NUCL 1

Total kinetic energy release and fission product mass distributions in the fast neutron induced fission of ^{235}U, ^{232}Th, ^{239}Pu and ^{233}U

***Walter Loveland**, lovelanw@onid.orst.edu. Oregon State Univ, Corvallis, Oregon, United States*

Using the WNR facility of the LANSCE, we have measured the total kinetic energy (TKE) release, its variance and the associated fission product mass distributions for the fast neutron induced fission of ^{235}U, ^{232}Th, ^{239}Pu and ^{233}U, The neutron energies, measured by time of flight, varied from 3 to 90 MeV. The TKE decreases modestly with increasing neutron energy (≤ 100 keV/MeV of neutron energy) indicating that the energy of the incident neutron does not go into the collective energy of fission and that the mean distance beteen the fragments at scission is roughly constant. The variances of the TKE distributions reflect the occurence of nthchance fission and act as a thermometer for the fissioning system at the scission point. The fission product mass and energy distributions can be described by a modal analysis reflecting the increasing probability of symmetric fission (with its lower associated TKE release) with increasing neutron energy.

NUCL 2

U-235 fission mass yield dependence on resonance and neutron energy

***Robert S. Rundberg**[3], rundberg@lanl.gov, Todd A. Bredeweg[2], Michael Koehl[4], Jenifer Braley[1]. (1) Chemistry Geochemistry/Nuclear Engineering, Colorado School of Mines, Golden, Colorado, United States (2) Nuclear & Radiochemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (3) Nuclear and Radiochemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (4) NA-221, Department of Energy, Washington, District of Columbia, United States*

The assymetric mass yield distribution is due to the lowering of the fission barrier by formation of a doubly magic Sn-132 core in the heavy fragment. Symmetric fission fragments increase in yield as neutron energy increases. This observation led to the two-mode fission hypothesis. The neutron energy dependence of the ratio of symmetric to asymmetric fission is surprisingly linear up to the onset of second chance fission. At low neutron energy, i.e., thermal and epithermal, nuclear structure affects the ratio of symmetric to asymmetric fission. The J = 3- resonances favor assymmetric fission. This is because the 3- state in the U-236 compound nucleus belongs to an octopole vibration, whereas the 4- state belongs to a two quasi-particle quadrupole state. We arrive at this conclusion using the mass yields from the "wheel" experiment and the ENDFB VII.1 fission cross sections. Our measured Cd-115g and Ag-111 to Mo-99 ratios can only be fit by assigning the J = 3- resonances to the more assymetric group from the "wheel" experiment.

NUCL 3

Energy dependence of fission product yields for ^{235}U, ^{238}U, and ^{239}Pu with monoenergetic neutrons between thermal and 14.8 MeV

Matthew Gooden[2], *m_gooden@lanl.gov, Todd A. Bredeweg*[2], *Malcolm M. Fowler*[3], *Dave J. Vieira*[2], *Jerry Wilhelmy*[2], *Anton Tonchev*[4], *Mark A. Stoyer*[1], *Megha Bhike*[5], *fnu Krishichayan*[5], *Werner Tornow*[5]. *(1) Lawrence Livermore Natl Lab, Livermore, California, United States (2) Nuclear & Radiochemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (3) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (4) Lawrence Livermore National Laboratory, Livermore, California, United States (5) Duke University, Durham, North Carolina, United States*

Under a joint collaboration between Triangle Universities Nuclear Laboratory (TUNL), Los Alamos National Laboratory(LANL) and Lawrence Livermore National Laboratory(LLNL), a set of absolute fission product yield measurements has been performed. The energy dependence of a number of cumulative fission product yields (FPY) have been measured using quasi-monoenergetic neutron beams for three actinide targets, ^{235}U, ^{238}U and ^{239}Pu, between 0.5 and 14.8 MeV. The FPYs were measured by a combination of fission counting using specially designed dual-fission chambers and γ-ray counting. Each dual-fission chamber is a back-to-back ionization chamber encasing an activation target in the center with thin deposits of the same target isotope in each chamber. This method allows for the direct measurement of the total number of fissions in the activation target with no reference to the fission cross-section, thus reducing uncertainties. γ-ray counting of the activation target was performed on well-shielded HPGe detectors over a period of two months post irradiation to properly identify fission products. Reported are absolute cumulative fission product yields for incident neutron energies of 0.5, 1.37, 2.4, 3.6, 4.6, 5.5, 7.5, 8.9 and 14.8 MeV. Preliminary results from thermal irradiations at the MIT research reactor will also be presented and compared to present data and evaluations.

NUCL 4

Theory of fission-fragment angular distributions

Walid Younes, *younes1@llnl.gov. Lawrence Livermore National Laboratory, Livermore, California, United States*

The angular distributions of fission fragments have been studied since the 1950’s as a probe of angular momentum in the fission process. The earliest models relied on the transition-state theory developed by Bohr in 1955. More recent theoretical approaches have sought to include the impact of dynamical effects during the fission process on the observed fragment angular distributions. In this talk I will present recent measurements of fission-fragment angular distributions obtained using the fission Time Projection

Chamber, and I will discuss their theoretical interpretation and what they can tell us about the fission process.

NUCL 5

Survival of excited nuclei produced in warm fusion reactions

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

Several new superheavy elements have been produced since the late 1990s using so-called “warm fusion” reactions, where compound nuclei with excitations of ~40 MeV are produced. The success of these reactions is largely a result of the use of neutron-rich ^{48}Ca projectiles reacting with actinide targets, which create relatively neutron-rich compound nuclei with higher probabilities of survival against fission. In contrast, more recent experiments using heavier projectiles to produce new elements have not been successful. The cross sections for all of these reactions are extremely small, so recent work at Texas A&M University has studied the reactions of similar projectiles with lanthanide rather than actinide targets to investigate the influence various quantities. Excitation functions for the *xn* and *pxn* exit channels of a large number of projectile/target combinations have been measured using the MARS spectrometer. A theoretical model has been developed that estimates the fission and particle emission widths for the excited compound nuclei. It adequately describes the cross sections of ^{48}Ca-induced reactions using only the fission and neutron emission widths, but describing the cross sections of reactions induced by ^{44}Ca and ^{45}Sc projectiles requires the inclusion of the proton and alpha emission widths. In most cases, there is also a significant reduction in fission survival due to collective effects. These results suggest that the discovery of new elements will largely be controlled by the ability of the compound nucleus to survive against fission. This talk will summarize the previous work, the most recent results using ^{40}Ar projectiles, and the theoretical model.

NUCL 6

Award Address (Glenn T. Seaborg Award for Nuclear Chemistry sponsored by the ACS Division of Nuclear Chemistry & Technology). Bonding trends across the actinide series

David L. Clark, *dlclark@lanl.gov. Natl Security Education Center, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

In 1944, Glenn Seaborg formulated the 'actinide concept' of heavy element electronic structure that predicted that actinide elements would form a transition series marked by the filling of electrons into the 5f shell. Whether the 5f-electrons in actinide molecules, compounds, metals, and some alloys are involved in chemical bonding has been a central and integrating focus for the fields of actinide chemistry and physics.

I will discuss fundamental studies aimed at understanding the molecular and electronic structure of the light actinide elements from U - Cm, that make use of systematic trends revealed through a variety of spectroscopic techniques and electronic structure calculations to probe the nature of chemical bonding. While these studies provide many new insights into the relative roles of 5*f* and 6*d* orbitals in actinide metal-ligand bonds, they often highlight the enigmatic nature of the actinide elements, and underscore the need for deeper understanding.

NUCL 7

Some bits and pieces of Dave Clark 5d and 5f chemistry

***Bruce E. Bursten**, bbursten@wpi.edu. Chemistry, University of Tennessee, Knoxville, Tennessee, United States*

The author will recount some of the contributions that Dave Clark has made in synthetic, structural, and electronic structural investigations of complexes of the heavy transition elements and the early actinides. The paper will start with our mutual work on the electronic structure of $W_2(O_2CR)_4(R)_2$, a d^3-d^3 complex with a proposed quadruple metal-metal bond that made us glad all over. It will continue with some of our work of mutual interest in the elctronic structure of actinide complexes and the relative roles of the 5*f* and 6*d* orbitals.

NUCL 8

Technetium oxide chemistry

***Alfred P. Sattelberger**[1], asattelberger@anl.gov, Bradley Childs[3,2], Keith V. Lawler[3,2], Frederic Poineau[3,2], Paul Forster[3,2], Ken Czerwinski[3,2]. (1) Argonne National Lab, Lemont, Illinois, United States (2) Chemistry, University of Nevada Las Vegas, North Las Vegas, Nevada, United States (3) UNLV, Las Vegas, Nevada, United States*

This talk will cover the chemistry and physical properties of technetium oxides, including TcO_2, Tc_2O_5, and Tc_2O_7, and describe synthetic methods, characterization techniques, structural data, and electronic structure calculations.

NUCL 9

Recent advances in the chemistry of the rare-earth metals in the formal +2 oxidation state

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

The discovery that reduction of Cp'_3Ln ($Cp' = C_5H_4SiMe_3$) by potassium graphite in the presence of 2.2.2-cryptand (crypt) could generate the complexes $[K(crypt)][Cp'_3Ln]$

provided the first crystallographically-characterizable molecules containing yttrium, holmium, erbium, praseodymium, gadolinium, terbium, and lutetium in the formal +2 oxidation state. This Cp'_3Ln/K reaction originated from earlier studies of dinitrogen reduction using a combination of a Ln^{3+} complex and an alkali metal in reactions designated as LnA_3/M (A = anion; M = alkali metal) since the mechanism was unknown. The LnA_3/M dinitrogen reduction studies, primarily with A = $N(SiMe_3)_2$, generally formed $(N{=}N)^{2-}$ and $(N_2)^{3-}$ complexes and not isolable Ln^{2+} complexes of formula $MLnA_3$ as found for A = Cp' with the $[K(crypt)][Cp'_3Ln]$ complexes. The isolation of $[K(crypt)][Cp'_3Ln]$ allows an evaluation of bona fide Ln^{2+} complexes, $MLnA_3$, as intermediates in the dinitrogen reductions. The synthesis and reactivity of $MLnA_3$ complexes with A = amides and cyclopentadienyls will be compared with the results of analogous LnA_3/M reactions in efforts to connect these two areas of reductive rare-earth metal chemistry.

NUCL 10

New divalent manganese complexes supported by imine-amide ligands

***John C. Gordon**, jgordon@lanl.gov, Doug Kindra, Brian Scott, Nathan C. Smythe. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Precious metals are commonly used for homogeneous catalysis in industrial processes due to their high activities and ability to promote two electron transformations. These metals are expensive however, thus searches are underway for cheaper, environmentally friendly alternatives with comparable activities, selectivities, and stabilities. To this end, a plethora of reports have described the catalytic activities of Fe, Co and Ni compounds as first row surrogates for the ubiquitous, industrially used metals Ru, Rh, and Pt/Pd. Despite this, limited attention has been given to manganese, a low cost metal that is environmentally benign. Some new chemistry of manganese (II) supported by imine-amide ligands as well as some applications in catalysis will be discussed.

NUCL 11

Uranium (IV -VI) imido and amido chemistry: Synthesis, reactivity and bonding

***James M. Boncella**[1], boncella@lanl.gov, Aaron M. Tondreau[1], Neil C. Tomson[2], Nickolas H. Anderson[1], Brian Scott[3]. (1) Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States (3) Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

We have been exploring the chemistry of uranium (IV – VI) mono and bis(imido) complexes. Recently, we have discovered a simple and convenient method for the preparation of U(VI)bis(imido) complexes starting from UCl_4. This procedure involves treating UCl_4 with four equiv. of amide in THF. This reaction rapidly generates two equiv. of amine and a species that behaves as a U(IV)bis(imido)(L)n equivalent. If treated with an oxidant such as I_2 or Ph_2S_2, the corresponding U(VI)bis(imido)$X_2(L)_n$ complex can be isolated in high yield. This oxidation reaction proceeds via a single electron transfer pathway rather than a concerted 2 e^- oxidative addition mechanism. The synthetic usefulness in the preparation of novel U(VI)bis(imido) complexes from U(IV) precursors suggests a variety of novel possible reactions. We have synthesized a variety of Me_3SiNR amide derivatives of U(IV) and have been exploring their redox reactivity with respect to generating new U(VI) or U(III) complexes. These results will also be discussed.

NUCL 12

Structural chemistry of UO_2, NpO_2, and PuO_2

***Steven Conradson**, st3v3n.c0nrads0n@icloud.com. Department of Complex Matter, Institut Josef Stefan, Ljbuljana, Slovenia*

The fluorite structured binary oxides of the light actinides are central to all aspects of their nuclear fuel application. Twenty years ago their chemistry was “known.” The binary U-O phase diagram was perhaps the most complicated of any element, with > 20 phases across UO_x with x continuous between 3/2 and 3. In contrast, NpO_{2+x} did not exist, resulting in a gap between NpO_2 and the highest valence Np_2O_5, and Pu terminated at the (IV) state of PuO_2. Then, in 2000, PuO_{2+x} with $x \leq 0.26$ was confirmed, with a similar result just this year for NpO_{2+x}, demonstrating that mixed valence and disorder are displayed for all three actinides and not just U. The question, then, is whether the An(V) within the oxide behaves analogously to its corresponding species in molecular complexes or its presence in the lattice modifies its chemical properties. The corollary is to what extent UO_{2+x}, NpO_{2+x}, and PuO_{2+x} are similar differ from each other? The proposed cuboctahedral or quad- and di-interstitial structures for U_4O_9 derived, respectively, from neutron scattering and calculations give no indication of the formation of uranyl species and the associated layered compounds as in U_2O_5. Surprisingly, XAFS experiments have demonstrated the opposite, showing terminal and possibly bridging U(VI)- and Np/Pu(V)-oxo moieties. This has been interpreted in U as originating in tunneling polarons. Without comprehensive neutron diffraction data from the Np and Pu oxides this same putative contradiction resulting from the differing time domains of the measurements cannot be discerned. However, we have found that Pu displays two types of H_2O-induced disorder, oxidation but also simply a disruption of the Pu-O bonds that may be hydrolysis, leading to the proposal that PuO_{2+x} is perhaps best described as $PuO_{2+x-y}(OH)_{2y} \times zH_2O$. In addition, the distribution of the near neighbor Pu-O bonds is affected by whether the material has been thermally treated. Disorder without oxidation has not been observed with U, with too few samples of NpO_2 to know. Another significant difference among them is the absence of long range order for U_4O_9, where PuO_{2+x} and NpO_{2+x} with large x both showing the likely continuation of the fluorite structure with some additional features. Continued research on these compounds is essential for further identification and characterization of their structures and properties.

NUCL 13

Reactivity of +3 actinides

Stosh A. Kozimor[2], *stosh@lanl.gov, Enrique R. Batista*[1], *John M. Berg*[3], *Eva R. Birnbaum*[3], *Justin N. Cross*[3], *Jonathan W. Engle*[3], *Juan Lezama Pacheco*[4], *Maryline G. Ferrier*[3], *Benjamin W. Stein*[3]. *(1) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Los Alamos Natl Lab, Los Alamos, New Mexico, United States (3) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (4) Stanford, Palo Alto, California, United States*

There is pressing need to advance fundamental understanding of trivalent actinide coordination chemistry. Unfortunately, two main technical challenges have impeded developing chemistry for actinide elements. These include (1) obtaining sufficient quantities of actinium for study, and (2) safely handling the highly-radioactive actinide elements. This talk will describe our recent efforts to make use of upgrades at the SSRL synchrotron facility to overcome the challenges associated with conducted studies on highly-radioactive Ac, Am, and Cm elements.

NUCL 14

Actinide coordination chemistry with environmental and biological applications

Mary Neu, *nmmneu@gmail.com. Global Security, Los Alamos National Lab, Los Alamos, New Mexico, United States*

In the early 1990s Dave Clark was expanding from his tremendous foundations and contributions in f-element organometallic and alkoxide chemistry into the aqueous chemistry of uranyl. Joining Dave's research team then was akin to joining an adventurous journey, using modern inorganic chemistry methods not yet applied to most actinides, to explore and map uranium chemistry and carve out new paths in transuranic science. We took direct and indirect routes to characterize carbonate, hydroxide, chloride complexes and to quantify their speciation.

It was simply a joy and a privilege to work with Dave! His enthusiasm was infectious and his energy boundless: Every day was an opportunity to make a new discovery. (And to overcome the technical and bureaucratic obstacles to conducting our experiments with toxic radionuclides.) To advance our expedition we brought modern inorganic chemistry methods and tools, used in bioinorganic and organometallic research, to our experiments with aqueous actinyl and actinide complexes. Dave learned from others, and fashioned his own approaches to prepare, contain, transport and examine radioactive samples using laboratory and synchrotron-based spectroscopic methods. These fundamental studies served as a platform for a generation of researchers to learn from and extend. Examples of our early work and how it led to branching studies of highly-coordinated plutonium complexes, bioinorganic transformations and environmental species will be discussed.

NUCL 15

Actinide organometallic chemistry: A meeting with David Clark at the bottom of the periodic table

***Jaqueline L. Kiplinger**, kiplinger@lanl.gov. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Non-aqueous chemistry of the actinides has proved invaluable for gaining insight into the behavior and properties of these elements in a variety of chemical environments. These range from inert atmosphere syntheses of well-defined actinide materials for nuclear fuel applications and materials science to addressing purely fundamental questions such as the involvement of 5f-orbitals in bonding and reactivity. Using the bis(C_5Me_5) platform, we have discovered a variety of unusual reactivity patterns unique to the actinides. A benefit of working at LANL has been the ability to work with and learn from David Clark on how to couple our synthetic efforts with spectroscopic and theoretical studies to gain insight into the role that f-orbitals and electrons play in the reaction chemistry, electronic structure and bonding of actinide complexes. Developments in these exciting areas of chemistry will be presented.

NUCL 16

Fission yield measurements for Th-232, U-238 and HEU at the National Ignition Facility

***Narek Gharibyan**[1], gharibyan1@llnl.gov, K. Moody[1], J. Despotopulos[1], S. Faye[1], P. Grant[1], K. Kmak[2], K. Roberts[1], C. Yeamans[1], Dawn A. Shaughnessy[1]. (1) Lawrence Livermore National Laboratory, Livermore, California, United States (2) UC Berkeley, Berkeley, California, United States*

The indirect-drive inertial-confinement fusion of a deuterium-tritium (DT) filled capsule at the National Ignition Facility (NIF) provides a unique platform for measuring fission yields from a high-intensity instantaneous neutron source. The 14.1 MeV DT fusion neutrons dominate the neutron energy spectrum at NIF with lower energy contributions from the DD and TT fusion neutrons. As part of the Solid Radiochemistry nuclear diagnostic at NIF, various irradiation locations at 10-50 cm from the capsule have been developed for exposing materials of interest to the NIF DT fusion neutrons. Several irradiation experiments were performed at NIF in an effort to measure the fission yields for Th-232, U-238 and HEU. The irradiated samples were analyzed directly via gamma-spectrometry for short-lived and peak fission products while radiochemical separations were necessary for the difficult-to-measure and low-yield fission products. Detailed decay-curve analyses allowed for a more accurate identification and quantification of the fission products. Results from the fission yield measurements of these actinide isotopes will be presented.

NUCL 17

Application of the Bohr-independence hypothesis for the measurement of fission yields

***Narek Gharibyan**, gharibyan1@llnl.gov, K. Moody, S. Tumey, T. Brown, Dawn A. Shaughnessy. Lawrence Livermore National Laboratory, Livermore, California, United States*

A new proposed method for measuring 14-MeV neutron fission yields is through a fission-proxy reaction method, an indirect process for creating the same compound nucleus as that produced from 14-MeV neutrons. It is based primarily on the Bohr-independence hypothesis, also known as the compound-nucleus model, which states that the compound nucleus will decay into its reaction products independent of its formation process. This proposed fission-proxy method may be validated by measuring fission yields from 25.6 MeV α-induced fission of Th-232, which simulates the same excited compound nucleus (U-236*, E*=20.6 MeV) as that produced from 14-MeV neutrons on U-235 with a large overlap in the angular momentum distributions. Since the literature data for the Th-232 system is limited, a series of α-induced fission yield measurements on Th-232 were performed using the accelerator located at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. These experimentally measured fission yields were compared to the evaluated England and Rider fission yields for 14-MeV neutrons on U-235 in order to assess the validity of the fission-proxy approach. The results from this detailed comparison will be presented.

NUCL 18

Addressing nuclear data needs with FIER

***Eric Matthews**[2], efmatthews@berkeley.edu, Bethany L. Goldblum[2], Walid Younes[1], Lee A. Bernstein[3]. (1) Lawrence Livermore National Laboratory, Livermore, California, United States (2) Nuclear Science and Security Consortium, University of California, Berkeley, Berkeley, California, United States (3) Lawrence Berkeley National Laboratory, Berkeley, California, United States*

The Fission Induced Electromagnetic Response (FIER) code has been developed to predict delayed gamma-ray spectra following fission of nuclei with evaluated independent yield libraries. FIER calculates the time-dependent populations of fission products arising from a user-specified irradiation of a fissionable isotope using evaluated nuclear data libraries and solutions to the Bateman equations. The resulting populations provide the beta-delayed gamma-ray activity of each fission product. The predictions of FIER were benchmarked against an experiment performed where a U-235 sample was irradiated in the Godiva critical assembly. While FIER generally agrees with the experimental results, discrepancies between the time-dependent FIER output and the experimental data show the utility of the code to highlight deficiencies in the underlying nuclear data. Methods by which to improve existing nuclear data libraries are explored.

NUCL 19

Delayed neutron spectroscopy for characterization of special nuclear material

*J Ocampo, J Wallick, George E. Miller, **A Shaka**, ajshaka@uci.edu. Chemistry, University of California, Irvine, California, United States*

Fission products are neutron rich and typically undergo *b*⁻-decay. In a few cases, the daughter is produced in an excited nuclear state and itself emits a neutron. These *b*-delayed neutrons provide a highly selective and quantitative means to interrogate fissile material. Several groups have proposed numerical methods to try to ascertain the composition of an unknown that may contain, e.g. ^{239}Pu and/or ^{235}U by exploiting the small differences in the populations of the delayed neutron precursors and analyzing the tally of delayed neutrons versus the time after irradiation. We have taken a slightly different approach, optimizing the figure of merit for the technique by maximizing detectable neutrons per unit experiment time, and altering the irradiation conditions to achieve discrimination. We will show that even with relatively low-flux irradiation conditions it is possible to get quantitative information on samples containing less than 100 ng of fissile material.

NUCL 20

Tribute to an esteemed colleague: Young Doctor Clark

***David E. Hobart**[1,2], dhobart15@gmail.com. (1) National Security Education Center, Los Alamos National Laboratory, Santa Rosa Beach, Florida, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

The Glenn T. Seaborg Award in Nuclear Chemistry, sponsored by the ACS Division of Nuclear Chemistry and Technology, recognizes outstanding contributions in nuclear or radiochemistry or their applications. This year’s recipient, David L. Clark, is well deserving of this prestigious recognition. He is best described as a Renaissance Man in heavy element chemistry who has performed as laboratory researcher, author, editor, mentor, educator, manager, incident investigator, technical advisor, international program reviewer, international conference chair, policy maker and architect of the next generation of nuclear scientists. I have had the pleasure of collaborating with Dave for nearly 30 years. I approved hiring of this bright young post-doc into my research team at Los Alamos in 1989 to study actinide solubility in candidate nuclear waste site ground waters. The rest is history. I will share memories of our continued interactions, highlight our technical discoveries and include some of our latest endeavors.

NUCL 21

Coordination of N-heterocyclic ligands to actinides: A joint theoretical and experimental study

Ping Yang[2], *pyang@lanl.gov, Jing Su*[2]*, Enrique R. Batista*[2]*, John K. Gibson*[1]*, Andrew Gaunt*[2]*, Stosh A. Kozimor*[2]*. (1) Lawrence Berkeley National Laboratory, Emeryville, California, United States (2) Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Nuclear energy represents a critical tool available to meet the demand for increasing energy supply, at the same time reducing green-house gas emissions. However, this form of energy produces long-lived radioactive waste. To reduce the need for long-term nuclear waste storage, it is important to develop efficient separation strategies that require high chemical selectivity. A molecular-level understanding of the coordination modes and affinity of ligands with multiple binding sites to actinides can pave the way to designing new ligand with improved extraction efficiency and selectivity. We will discuss the coordination chemistry to actinide centers with ligands composed of multiple competitive binding sites including sulfur, nitrogen and oxygen chelating groups. We will present the interactions between actinide centers and the selected nitrogenous heterocyclic ligands using first-principle methods that include relativistic effects and electron correlation. The theoretical results will be further validated by experimental synthetic and spectroscopic characterizations.

NUCL 22

Probing actinide-ligand chemical bonds: Hand shake between quantum mechanical calculations and experimental measurements

Enrique R. Batista[2], *erb@lanl.gov, Ping Yang*[2]*, Richard L. Martin*[4]*, Stosh A. Kozimor*[3]*, David L. Clark*[1]*. (1) Natl Security Education Center, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (3) Los Alamos Natl Lab, Los Alamos, New Mexico, United States (4) MS B214 Theoretical Div, Los Alamos Natl Lab, Los Alamos, New Mexico, United States*

The presence or absence of significant participation in chemical bonding by the f-element materials and molecules had been a subject of much debate for many years. Although computational studies could be carried out to calculate orbital mixings, direct experimental validation of this purely quantum mechanical effect was hard to attain. The developments of Dave Clark and his team of experimentalists lead to a clean hand shake between theoretical calculations and measurements by means of ligand K-edge X-ray absorption spectroscopy. Whereas this technique had been pioneered for lighter elements, extension to actinide complexes was not easy, eventually changing the way people understand these systems. In this talk we will recap this exciting trip with Dave

Clark and his team and present studies of actinide-ligand bonds, from the computational side and its mapping to the experimental measurements.

NUCL 23

Interpretation of morphologic and chemical signatures from actinide oxide materials

***Marianne P. Wilkerson**, mpw@lanl.gov. Chemistry-Nuclear and Radiochemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

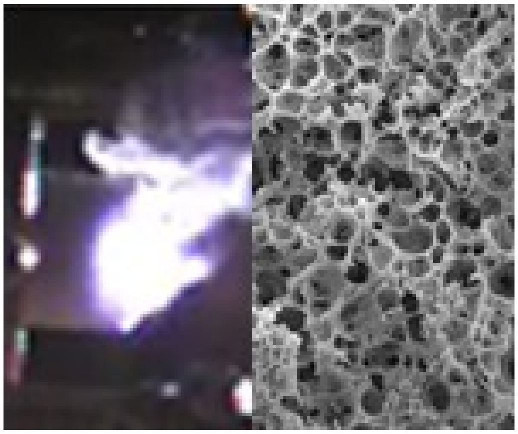
A number of publications and reports have identified a need to develop new signatures for characterizing the chemical history of actinide materials. Evaluation of morphology as a clue for understanding the process history of material has been suggested as well. Chemical signatures of actinide oxides may be indicative of nuclear processing conditions or may be modified following storage of the material under controlled conditions. We have engaged experimental and modelling tools to understand these signatures in bulk actinide oxide materials and to evaluate how the signatures could be modified over time. In comparison, signatures from released particulates may be sensitive to the release scenario and deposition conditions in the environment, and we have reported on the characterization of environmental actinide samples. Our studies to measure morphologic and chemical signatures from both bulk measurements and images sensitive to spatial relationships on mesoscale materials will be discussed.

NUCL 24

New methods for the preparation of high purity transition metal, lanthanide, and actinide nanomaterials: Synthesis and applications of nitrogen-rich metal complexes

***Jacqueline M. Veauthier**, veauthier@lanl.gov. Los Alamos National Laboratory MS C920, Los Alamos, New Mexico, United States*

Our team has developed new synthetic strategies for the preparation of high purity, high surface area, low density transition metal, lanthanide nitride, and actinide oxide nanomaterials. Our methodology utilizes nitrogen-rich metal precursors that undergo self-sustained combustion reactions (under argon or nitrogen atomospheres) to yield high purity nanomaterials. Successful application of this new technique for the preparation of Fe, Co, Ni, Cu, Zn, Pd, Ag, Pt, and Au metal foams, LnN_x and CeN_x nitride foams, and for ThO_2 and UO_2 oxide foams has been demonstrated. Preparation, characteization, and potential applications of these new nanoporous materials will be discussed.



NUCL 25

Factors affecting the sorption of uranyl at mineral-aqueous solution interfaces

Gordon E. Brown[1], *gordon.brown@stanford.edu, Gabrielle Dublet*[4], *Vincent Noel*[1], *Scott E. Fendorf*[3], *John R. Bargar*[2], *Kate Maher*[5]. *(1) Geological Sciences, Stanford Univ, Stanford, California, United States (2) Stanford Synchrotron, Menlo Park, California, United States (3) EESS--Suite 140, Stanford University, Stanford, California, United States (4) Environmental Microbiology Lab, EPFL, Lausanne, Switzerland (5) Geological Sciences, Stanford University, Stanford, California, United States*

Uranyl is an important environmental contaminant at high-level nuclear waste storage facilities, such as Hanford, WA, at former uranium milling facilities, such as Rifle, CO, and at natural uranium deposits, such as the Powder River Basin in Wyoming. Sorption of uranyl on mineral surfaces or its incorporation in mineral structures help reduce the hazard of this highly mobile ion in groundwater and surface waters. Many factors impact the sorption of uranyl to mineral surfaces including solution pH, reduction-oxidation conditions, intrinsic differences in reactivity of different mineral substrates, natural organic matter (NOM) and microbial biofilm coatings on mineral surfaces, and the presence of CO_2 dissolved in natural waters, among others. We will review the results of studies of sorption reactions of uranyl with minerals in subsurface sediments at the Hanford site and in surface waters and sediments at Rifle, CO. We will also discuss the results of a recent laboratory study of the effect of NOM (humic and fulvic substances) on the sorption of uranyl on 2-line ferrihydrite (Fh), a common, naturally occurring nano-Fe(III)-hydroxide. In order to determine the effect of NOM associated with Fh nanoparticles on the sorption of aqueous uranyl ions, uranyl was reacted with Fh at pH 4.6 and 7.0 in the presence and absence of Elliott Soil Humic Acid (ESHA) (0–835 ppm) or Suwanee River Fulvic Acid (SRFA) (0–955 ppm). No evidence was found for reduction of uranyl by either form of NOM after 24 hours of exposure. We used x-ray absorption spectroscopy to characterize molecular-level changes in uranyl complexation resulting from sorption to Fh-NOM aggregates. The results of this study will be discussed.

NUCL 26

Molecular controls over uranium mobility in complex redox-active sediment systems

John R. Bargar[3]*, bargar@slac.stanford.edu, Vincent Noël*[3]*, Sharon Bone*[3]*, Noemie Janot*[1]*, Scott Roycroft*[2]*, Kristin Boye*[3]*. (1) Laboratoire Interdisciplinaire des Environnements Continentaux, University of Lorraine, Nancy, Nancy, France (2) Earth System Science, Stanford University, Stanford, California, United States (3) Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States*

Organic-rich anoxic sediments accumulate uranium globally in marine sediments, ore bodies, and in shallow contaminated near-surface environments. Natural organic matter is increasingly being recognized as playing multiple and important roles mediating uranium behavior in these environments. To better understand the roles of organic-enriched sediments at the regional scale of the upper Colorado River Basin, we sampled multiple field sites along a 700 km north-south transect in New Mexico, Colorado, and Wyoming, USA. This work shows that organic-enriched sediments are prevalent, strongly accumulate uranium, and moreover are important reservoirs for nutrients and biogeochemical critical elements, including C, N, S, and Fe. Sulfate reducing conditions appear to be particularly important for uranium accumulation, suggesting at least a strong indirect control of sulfide on U(VI) reduction. Indeed, the nominal oxidation state of water-soluble soil organic carbon was found to be correlated to sulfide concentration, suggesting that sulfide plays a major role in poising the redox conditions of organic-enriched sediments across this region.

To better understand molecular controls over uranium behavior in NRZs, we performed controlled microcosm experiments designed to mimic sulfate reducing conditions in NRZs and to more clearly define the potential roles of organic functional groups as uranium binding sites. U(IV) was found to be dominantly associated with surfaces of particulate organic carbon and to exhibit local molecular structure consistent with sorbed complexes. Moreover, we show that solid-phase U(IV) formation can be inhibited under groundwater-relevant conditions by decreasing the total concentration of U, while maintaining the same concentration of sorbent. Thus, the number and type of surface ligands can infleunce U(IV) speciation subsequent to U(VI) reduction. An important implication of this finding is that U(IV) will be readily mobilized in the presence of complexing agents and oxidants. Such conditions are common in NRZ sediments, which experience large variations in saturation state and redox conditions throughout the annual winter (base flow) / summer (meltwater discharge) cycle within the upper CRB. In ensemble, these studies suggest more nuanced conceptual models that help to explain uranium biogeochemical behavior in the present and through geological time.

NUCL 27

Swift heavy ion irradiation of actinide materials

***Rodney Ewing**, rewing1@stanford.edu. Geological Sciences, Stanford, Menlo Park, California, United States*

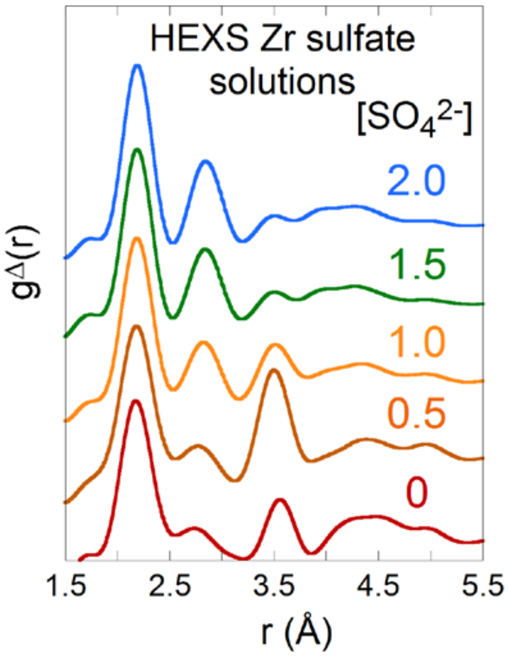
Actinide materials, perhaps more than any other material composition class, often find applications in which they are subjected to extreme environments – usually combinations of high temperatures and intense radiation fields. In this presentation, I will summarize recent work done as part of the Center for the Materials Science of Actinides, an Energy Frontier Research Center. The presentation will focus on actinide oxides, related rare-earth oxides and ceramic oxides that may incorporate transuranium elements. We will examine the effects of swift heavy ion irradiations, particularly in combination with high-temperature and high-pressure irradiations of actinide materials. Of particular importance is the observation that under these extreme conditions, phase transformation pathways that are otherwise energetically or kinetically precluded can become accessible. As an example, irradiation of bixbyite-structured (C-type) compounds in the lanthanide sesquioxide (Ln_2O_3) system with swift heavy ions yields transformations to various crystalline and amorphous phases, with the final structure formed showing dependence on material composition and ion velocity. A remaining challenge is the characterization of these nano-scale modifications. The complete characterization requires a unique combination of very different analytical techniques, such as transmission electron microscopy, synchrotron x-ray diffraction, small angle x-ray scattering, and neutron scattering.

NUCL 28

Synthesis, structure and bonding of tetravalent-metal (M^{IV}) oxide clusters

***Lynda Soderholm**, ls@anl.gov, S. Skanthakumar, Shanna L. Estes. Argonne Natl Lab, Argonne, Illinois, United States*

The structural analyses of tetravalent metal (M^{IV}) hydrolysis products are providing a new window into the different bonding requirements of *d*- and *f*-ions. By probing the metal correlations *in situ* using high-energy X-ray scattering (HEXS), we are able to interrogate how metal oligomers develop and change with changing conditions. This information enables the selection of the solution conditions, such as pH, anion characteristics, and concentration, which are necessary to target and isolate a crystalline metal hydroxo, oxyhydroxo, or oxide. Analyzing the single-crystal structures of the resulting nanoclusters and extended solids in turn further informs solution speciation. More importantly, from the perspective of this talk, we are learning how similar solution conditions yield different condensation products, depending on the specific M^{IV} ion. Within the actinide series, we see trends consistent with those expected based on simple cation-hardness rules. Moving across the series from Th^{IV} to Pu^{IV} tends to increasingly favor oxo ligation and nanoclusters based on fluorite-type bonding. In contrast, even under much more acidic conditions transition-metal M^{IV} ions form predominantly hydroxo bonded species, even though they are much smaller cations than their *f*-ion counterparts. The general trends in these isolated structures are mirrored in their solution speciation. Our results are discussed in terms of the important contribution played by differences in symmetry and bonding requirements of the *d*- versus *f*-valence orbitals. Also included in the presentation will be our recent observations on Ce^{IV} hydrolysis, both in solution and in the solid. This ion is expected to behave similarly to Pu^{IV,}, based on hardness considerations and valence-bond considerations, contrary to our observations.



NUCL 29

Covalent interactions in actinide oxides

Paul S. Bagus[1]*, bagus@unt.edu, Connie J. Nelin*[2]*. (1) Chemistry, University of North Texas, Austin, Texas, United States (2) Consultant, Austin, Texas, United States*

The extent and the energetic importance of covalent interactions in actinide oxides is important for understanding their bonding and their electronic structure. However, the degree of the covalent mixing is controversial, in large part, because it is not easy to asses this from the results of theoretical studies of the electronic structure of these compounds. We have studied the importance of the covalent mixing using two novel approaches to the analysis of the orbitals and energetics of wavefunctions. The first provides estimates of the departures of the 5f and 6d occupations from the “nominal” values for the oxidation state of the actinide. This method, which is based on the projection of orbitals of suitable fragments on the total wavefunction makes it possible to provide an uncertainty for the estimated occupations. The second approach provides estimates of the energetic importance of the covalent mixing. This is achieved by constraining the variational space where the orbitals are determined so that the covalent mixing is either allowed or forbidden. In this way, we are directly able to estimate the energetic contribution of the covalent mixing between the O(2p) and the actinide 5f and

6d. Furthermore, the importance of the actinide 7s and 7p orbitals in the interaction with oxygen has also been examined. The covalent mixing will be examined for different oxidation states of U oxides and for actinyls formed with U, Np, and Pu. In particular, it will be shown that the importance of the 5f covalent mixing with O depends strongly on the nominal 5f occupation. This dependence is explained by a competition between the attraction to the actinide, which favors a higher 5f occupation, and the electrostatic repulsion between the 5f electrons, which does not favor this occupation.

NUCL 30

Impact of the nuclear and radiochemistry summer schools on the nuclear chemistry program at Michigan State University

Paul F. Mantica*, mantica@msu.edu. Chemistry and FRIB, Michigan State University, East Lansing, Michigan, United States*

The nuclear chemistry program at Michigan State University (MSU) has benefited tremendously from the Nuclear and Radiochemistry Summer Schools. I will discuss the involvement of alumni from the Summer Schools in the nuclear chemistry research programs at MSU. I will also provide an overview of the Facility for Rare Isotope Beams (FRIB), which is being constructed at MSU and will be a new national user facility for the study of rare isotopes. FRIB will require scientific expertise in nuclear and radiochemistry to realize its science mission. I will therefore advocate for the continued recruiting and training of outstanding undergraduates in nuclear chemistry and radiochemistry to meet future national needs.

NUCL 31

How the Nuclear and Radiochemistry Summer School shaped my career as a radiochemist in biotech

Charles A. Boswell*, boswell.andy@gene.com. MS 463-A, Genentech, South San Francisco, California, United States*

This presentation will focus on how the Nuclear and Radiochemistry Summer School shaped my career development from an undergraduate chemistry student at Tennessee Technological University to my current role as Senior Scientist and Postdoc Mentor in the Preclinical and Translational Pharmacokinetics Department at Genentech (A Member of the Roche Group) in South San Francisco. One of my undergraduate chemistry professors, Dr. Dale Ensor, gave me information about the summer school and encouraged me to apply. During the San Jose summer school in 1997, I was exposed to a variety of research topics in all aspects of nuclear and radiochemistry. I became particularly interested in research on synthesis and preclinical evaluation of radiotracers for nuclear medicine presented by Dr. Carolyn Anderson. I joined her lab as a graduate student, earning my PhD in Chemical Biology in 2004 at Washington University School of Medicine in Saint Louis, Missouri. Upon graduation, I received a

Cancer Research Training Award to perform postdoctoral research under the guidance of Dr. Martin Brechbiel on novel targeted molecular imaging agents for cancer at the National Cancer Institute in Bethesda, Maryland. In 2007, I joined Genentech where I have continuted to apply radiochemistry towards the development of biotherapeutic drugs.

NUCL 32

My career in nuclear science: From the nuclear and radiochemistry summer school to national security

John Freiderich, *freiderichjw@y12.doe.gov. Y-12 National Security Complex, Oak Ridge, Tennessee, United States*

I've enjoyed a decade long career in nuclear and f-element science with a jump start and humble beginnings at the Nuclear and Radiochemistry Summer School in Brookhaven. After graduate work and a post-doctoral position I now work for the U.S. Department of Energy.

NUCL 33

Nuclear science from the big apple to down under

Rachel Popelka-Filcoff, *rachel.popelkafilcoff@flinders.edu.au. School of Chemical and Physical Sciences, Flinders University, Adelaide, South Australia, Australia*

When I am asked to write or speak for the media, people often me how to define myself. I respond that I am an archaeological and radioanalytical chemist. My career is based around the inter-disciplinary study of radioanalytical methods to archaeology and cultural heritage, and more recently to forensic and environmental studies.

Currently, I am an Associate Professor in Chemistry at Flinders University, in Adelaide, South Australia. I currently lead a group of students in the areas of analytical, forensic, radiochemistry and archaeometry. I also have strong research collaborations with the Australian Nuclear Science and Technology Organisation (ANSTO) in Lucas Heights, New South Wales.

However, the beginnings of my career began at Washington University, and subsequently at the University of Missouri for my PhD. It was at Missouri that I had the opportunity to be a graduate assistant at the Summer School in Nuclear and Radiochemistry. It was a challenging summer of teaching students, keeping equipment running, preparing labs, assisting in logistics and coordinating social events. In many ways it prepared me for my own career in teaching students in the discipline, as well as giving me the opportunity to meet some of the leaders in the field, who all came to Brookhaven that summer. Personally, I enjoyed meeting leaders in archaeometry such as Gar Harbottle, as well as meeting other leaders in radiochemistry

and nuclear science. I was fortunate to be able to attend the other field trips and site visits as well as experience the many enjoyable activities of a Long Island summer.

Looking back over the 12 years since, I realize that the program gave me the opportunity to meet the next generation of students. I am pleased to see many of the graduates of the program present at ACS meetings since, and to hear of their successes in graduate school and employment. The program also gave me an excellent framework for how to design my own courses. I look forward to educating the next cohort of undergraduates and graduate students in Australia towards an international group of radiochemistry graduates, and developing radiochemical research.

NUCL 34

Structural and chemical changes in uranyl fluoride: A complementary spectroscopic and computational study

Marie C. Kirkegaard[1,2]*, mkirkegaard@hmc.edu, Andrew J. Miskowiec*[3]*, John Langford*[2]*, Brian Anderson*[2]*. (1) University of Tennessee, Claremont, California, United States (2) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Uranyl fluoride, the product of the hydrolysis of UF_6, has previously been shown to undergo structural changes in the presence of gas phase water. Water sorbs between the layers of the anhydrous crystal, resulting in a stable, partially-hydrated state with a distinct spectroscopic signature. Another stable hydrate form, $[(UO_2)_7F_{14}(H_2O)_7]*4H_2O$, is produced via further hydration and subsequent desiccation, but has not been fully characterized previously. Clarifying how these structural and chemical changes can be induced by environmentally relevant perturbations is important for the detection of uranyl fluoride, i.e. in nuclear forensics applications.

Raman spectroscopy with humidity and temperature control was used to conduct a time-dependent analysis of the induced structural and chemical changes in uranyl fluoride. A complementary computational study was also undertaken to help interpret the Raman spectra. Static DFT calculations were previously shown to accurately predict vibrational frequencies of the “pristine” anhydrous state. Expanding on this work, Born-Oppenheimer molecular dynamics simulations were performed to show how the predicted vibrational states change with temperature and the introduction of water. These simulations show hydrogen bonding interactions that provide insight into the water-phonon coupling previously observed with inelastic neutron scattering.

NUCL 35

Path to a PhD: From a summer to a career

Andrew J. Swift[1]*, swifta2@unlv.nevada.edu, Ken Czerwinski*[2]*, Daniel J. Koury*[1,2]*. (1) Chemistry, UNLV, Las Vegas, Nevada, United States (2) UNLV Dept of Chemistry, Las Vegas, Nevada, United States*

In 2011, I arrived at the Nuclear Chemistry Summer School (NCSS) Brookhaven National Laboratory site with a limited working knowledge of nuclear and radiochemistry and the potential research opportunities associated with the field. Over the course of the school, nuclear and radiochemistry topics were discussed through a series of academically rigorous classroom discussions and hands on laboratory experiments with nuclear professionals from around the country. The school extended outside the bounds of the classroom through tours of lab facilities and personal interactions with visiting lecturers. It was through this design that NCSS sparked my interest in nuclear fuel cycle research and introduced me to my current research advisor. After graduating the school and obtaining my undergraduate in chemistry from Huntingdon College, I began working towards my PhD in Radiochemistry at UNLV in 2012. My current research focuses on the nuclear fuel cycle and uranium metallic fuels and their fuel cladding chemical reactions with respect to burnup.

NUCL 36

Finding my place in radiochemistry: A recent grad’s letter of gratitude to the NCSS

***Erin M. May**, erin.m.gantz@gmail.com. Chemistry, University of California, Berkeley, Berkeley, California, United States*

The ACS Nuclear and Radiochemistry Summer School formed the foundation of my career as a radiochemist. This talk will discuss the facets of the NCSS program that inspired me to attend graduate school, succeed within my doctoral program, and find a post-doctoral appointment that complemented my interests. While the content of the classroom training provided during NCSS was vital to attaining undergraduate internships and admission to graduate school, I would like to highlight the aspects of the NCSS experience that can be less easily quantified, such as the location, the instructors, and my fellow students. I would consider these elements to have influenced my decisions about my career to the greatest extent. As a recent graduate, I would also like to comment on the continued need for radiochemistry education at the undergraduate level and why the NCSS program remains relevant even amidst other new summer opportunities in radiochemistry.

NUCL 37

Impact of the Nuclear Chemistry Summer School on one student from a small, undergraduate liberal arts college

***Andrew Klose**, aklose@augie.edu. Department of Chemistry, Augustana University, Sioux Falls, South Dakota, United States*

The Nuclear and Radiochemistry Summer School (NCSS) has had a significant impact on promoting the field to undergraduate students. Here, I will share my anecdotal success story of the program. I had no knowledge of the field of nuclear chemistry before seeing a flyer describing the NCSS on a bulletin board at my undergraduate liberal arts institution. I was interested in the intersection of chemistry, mathematics, and physics, and the program seemed like an attractive opportunity. After being accepted and attending the summer school program, I became interested in nuclear science and found my way back to the NCSS as a teaching assistant. Being hooked on the field at this point, I decided to attend Michigan State University for graduate school. I joined the group of a nuclear chemist there, and was one of the students that help build and commission a new precision laser spectroscopy facility at the National Superconducting Cyclotron Laboratory (NSCL). After completing a postdoctoral fellowship studying precision laser spectroscopy at NIST, I accepted a position at a small liberal arts undergraduate college. Currently, a major portion of my research program revolves around a collaboration with colleagues at NSCL. My role has come full circle, as I now introduce undergraduate students to nuclear and radiochemistry in our undergraduate curriculum, and encourage the next generation of students to attend the NCSS.

NUCL 38

Coordination chemistry of uranium with thioethers and selenoethers: Investigation of neutral heavy donor binding to heavy metals

Anastasia V. Blake, Zachary Theiler, ***Scott R. Daly****, scott-daly@uiowa.edu. Chemistry, University of Iowa, North Liberty, Iowa, United States*

Spectroscopic, structural, and theoretical studies of actinide-chalcogen bonding continue to emerge in the quest to understand the fundamental role that metal-ligand covalency plays in minor actinide/lanthanide separations and actinide electronic structure. Like dithiophosphinates that show exceptionally high selectivity for Am^{3+} over lanthanides (*i.e.* $S_2PR_2^{1-}$), most of the S, Se, and Te ligands that have been studied with actinides are negatively charged. As a result, there are significant electrostatic contributions that influence the ligand bonding with actinide cations, which makes it difficult to tease out how variations to metal-ligand covalency contribute to solution binding affinities. To address this challenge, we have been exploring the coordination chemistry and bonding of neutral thioether and selenoether ligands to f-elements to evaluate systematic structural and spectroscopic variations as the identity of the chalcogen is changed. Given that the neutral actinide-chalcogen bonding interactions were expected to be weak (especially with Se and Te), we prepared new multidentate amine-bis(phenolate) ligands containing pendant heavy ethers. The harder amine-bis(phenolate) donor groups were selected to ensure that the ligand remains bound to the metal so that we can evaluate the local bonding affinity of the heavy ether even if it is hemilabile or too weak to bind to the metal on its own. Several new crystal structures with uranium will be presented along with supporting spectroscopic data. The aim of these studies is to provide the foundation necessary for future transuranic work, which will require more specialized radiological facilities and controls.

NUCL 39

Harnessing the principles of coordination chemistry to control the growth of actinide materials

***Stefan G. Minasian**[2], minasian@gmail.com, Alexandre Herve[5], Augustin Braun[4], Selim Alayoglu[3], Alison B. Altman[7], Corwin Booth[1], Daniel Olive[6]. (1) LBNL, Berkeley, California, United States (2) 70A-1150, Lawrence Berkeley Laboratory, Berkeley, California, United States (3) Lawrence Berkeley National Laboratory, Berkeley, California, United States (4) Chemical Science, Lawrence Berkeley National Laboratory, Berkeley, California, United States (5) Chemical Science Division , Lawrence Berkeley National Laboratory, Walnut Creek, California, United States (6) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (7) Chemistry, UC Berkeley, Berkeley, California, United States*

The design of accident tolerant fuels poses considerable challenges in terms of understanding and controlling chemical and physical phenomena in complex systems under extreme conditions, over length scales from the atomic to the macroscopic, and time scales from femtoseconds to years. A growing body of knowledge shows that changing fuel composition and structure on the nanoscale can increase resistance to radiation damage and facilitate higher burn-ups. Controlling growth mechanisms is a critical aspect of these efforts to synthesize ordered actinide materials. However, the building blocks of actinide materials often lack the directional bonding needed to promote the stereochemical orientations of atoms needed for growth.

This work shows that new synthetic methodology can be invented by developing a conceptual framework that accounts for the role of the coordination chemistry on material growth mechanisms. Our work leverages recent studies from LANL and LBNL, which showed that ligand K-edge X-ray absorption spectroscopy provides a direct and quantitative probe of electronic structure and bonding in actinide molecules. These molecular-level insights provided a basis for efforts to control the volatility and decomposition chemistry of precursors used in materials synthesis. 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. This presentation will also discuss our preliminary efforts to show how controlling properties including particle size and composition in well-defined actinide materials can affect the outcome of chemical and physical processes relevant to the use and storage of advanced nuclear fuels.

NUCL 40

C-term magnetic circular dichroism spectroscopy: From transition metals to f-element chemistry

***Michael L. Neidig**, neidig@chem.rochester.edu. Department of Chemistry, University of Rochester, Rochester, New York, United States*

C-Term MCD Spectroscopy is a powerful method for evaluating electronic structure and bonding in paramagnetic compounds. In particular, this method has been widely developed and utilized in transition metal chemistry, especially in bioinorganic chemistry. Following a discussion of recent applications of this method to understanding electronic structure, bonding and speciation in iron organometallic catalysis, this presentation will focus on recent efforts in our group towards the development and application of *C*-term MCD spectroscopy in f-element chemistry, particularly attractive due to the significance of spin-orbit coupling in both f-element complexes and in the intensity mechanisms in *C*-term MCD spectroscopy. Examples of the application of this technique in both 4f and 5f complexes will be discussed as well as efforts towards the development of theoretical methods for the simulation of *C*-term MCD spectra in f-element systems.

NUCL 41

Synchrotron radiation for the investigation of heavy element science

***David K. Shuh**, dkshuh@lbl.gov. Lawrence Berkeley Natl Lab, Berkeley, California, United States*

Advanced synchrotron radiation investigations utilizing both soft and hard X-rays have been pivotal for an improved understanding of fundamental heavy element chemistry issues over the past several years. The scientific impact of synchrotron radiation studies in heavy element chemistry has led to the regular utilization of many state-of-the-art synchrotron techniques to address a wide range of diverse topics within heavy element science. Early studies frequently used hard X-ray X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure to obtain speciation information from radionuclide systems. More recent studies have employed the full gamut of available synchrotron methodologies from small angle X-ray scattering to resonant inelastic X-ray scattering to microspectroscopies, and even including small molecule X-ray crystallography. Developments for heavy element science at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory have focused on the use of the Molecular Environmental Sciences soft X-ray scanning transmission X-ray microscope at Beamline 11.0.2 for spatially-resolved XANES whereas X-ray emission spectroscopy has been conducted at several beamlines. The recent focus of the ALS investigations has been on fundamental heavy element chemistry studies with the STXM, however, spectromicroscopy capabilities of the STXM provide the means to investigate and determine the speciation in a range of actinide materials, particularly those of

technological and environmental interest with spatial resolution that reaches towards the true nanoscale.

NUCL 42

Activation of uranyl in gas-phase complexes

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

The strong uranium-oxygen bonds in the ubiquitous uranyl moiety, UO_2^{2+}, are notoriously inert. The challenging goal of activation of $U{=}O_{yl}$ bonds concomitant with formation of new bonds has met with limited success in condensed phase chemistry. We approach uranyl oxo-activation by employing gas-phase complexes in which UO_2^{2+} is coordinated by strongly bound anionic ligands. Thermal excitation of complexes with suitable ligation can result in endothermic decomposition processes that result in U=O bond activation. An example is the conversion of a UO_2^{2+}/NCO^- complex to NUO^+ by elimination of CO_2. Activation by less predictable routes has been observed and confirmed by IR spectroscopy, which shows disappearance of the characteristic uranyl asymmetric stretch.

NUCL 43

Separating technetium from nitric acid by trapping in iron oxides

***Wayne W. Lukens**, wwlukens@lbl.gov. Chemical Sciences Division, Lawrence Berkeley National 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 volatilize out of the glass melt unless the electrochemical potential of the glass is sufficiently reducing. The advent of new reprocessing schemes, especially the UREX family, offers the possibility of incorporating ^{99}Tc into a custom waste form since ^{99}Tc is separated as its own waste stream in nitric acid. Work by Skrob and co-workers at Argonne has demonstrated that metallic zinc can be used to reduce and trap Tc(IV) in $Zn(OH)_2$, which provides a blueprint for removal of TcO_4^- from nitric acid by coprecipitation with transition metal oxides. In this case, the resulting material is not a viable waste form due to the solubility of $Zn(OH)_2$. To examine whether a related approach could be a valid route to Tc(IV) doped into environmentally durable iron oxides, the denitration of TcO_4^- in 5 M HNO_3 by formic acid, hydroxylamine, and hydrazine was studied alone and in the presence of iron compounds. The resulting solid materials were characterized by a combination of powder X-ray diffraction and Tc K-edge extended X-ray absorption fine structure

(EXAFS) spectroscopy. The rates of Tc leaching from the resulting iron oxide nanoparticles suspended in deionized water was determined.

NUCL 44

Water adsorption on AnO_2 (An = U, Pu) surfaces

*Joseph Wellington[3], Bengt Tegner[1], Andrew Kerridge[2], **Nikolas Kaltsoyannis**[1], nikolas.kaltsoyannis@manchester.ac.uk. (1) School of Chemistry, The University of Manchester, Manchester, United Kingdom (2) Department of Chemistry, University of Lancaster, Lancaster, United Kingdom (3) Department of Chemistry, University College London, London, United Kingdom*

Over 100 tonnes of separated Pu are stored at Sellafield in the UK as PuO_2 powder in sealed steel cans. Under certain circumstances, gas generation may occur in these cans, with consequent pressurization. Many routes to gas production have been suggested, several of which involve complex, inter-connected and poorly understood PuO_2/H_2O interactions. We are studying these interactions computationally, using DFT within the Hubbard corrected periodic boundary condition (PBC) framework ("GGA+*U*") and also employing an embedded cluster approach (the periodic electrostatic embedded cluster method). In this contribution I will report the latest results from both of these approaches, comparing the geometries and energies of water adsoprtion on both stoichiometric and defect low index surfaces. I will also present our calculations of the water desorption temperatures from these surfaces as a function of pressure.

NUCL 45

Electronic structures and photoelectron spectra of uranium halides and oxides

*Jing Su[1], Lai-Sheng Wang[2], **Jun Li**[1], junli.thu@gmail.com. (1) Department of Chemistry, Tsinghua University, Beijing, China (2) Department of Chemistry, Brown University, Providence, Rhode Island, United States*

Theoretical studies of electronic structure and electronic spectra of actinide complexes are challenging because of significant relativistic effects and complicated electron correlation effects of actinides. Photoelectron spectroscopy (PES) can provide detailed information about the electronic structures of ground states and excited states of actinide species.

In this talk we will present our recent results from a series of joint relativistic quantum chemical and photoelectron spectroscopy studies on actinyl complexes and uranium halides, including $UO_2X_3^-$, $UO_2X_4^{2-}$ (X = F, Cl, Br, I) and UF_x (x = 1-6). Theoretical results from ab initio wavefucntion theory (WFT) calculations agree well with experiments. Extensive bonding analyses show that the U-halogen bonds are dominated by ionic interactions with weak covalency. Further theoretical calculations show that the gaseous $UO_2X_4^{2-}$ complexes are thermodynamically unstable against dissociation to $UO_2X_3^- + X^-$ with decreasing dynamic stability from X = F to I. The competition between the U-X bonding and the Coulomb repulsions determines the kinetic stability of $UO_2X_4^{2-}$.

NUCL 46

Broadening student experiences: Research internships with Los Alamos National Laboratory and the interesting Pu chemistry they performed

Peter K. Dorhout, *dorhout@ksu.edu. Chemistry, Kansas State University, Manhattan, Kansas, United States*

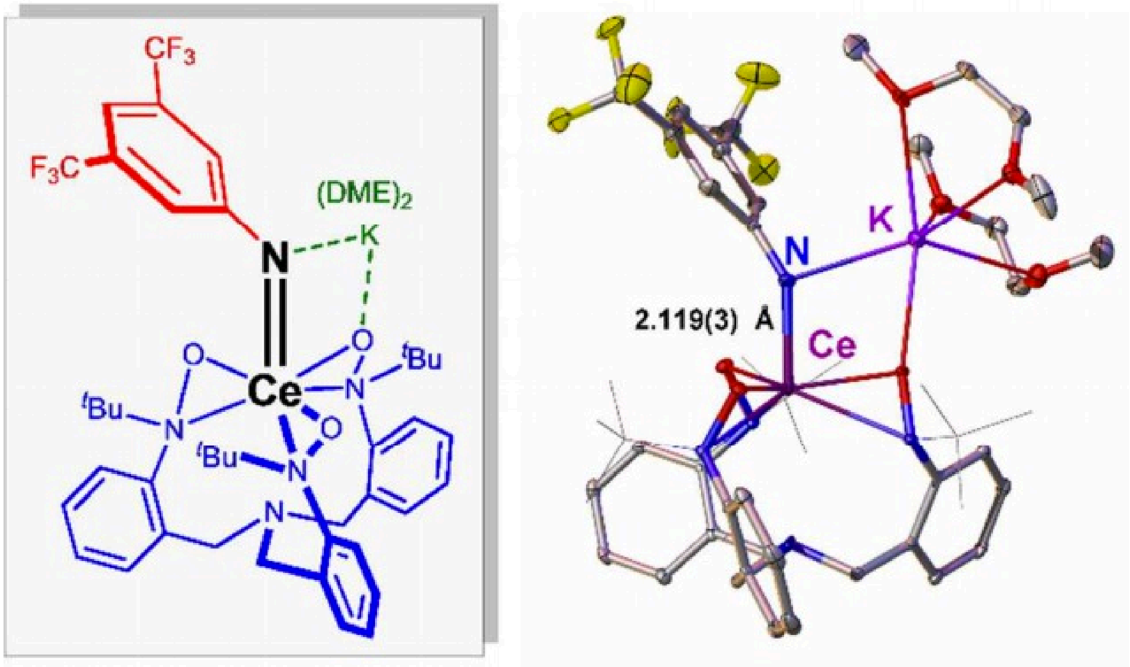
Enriching the student experience in order to prepare the next generation of chemists should involve complex problem solving, working with diverse teams, and moving out of one’s comfort zone. This is especially true for graduate students, the majority of whom continue to seek jobs outside of the halls of academics. A variety of recent reports on graduate education point to the value of industrial internships and study abroad research experiences, including two recent ACS Presidential Task Force analyses. From the perspective of an academic leader in undergraduate and graduate education and research, collaborations with National Laboratories like Los Alamos, the Seaborg Institute, and the National Security Education Center offer a wealth of opportunities to explore the chemistry of plutonium. This talk will focus on our Pu chemistry and the students and postdocs it engaged.

NUCL 47

Realizing cerium(IV)-ligand multiple bonds: Cerium is a 5d element after all?

Eric J. Schelter, *schelter@sas.upenn.edu, Lukman Solola, Alexander V. Zabula, Walter L. Dorfner, Brian Manor, Patrick Carroll. Dept of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Group 3 metal-ligand bonds are challenging synthetic targets but are likewise expected to be reactive for small molecule transformations. Recently, we reasoned that by applying a tailored ligand framework, namely one that electronically supports high oxidation states and provides steric protection, that Ce(IV)=E targets should be accessible. By leveraging the higher oxidation state, the Ce(IV)=E targets are expected to be less reactive and isolable. This hypothesis was a direct extension of insights offered by Dave Clark and co-workers in seminal DFT studies of cerium(IV)-ligand multiple bonds. Their work showed that, in low symmetry settings, such compounds should be stabilized by combinations of both 4f and 5d orbital character in their valence electronic structures. We have contributed to realizing the goal of Ce(IV)-ligand multiple bonds in a recent isolation of the first Ce(IV)-imido complex. The structural and reactivity of this and related compounds will be presented.



NUCL 48

Heavy actinide thermodynamics: Research enabled by the Nuclear Chemistry Summer School

Jenifer Braley, *jenifer.braley@gmail.com, Morgan Luckey, Matt Urban, Nathan Bessen. Chemistry Geochemistry/Nuclear Engineering, Colorado School of Mines, Golden, Colorado, United States*

The Nuclear Chemistry Summer School has provided an introduction to nuclear science for many currently active scientists and, consequentially, has fostered the development of numerous lines of scientific inquiry, in the nuclear field. A recently reinvigorated vein of research has focused on the chemistry of the heaviest available actinides (Am, Cm, Bk, Cf). Certain systems suggest that covalency becomes increasingly important in actinide interactions with increasing atomic number. This is in direct contrast to the common understanding that the actinides become more, not less, lanthanide-like and ionic in their interactions with increasing atomic mass. Spectroscopic and magnetic experiments have provided the basis for the suggestion of increasing covalency for the heaviest actinides, but these measurements do not indicate how or if the covalency strengthens or weakens the given actinide-ligand complex. Resolution of such questions may indicate: 1) If orbital overlap (aka strong) or degeneracy driven (aka weak) covalency is observed in these systems and 2) the possible origin of the covalent interaction. The trans-actinide thermodynamic complexation trends will be considered for a variety of actinide-ligand systems with an eye towards unraveling these questions and highlighting the role the Nuclear Chemistry Summer School had in advancing this research.

NUCL 49

Radiochemistry Center of Excellence and the NCSS: To infinity and beyond

John D. Auxier[2,1]*, jdauxier2@yahoo.com, Matthew T. Cook*[2,1]*, Maik Lang*[1]*, David C. Donovan*[1]*, Howard L. Hall*[2,1]*. (1) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (2) Institute for Nuclear Security, University of Tennessee, Knoxville, Tennessee, United States*

The ACS Nuclear Chemistry Summer School (NCSS) program is widely known as one the best options for undergraduate students to learn about the science of nuclear and radiochemistry. In spite of this success, there continues to a be significant gap in getting undergraduate students from the NCSS program to a graduate program that will ultimately lead to placement in the national laboratory community. In response to this need the Radiochemistry Center of Excellence (RCoE) at the University of Tennessee, Knoxville was established by the National Nuclear Security Administration (NNSA) as a way of providing students opportunities to perform research that could also be dovetailed into a possible entry point into a national laboratory. In this presentation, the focus will be on a number on the ongoing research efforts at the RCoE. In particular, the projects that will be highlighted will be the on-going efforts with rapid separations, development of nuclear codes to predict the fallout in urban environments, surrogate special nuclear material alloys, and the development of new analytical techniques to characterize the fusion reactor experiments.

NUCL 50

From Brookhaven to the Bronx: Radiochemistry and education

Melissa A. Deri*, mderi@gradcenter.cuny.edu. Chemistry, Lehman College CUNY, Holtsville, New York, United States*

Scientific outreach and recruitment, such as that being offered by the Nuclear and Radiochemistry Summer School (NCSS), is incredibly important to the continuing health of the field. I had the opportunity to participate in NCSS at Brookhaven National Laboratory (BNL) in 2009 and it definitely shaped my career since. NCSS played a major part in my decision to apply to graduate school and was entirely responsible for me applying to and ultimately choosing a radiochemistry program in particular. Additionally, I went back to BNL in 2010 as a teaching assistant for the next cohort in NCSS which helped to cement not only my interest in radiochemistry, but also my passion for teaching.

As a doctoral student, my research focused on building a better chelator for zirconium-89 to build improved positron emission tomography imaging agents for use in cancer imaging. My interest in radiopharmaceutical research was spawned during my tenure in NCSS and, in fact, I met both of my PhD mentors during the program. While in graduate school, I helped to develop a new graduate radiochemistry course and taught a few

undergraduate courses that reinforced my interest in teaching and in the field of education.

Since completing my PhD work, I started a postdoctoral fellowship doing research on chemical education and the efficacy of different methods of teaching. While my current focus is on education and science communication, radiochemistry remains a part of my future career goals and it will inform the next steps in my career path which, to a large extent, began with NCSS.

NUCL 51

NCSS to doctoral candidate: Determination of radioisotopes in complex saline matrices

Jaimie K. Daum[1]*, daumj2@unlv.nevada.edu, Ralf Sudowe*[2]*. (1) Radiochemistry, University of Nevada Las Vegas, Las Vegas, Nevada, United States (2) Department of Environmental & Radiological Health Sciences, College of Veterinary Medicine & Biomedical Sciences, Colorado State University, Fort Collins, Colorado, United States*

The 2012 Nuclear and Radiochemistry Summer School at Brookhaven National Laboratory provided an introduction into the foundations of modern nuclear chemistry, which was what initially sparked my passion to pursue a career in the radiochemistry field. The summer school provided the students with the opportunity to interact/learn from principal lecturers and speakers from industry, government, and academics. It was these networking opportunities that solidified my decision to apply to a radiochemistry graduate program. The summer school also offered a hands-on laboratory experience that familiarized the students with the properties and applications of radioisotopes. The procedures and instrumentation utilized within the laboratory course provided a strong foundation for the research that I am currently pursuing through the Radiochemistry Ph.D. Program at the University of Nevada Las Vegas. My work focuses on the development and optimization of radioanalytical separation techniques for the isolation and quantification of radioisotopes within complex matrices. The motivation for this research originates from the environmental impact of contamination from anthropogenic radionuclides on natural resources. Natural waters are the largest recipient of environmental contamination by anthropogenic radionuclides. The elevated salinity of sea and ocean water results in a complex matrix that hinders the isolation, characterization, and determination of the radioisotopes of interest. The work employs novel extraction chromatographic resins in order to determine the effect of matrix constituents, such as those found within sea and ocean water, on their retention capabilities for the radioisotopes of interest. In the aftermath of the reactor accident in Fukushima, it has become obvious that there is a severe lack in methods that would allow the rapid determination of alpha and pure beta-emitting radionuclides in ocean water. This research can be expanded into optimizing the isolation and purification of an array of radioactive species from any type of target/matrix.

NUCL 52

Education blended with inspiration: Nuclear chemistry summer schools

Amanda L. Werlein[1,2]*, awerlein@gmail.com. (1) Department of Chemistry, University of Missouri, Columbia, Missouri, United States (2) University of Missouri Research Reactor, Columbia, Missouri, United States*

For students of nuclear and radiochemistry, opportunities to study at world class intuitions are rare and yet crucial to the development of essential knowledge and skills. Experience gained in the summer school programs cultivates these skills in unique ways and more thoroughly prepares students for future engagements in their field. This talk will summarize personal career influences and the tremendous advantages gained from the high quality classes and mentors found at the nuclear chemistry summer school at Brookhaven National Lab. Current research in archaeometry and past research on separation chemistry will also be briefly covered.

NUCL 53

Thermodynamic analysis of lanthanide halides and oxyhalides

Dorothy Miller[2]*, dj10mill@siena.edu, John D. Auxier*[1]*, Howard L. Hall*[2]*. (1) Department of Nuclear Engineering, Institute for Nuclear Security, Jefferson City, Tennessee, United States (2) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States*

It is well-known that lanthanide elements are important in the area of nuclear forensics, particularly for post-detonation analysis. In the post-detonation arena, rapid separations are necessary to reduce the analysis time following the event. In the past, most of the rare earth separations are performed using traditional liquid methods, which can be time consuming. Therefore, this project seeks to expand the scientific efforts in the super-heavy elements community wherein significant progress has been made in the separation of elements while in the gas phase, such as $Sg(CO)_6$ or as Cn chloride derivatives. In this literature, there is some discussion of the fact that the halide motifs also form a metal oxyhalide (eg $MOCl_x$), and that these separations can be loosely predicted using thermodynamic equations based on the entropy and enthalpy of adsorption to a quartz column. Similarly, the adsorption entropy and enthalpy can be approximated with data from Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). A correlation can be drawn from the respective enthalpy of the complex and the atomic number of the lanthanide. The trend can be compared to that of its halide precursor. With this data, better estimates of retention times can be determined for both halides and oxyhaildes in the application of gas-phase separations.

NUCL 54

From the summer school to graduate school: Leveraging opportunities in nuclear chemistry

Rebecca Lewis[1,2]*, beckylewis17@gmail.com. (1) Department of Chemistry, Michigan State University, East Lansing, Michigan, United States (2) National Superconducting Cyclotron Laboratory, Michigan State University, East Lansing, Michigan, United States*

Research in nuclear science covers a wide range of topics, from radiochemistry to nuclear astrophysics. A student entering graduate school in nuclear science must be prepared to master one or more of these to perform research, usually without any previous exposure in undergraduate classes. The Nuclear Chemistry Summer School changed that for me by teaching the fundamentals of nuclear science through lectures, labs, and interactions with leading researchers. The relationships I formed with students and researchers through the program are very important to my personal and professional growth, and have helped me build a network that covers the entire field of nuclear science. My experience as both a student and a teaching assistant at the summer school gave me the confidence to jump right into a complex research project when I started as a graduate student at the National Superconducting Cyclotron Laboratory at Michigan State University. My work in determining neutron capture cross sections of r-process nuclei using beta decay involves aspects of nuclear structure, reactions, and astrophysics, all of which I had been introduced to before I arrived, thanks to the summer school. The conversations I had with visiting faculty and scientists at national laboratories helped me decide what science I wanted to pursue, and what graduate program would be the best fit for that science. My introduction to nuclear science at NCSS prepared me to be a successful graduate student by exposing me to all aspects of the field and the fundamental concepts that I can build on with my work.

NUCL 55

Nuclear and radiochemistry summer school: (Almost) six years later

Jacquelyn M. Dorhout[1,2]*, dorhoutj@unlv.nevada.edu. (1) UNLV, Las Vegas, Nevada, United States (2) Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

What happens after graduation from the Nuclear and Radiochemistry Summer School program? This talk will focus on my career path after the summer of 2011, including graduate work, fellowship awards, and summer internships, which has ultimately led to a full-time employment opportunity in radiochemistry. The research I plan present will focus on pseudo-post-detonation nuclear forensic signature examinations and organometallic synthetic investigations of thorium and uranium. Due in large part to the ACS Summer School, I was able to make connections and begin a career in radiochemistry that will hopefully enable me to pursue my career in the nuclear forensics field at Los Alamos National Laboratory.

NUCL 56

2016 Class of the DOE Radiochemistry Summer School in Oregon State University

***Alena Paulenova**, paulenoa@engr.orst.edu. School of Nuclear Science and Engineering, Oregon State University, Corvallis, Oregon, United States*

The OSU School of Nuclear Science and Engineering was responsible for hosting the Undergraduate Summer School in Radiochemistry. Conducted together with Department of Chemistry, the six-week laboratory-intense school focused on the back-end of the nuclear fuel cycle. The curriculum covered fundamentals of nuclear science, radiochemistry, detection, chemical properties of radionuclides, separations and actinide speciation in solution, radiation chemistry, reactor and fuel design, fuel cycle stages, different fuel cycle options and international efforts in used fuel management. Hanford site tour was the most appreciated event by students. For their own small research projects, students joined the research groups of Prof. W. Loveland, M. Nyman, A. Paulenova and A. Farsoni. For student professional development a visit from our graduate school and discussions hours with guest speakers with the aim to inform students about career opportunities in radiochemistry, improve their understanding of how to find and apply for graduate school, and boost their self-confidence to develop their own personal career path goals were organized.

NUCL 57

Development of actinide separations in alkaline solutions

***Gordon Jarvinen**, gdjarvinen@gmail.com, Wolfgang H. Runde, George Goff. Los Alamos Natl Lab, Los Alamos, New Mexico, United States*

The processing of used nuclear fuel in alkaline solution provides potentially useful new selectivity for separating the actinides from each other and from the fission products. Over the last decade, several research teams around the world have considered dissolution of used fuel in alkaline solution and further partitioning in this medium as an alternative to acid dissolution. Most work to date has focused on carbonate, peroxide, or carbonate-peroxide solutions and using selective precipitation methods. A limited amount of work on the use of liquid-liquid extraction, ion exchange, and extraction chromatography for actinide separations in alkaline solution has been reported. Most of the coordination chemistry in alkaline solution has been studied under conditions where only one major anionic ligand is present. There are many combinations of ligands that could provide new separation possibilities. A more intensive investigation of the area of actinide alkaline solution chemistry appears warranted.

NUCL 58

Subsurface containment and permanent disposal of nuclear waste: Role and contribution of fundamental actinide science

***Donald T. Reed**, dreed@lanl.gov. Repository Science & Operations, Los Alamos National Laboratory, Carlsbad, New Mexico, United States*

The contributions of fundamental actinide science to the design and implementation of containment and disposal strategies for actinide contaminants and waste are discussed. This understanding is critically needed to support the safety case and provide assurances to the public that the environment will be protected. The real-system application of fundamental scientific results in this instance has led to many remediation and containment approaches to manage nuclear waste issues.

Three areas will be highlighted in this presentation. The first and most important is the role and understanding of the many linkages between oxidation state distribution and the environmental chemistry of the multivalent actinides such as U, Np, Pu and Am. Oxidation state determines the likely solubility, the key interactions, the role and relative importance of complexants, sorptive behavior, and the likelihood of microbial interactions. The second area impacted by basic studies is the colloidal transport of actinides and the role it plays in long-term performance assessment. In many subsurface environments, colloidal transport of transuranics, although very low, is the most likely mechanism for radionuclide migration. Recent progress on the structure and stability of colloidal species will be summarized. Lastly, there are many impacts of the several recent advances in our understanding of the structure of actinide solids and aqueous species based on recent synchrotron-based studies (XANES, EXAFS, etc.) and supporting theoretical calculations. These results confirm the speciation schemes and provide insight into the overall structure and stability of species and solid phases to support long-term modeling predictions.

Throughout this presentation, technical results that also reflect on the many contributions Dr. Dave Clark has made to the Waste Isolation Pilot Plan repository and waste cleanup and remediation of Rocky Flats will be highlighted.

NUCL 59

Recent progress in studies of internuclear interactions in heavy element systems by solid-state NMR and NQR spectroscopy

Herman Cho[1]*, hm.cho@pnl.gov, Cigdem Capan*[2]*, Richard Dempsey*[2]*, Bruce K. McNamara*[1]*, Sergei Sinkov*[1]*, Chuck Soderquist*[1]*. (1) Pacific Northwest National Laboratory, Richland, Washington, United States (2) Physics and Astronomy, Washington State University, Richland, Washington, United States*

A number of important radioisotopes, including ^{99}Tc, ^{227}Ac, ^{229}Th, ^{231}Pa, ^{233}U, ^{235}U, ^{237}Np, and ^{239}Pu, have non-zero nuclear spin, and can in principle be detected by nuclear magnetic resonance (NMR) or nuclear quadrupole resonance (NQR) spectroscopy. We will review advances in instrumentation and experimental techniques that make it possible to probe the electronic structure of transition metals and actinide elements by state of the art NMR and NQR measurements of these nuclides.

NUCL 60

Amplification in late actinides: How the minor nuances of electronic structure create bulk effects

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

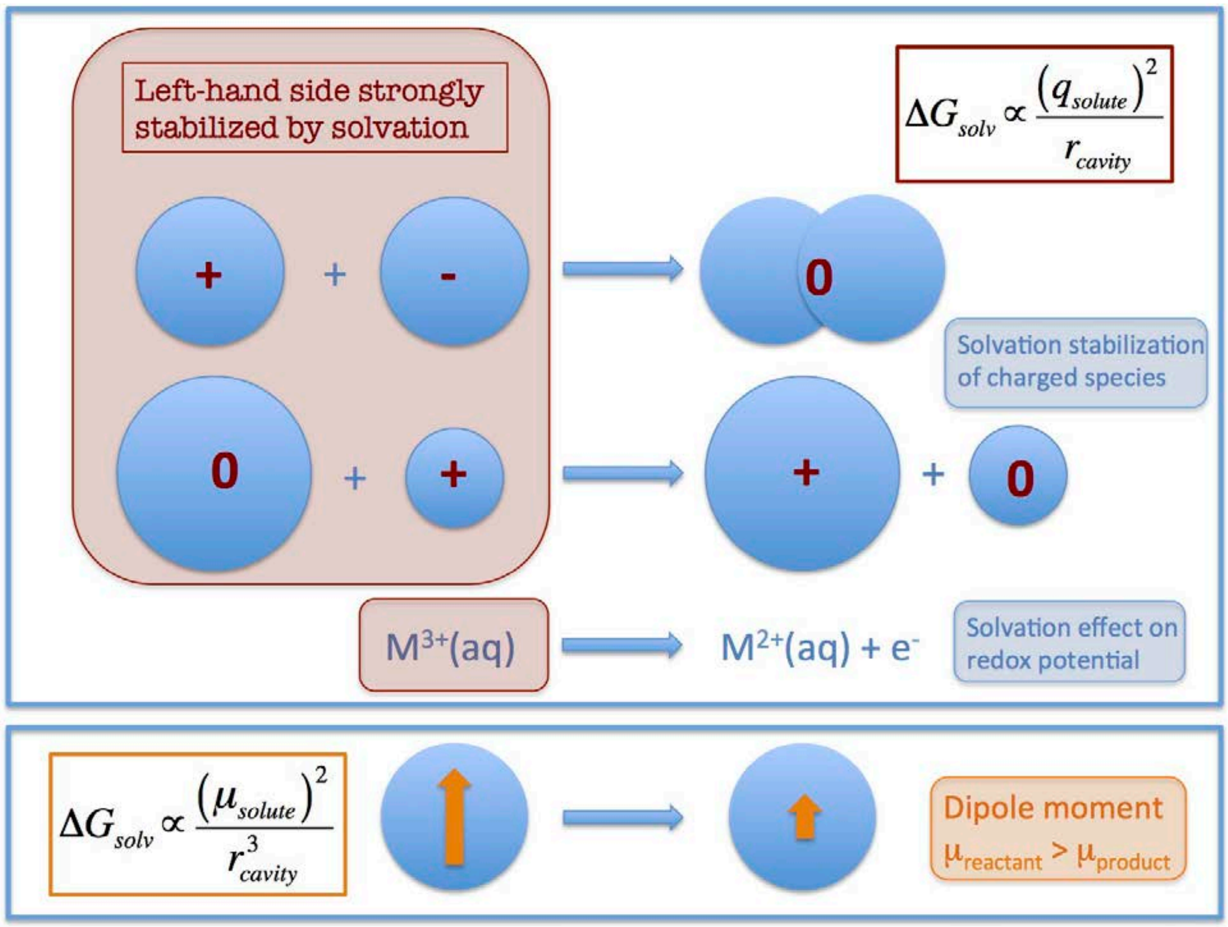
This talk will focus on the fine details of electronic structure in berkelium and californium compounds. Specifically, we will examine the roles of the ligand-field splitting, spin-orbit coupling, and covalency in determining the magnetic and optical properties of these elements in several divergent chemical systems. We will demonstrate that minute changes in bond distances that are barely statistically significant create rather large changes in observable bulk properties, especially at low temperatures. We will also demonstrate that the properties of molecules containing these elements can be quite different from that observed in materials with extended structures. We will conclude with a broad overview of the electronic properties of actinide compounds that will demonstrate that the broad swath often used to descibe lanthanides extends rather poorly to actinides.

NUCL 61

Differential solvation effects on reaction energetics

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

Computational chemistry, and science in general, produce large amounts of data, and it becomes increasingly important to add understanding to these. This presentation will focus on the effect of solvation on reaction equilibria. For reactions containing ions, the Born equation can be used for qualitative - and sometimes even semi-quantitative - interpretation of differential solvation effects (preferred solvation stabilization of one side of the reaction over the other), noting that the free energy of solvation in the Born approximation is proportional to the charge squared and inversely proportional to the cavity radius. We will illustrate these ideas with several examples, including redox potentials and the preference of macrocycles for actinyl(V) over actinyl(VI) inclusion complexes. For reactions containing only neutral species, a similar approach can be based on the Kirkwood-Onsager equation, provided that the molecular charge distribution is well described by the dipole moment.



NUCL 62

Actinide-sulfilimine chemistry

__Justin R. Walensky__, walenskyj@missouri.edu. Chemistry, University of Missouri, Columbia, Missouri, United States

Besides one report by Gilje, the chemistry of the actinides with sulfilimines is nonexistent. There are interesting class of ligands since they have the ability to donate electron density to the metal center to stabilize higher oxidation states in a similar manner to ketimides. Our results with sulfilimine and sulfone ligands in organoactinide chemistry will be presented.

NUCL 63

Preparation and reactivity of the $[Re_2F_8]^{2-}$ anion

__Frederic Poineau__[2], poineauf@unlv.nevada.edu, Samundeeswari Mariappan Balasekaran[2], Alfred P. Sattelberger[1]. (1) Rm A210, Argonne Nat Laboratory, Lemont, Illinois, United States (2) UNLV, Las Vegas, Nevada, United States

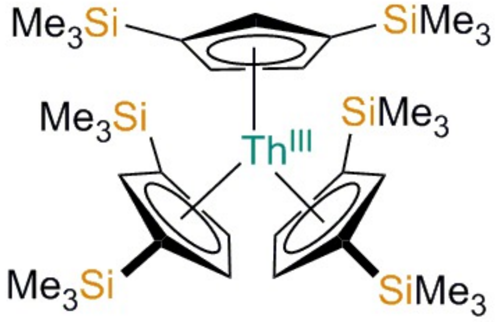
The octachlorodirhenate(III) anion is the archetypal quadruply metal-metal bonded complex. The study of its molecular and electronic structure, and its spectroscopic properties, was key to the development of multiple metal-metal bond chemistry. Studies of the lighter halogen derivative, $[Re_2F_8]^{2-}$ are sparse and since its discovery, only a few reports have been published.
Here, a simple and high yield method for the preparation of $(NH_4)_2[Re_2F_8].2H_2O$ is presented. The method involves the reaction of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ with molten ammonium bifluoride. The new $(NH_4)_2[Re_2F_8].2H_2O$ salt was characterized in solution and in the solid-state by spectroscopic and diffraction techniques. The $[NH_4]_2[Re_2F_8].2H_2O$ salt was used as a precursor in synthetic chemistry and new rhenium dinuclear complexes were obtained.

NUCL 64

Thorium redox chemistry and a new way to measure actinide covalency by pulsed EPR spectroscopy

David Mills[3]*, david.mills@manchester.ac.uk, Eric McInnes*[3]*, Floriana Tuna*[3]*, Andrew Kerridge*[4]*, Laurent Maron*[2]*, Alasdair Formanuik*[3]*, Ana-Maria Ariciu*[3]*, Fabrizio Ortu*[3]*, Jingjing Liu*[3]*, Reece Beekmeyer*[5]*, Ludovic Castro*[1]*. (1) LPCNO, Toulouse Cedex 4, France (2) Dept de Genie Physique, LPCNO, Toulouse, France (3) School of Chemistry, The University of Manchester, Manchester, United Kingdom (4) Chemistry, Lancaster University, Preston, United Kingdom (5) Chemistry, University College London, London, United Kingdom*

In contrast to molecular uranium redox chemistry, which has blossomed in recent years due to the relatively facile interchange between a variety of oxidation states, the corresponding thorium chemistry is underdeveloped as the +4 oxidation state predominates and strong reducing agents are often necessary to access subvalent compounds. Inspired by the remarkable small molecule activation properties of U(III) compounds, we have embarked upon full reactivity studies of Lappert's Th(III) complex $[Th\{C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**1**) and its hydrocarbyl analogue, $[Th(C_5H_3{}^{t}Bu_2\text{-}1,3)_3]$ (**2**). For **1**, we are discovering reactivity profiles that complement and contrast with better understood homoleptic U(III) substituted cyclopentadienyl complexes. For **2**, we have employed pulsed EPR spectroscopy to determine spin density at ligand C_5 ring ^{13}C nuclei, and therefore the covalency of Th-C bonds in this molecule. Our recent progress will be discussed here.



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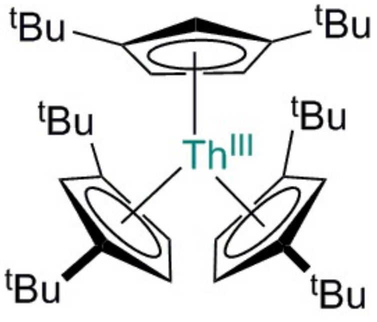

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NUCL 65

Structures and phase transitions of the actinide hexachlorides

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

The actinide hexachlorides of Th, Pa, U, Np, and Pu have been used as model systems for the study of f-element electronic structure, magnetic properties and as benchmarks in computational studies. Despite their simple chemical compositions and generally high symmetry, these salts exhibit complex structural properties including phase transitions with isotope effects observed for the transition temperatures. Such effects are not uncommon in transition metal and semi-metal hexahalides, but are until recently uncharacterized for the tetravalent actinides. This presentation will focus on the structures and dynamics of these fundamentally important chemical model complexes of the tetravalent actinides, their structures, phase transitions, and their vibrational spectroscopy. As a group these molecules are fundamentally important to understanding periodic properties across the early actinide series of elements.

NUCL 66

Why does solid PuO_2 possess no magnetic moment?

***Richard L. Martin**, bonsainouka@gmail.com. Theoretical Division, Los Alamos Natl Lab, Los Alamos, New Mexico, United States*

PuO_2 is now known to be a charge transfer insulator with a significant band gap (~2.8eV). While conventional DFT approaches incorrectly predict it to be a metal, hybrid DFT yields predictions in excellent agreement with experiment as regards the magnitude and nature of the gap, the lattice constants, and the x-ray absorption and photoemission spectra. In particular, hybrid DFT predicted, and photoemission experiments found, unexpected covalency (dispersion) in PuO_2. In addition, hybrid DFT predicts PuO_2 to have sizeable magnetic moments (high-spin f^4) on the Pu sites ordered

antiferromagnetically. In fact, PuO_2 has no magnetic moment. Neither does metallic δ-Pu, also a long-standing challenge to theory and in disagreement with DFT predictions. In this talk I will present wave-function based calculations for a single site cluster model of PuO_2. The ground state of the cluster is found to be J=0. Metal-ligand mixing is shown to be responsible for quenching the moment from the J=4 ground state predicted in a purely ionic model. The extent to which these local effects may play a role in the extended solid are discussed.

NUCL 67

Electronic structures of F_3UAH (A = C - Fl) molecules: Lewis Electron-Pair (LEP) model revisited

*Han-Shi Hu[1], Wan-Lu Li[1], **Jun Li**[1,2], junli.thu@gmail.com. (1) Department of Chemistry, Tsinghua University, Beijing, China (2) Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland 99352, Washington, United States*

Lewis electron pair (LEP) model has established electron pair as one of the most useful concepts in chemistry in the 20th century. The importance of this model can hardly be overstated because of the role it plays in chemistry in interpreting structures and bonding of chemical compounds, although it was established prior to the finding of quantum mechanics. In the Periodic Table, each period row corresponds to the filling of electrons in quantized shells. The elements in the same group column usually have similar properties due to the same electron configuration in their valence shell. However, heavier p-block main-group elements tend to have more or less different chemical bonding from those of 2p elements partly due to *quantum primogenic effect*. Here we discuss the U-A (A = C, Si, Ge, Sn, Pb, Fl) chemical bondings of F_3UAH complexes based on quantum chemical analyses of density functional theory (DFT) and *ab initio* wavefunction theory (WFT). We have shown that while U-C maintains perfect multiple bonds in F_3UCH, the naively anticipated “Lewis electron pairs” between U-A in F_3UAH (A = Si, Ge, Sn, Pb, Fl) were broken, leading to a multi-radical bonding scenario. The implication of this finding to chemical bonding in heavy-elements will be discussed.

NUCL 68

Experimental and computational study of protactinium, the transition metals and the actinides

***Richard Wilson**[1], rewilson@anl.gov, Valerie Vallet[2]. (1) Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois, United States (2) UFR de Physique, CNRS - University Lille 1, Villeneuve dAscq, France*

The periodic stabilization of the 5f orbitals across the early actinide series gives rise to the complex and fascinating chemical behavior that is the hallmark of these elements’ chemistry. Often overlooked, both experimentally and computationally, is the chemistry of protactinium, Z = 91. Our hypothesis has been that protactinium sits at a chemical

intersection of transition metal d- and actinide f- like chemistries that can be demonstrated experimentally and computationally. Recently, we have explored by experiment, whether or not protactinium may form a hexametalate, like that observed for niobium and tantalum. Complementary computational studies have explored whether or not such a complex would be stable. Additionally the electronic properties of our experimentally synthesized protactinium complexes, along with those of Nb, Ta, and U have been studied to explore the periodic chemical differences between these elements. Presented here will be our combined experimental and computational study of the changing chemistries between the transition metals and the actinides, highlighting their intersection at protactinium.

NUCL 69

Still thoroughly modern at 25: The FEUDAL bonding model

Jason L. Sonnenberg, *sonnenberg.11@osu.edu. Gaussian Inc., Wallingford, Connecticut, United States*

The FEUDAL description of actinide bonding was one of the first qualitative models for bonding in actinide complexes. Built from synergistic experimental and computational work on a variety of organoactinide complexes containing formally anionic ligands, it was later extended to neutral ligand sets. The continued relevance of the FEUDAL model is described in the context of organometallic complexes containing naturally occurring siderophores. Results from scalar-relativistic density functional theory calculations will be presented.

NUCL 70

Magic journey in metal-metal multiple bonds

Laura Gagliardi, *gagliard@umn.edu. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, United States*

I will describe how our theoretical studies on metal-metal multiple bonds have been inspired by Bruce Bursten’s pioneering work. The challenges of modeling electron correlation and relativistic effects in systems containing actinides and transition metals will be discussed and some recent results will be presented.

NUCL 71

Covalency in 4f-element complexes probed with quantum mechanics and ligand K-edge x-ray absorption spectroscopy

Enrique R. Batista[2], *erb@lanl.gov, Ping Yang*[2], *Richard L. Martin*[4], *Stosh A. Kozimor*[3], *David L. Clark*[1]. *(1) Natl Security Education Center, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Theoretical Division, Los Alamos National*

Laboratory, Los Alamos, New Mexico, United States (3) Los Alamos Natl Lab, Los Alamos, New Mexico, United States (4) MS B214 Theoretical Div, Los Alamos Natl Lab, Los Alamos, New Mexico, United States

The presence or absence of significant participation in chemical bonding by the f-orbitals in lanthanide and actinide materials has been a subject of debate for many years. This discussion stems from the clear evidence that the 4f electrons in the lanthanide series are contracted act core like. The FEUDAL model presented by Bursten hypothesized that the f orbitals store electrons but do not participate in bonding, whereas it is the d electrons that do the heavy lifting. In this talk, we will discuss computational studies in synchronicity with spectroscopic probe measurements on a series of electronic structure description of bonding in a series of lanthanide compounds. We found that the FEUDAL model can successfully explain most of most of the systems with a few exceptions where the participation of 4f electrons in the metal-ligand bond is non negligible and unexpected.

NUCL 72

Theory enables soft x-ray synchrotron radiation spectroscopy of heavy element materials

***David K. Shuh**, dkshuh@lbl.gov. Lawrence Berkeley Natl Lab, Berkeley, California, United States*

An absolutely critical and key enabling component for soft X-ray synchrotron radiation investigations is the contribution of theory when combined with and or leading experiments, has served to provide much more detailed understandings of electronic structure in heavy element materials. Soft X-ray experimental studies of heavy element materials have centered on the use of the scanning transmission X-ray microscope (STXM) at the Molecular Environmental Sciences (MES) Beamline 11.0.2 for near-edge X-ray absorption spectroscopy (XAS), and on X-ray emission spectroscopy (XES) at several beamlines, focusing primarily on light atom constituents (C, N, O, F) for ligand K-edge XAS, and on metal-ion centers plus light-atom signals for XES. Recent results for heavy element oxide systems benefit from the combined use of XAS and XES techniques to garner information about the unoccupied and occupied partial density of states, respectively. The collaborative soft X-ray investigations have begun to yield valuable knowledge from which to understand the overall reactivity of heavy element materials, thereby providing improved starting points for the enhanced design of special-purpose heavy element materials. Furthermore, the effective combination of theory and soft X-ray experiments has significantly lessened the barrier to new, future investigations of heavy element chemistry in the soft X-ray regime.

NUCL 73

Photoelectron spectroscopy and density functional theory: The interplay of experiment and theory

***Jennifer C. Green**, jennifer.green@chem.ox.ac.uk. Chemistry, Oxford University, Shipston-on-Stour, United Kingdom*

Case studies are presented of metal-metal bonding, spin-orbit coupling and t_1 interactions where both spectroscopy and theory have built models for the electronic structure of heavy element compounds.

NUCL 74

Stabilities of actinide oxidation states in gas-phase complexes

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

The wide range of accessible oxidation states, from II to VII, is a distinguishing feature of actinide chemistry. The objective of evaluating intrinsic stabilities of actinide oxidation states, particularly extreme oxidation states, is pursued in the gas phase absent stabilizing effects imparted by complex interactions in liquids or solids. The extreme high oxidation states, Np(VII) and Pu(VII), have been assessed in elementary gas-phase complexes and molecules by reactivity, and complementary computations. Other unusual oxidation states of interest include Bk(IV) and Cf(II), and that in “protactinyl”, PaO_2^{2+}. The results provide insights into fundamental actinide chemistry, including the role of 5f electrons in bonding and redox behavior.

NUCL 75

Complexation of Am^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+} with DPA ligand in water: A theoretical study

***Ping Yang**[1], pyang@lanl.gov, Morgan Kelley[1], Enrique R. Batista[1], Jenifer Braley[1]. (1) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (1) Chemistry Geochemistry/Nuclear Engineering, Colorado School of Mines, Golden, Colorado, United States*

We will present recent results in quantum chemical computations applied to heavy element chemistry and demonstrate how the synergy between theory and experiment has greatly accelerated progress in this field. Particularly, we will focus on the complexation of trivalent americium, curium, berkelium, and californium in aqueous solution. We will show the predictive capability of first-principle methods in the structures of the complexes and the binding affinity of ligands composed of multiple competitive binding sites to the actinide centers. The theoretical results compared well with experimental characterization data and provide insights into the nature of bonding, as well as solvent effects.

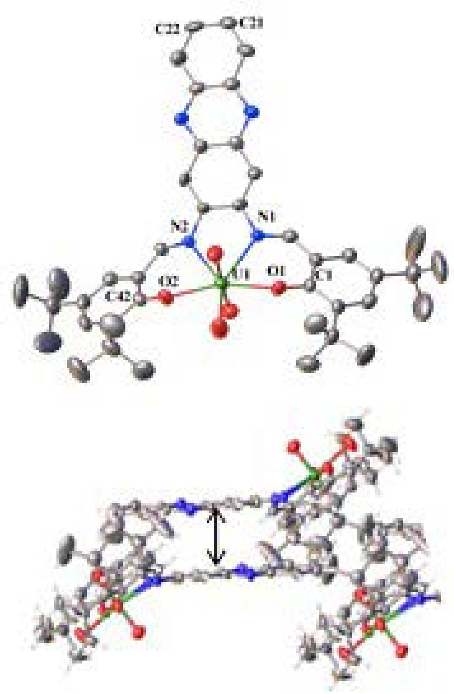
NUCL 76

Taking advantage of the chemistry of heterocycles in actinide coordination: Crystal packing, reactivity, and pi-pi interactions of nitrogen donor ligands containing naphthalene and phenazine

Anne E. Gorden*, gordeae@auburn.edu, Emily E. Hardy, Kevin M. Wyss, Madeleine A. Eddy, Rebecca J. Keller. Chemistry and Biochemistry, Auburn University, Auburn, Alabama, United States*

An increase in the use of nuclear fuels for electrical power production is one proposal to limit global dependence on fossil fuels; however, the environmental and health concerns that surround the use of nuclear fuels and the wastes generated still limits the acceptance of nuclear power by the public. New materials are required that can coordinate, sense, and isolate actinides both for use in chemosensors and decontamination applications.

In an effort to develop inexpensive ligands for selective colorimetric sensing of actinides, we have developed ligands incorporating quinoxalines, pyridines, phenazines and other imine aza-donors. We have used these complexes to probe the contributing factors toward selectivity, signal intensity, and the actinides uranium and thorium, and distinguish these from first row transition metals. We found that the hypsochromic shift upon UO_2^{2+} ion complexation of ligand is due to ligand to metal charge transfer, while the bathochromic shift observed with the addition of Cu^{2+} or other transition metal ions is metal to ligand charge transfer. Here, new complexes are reported containing lanthanides and thorium, and we describe the further expansion of these systems to include characterize other aromatic extended systems and their unique packing and pi-pi interactions.



Projections of UO_2^{2+} salphenazine complex featuring a tetradentate oxygen-nitrogen-nitrogen-oxygen coordination core. Solid-state dimers and pseudo 2-D sheets are also shown. Carbon atoms shown in grey, nitrogen shown in blue, oxygen shown in red, hydrogen (when not omitted for clarity) are shown in white. Interstitial solvents were removed for clarity.

NUCL 77

Unique advantages of organometallic supporting ligands

***Paula Diaconescu**, pld@chem.ucla.edu. UCLA, Los Angeles, California, United States*

Ancillary ligand design in organometallic chemistry is drawing increasingly on inducing ligand participation in reactions of the metal. Chelating ferrocene diamides possess unique electronic characteristics that make them especially versatile in supporting a wide range of reactivity behaviors for the resulting metal complexes. The reactivity of rare earth and actinide complexes supported by ferrocene diamides will be discussed. Redox reactions and unusual mechanisms will be emphasized.

NUCL 78

Complexes of uranium and thorium with multiple bonds to tetryl and pnictide centers

***Stephen T. Liddle**, steve.liddle@manchester.ac.uk, John Seed, Matthew Gregson, Ashley Wooles, Floriana Tuna, Eric McInnes. School of Chemistry, The University of Manchester, Manchester, United Kingdom*

Determining the electronic structure of actinide compounds remains one of the most complex challenges in molecular chemistry, and thus there is currently great interest in preparing and studying novel actinide-element multiple bonds. To achieve this endeavor it is necessary to prepared new metal-ligand linkages and study them in-depth. This contribution will overview our recent studies of uranium and thorium complexes that exhibit metal-carbon, -pnictide, and –oxo multiple bonds.

NUCL 79

Synthesis and x-ray crystallographic characterization of low valent organoplutonium complexes: Identification of plutonium in the +2 oxidation state

Cory J. Windorff[3,2]*, cjwindorff@gmail.com, Brian Scott*[1]*, Andrew Gaunt*[1]*, Stosh A. Kozimor*[2]*, William J. Evans*[4]*. (1) LANL, Los Alamos, New Mexico, United States (2) Los Alamos Natl Lab, Los Alamos, New Mexico, United States (3) Chemistry, UC-Irvine, Irvine, California, United States (4) Dept of Chemistry, University of California Irvine, Irvine, California, United States*

Although organometallic chemistry has been heavily studied 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, no full structural characterizations have been reported in the literature on any organoplutonium complexes. We now report the synthesis and crystallographic-characterization of the Pu(III) complex $Pu[C_5H_3(SiMe_3)_2]_3$. This complex was prepared for evaluation as a possible precursor to a Pu(II) product. Reduction of the silylcyclopentadienyl complexes $M(C_5H_4SiMe_3)_3$ and $M[C_5H_3(SiMe_3)_2]_3$ have recently provided the first examples of M(II) complexes for yttrium and all the lanthanides as well as uranium and thorium. Reduction of $Pu[C_5H_3(SiMe_3)_2]_3$ with potassium graphite in the presence of 2.2.2-cryptand proceeds similarly and gives crystals of the first example of Pu^{2+} as [K(2.2.2-cryptand)]$\{Pu[C_5H_3(SiMe_3)_2]_3\}$ which has been characterized by X-ray crystallography, UV-VIS-NIR and ^1H NMR spectroscopies.

NUCL 80

Pushing the limits with f element-ligand multiple bonding

Trevor W. Hayton*, hayton@chem.ucsb.edu. University of California Santa Barbara, Goleta, California, United States*

Complexes with f element-ligand multiple bonds are of interest for the insight they give into covalency and f orbital participation in bonding. Previously, we prepared a complete series of isostructural actinide chalcogenides, $[An(E)(NR_2)_3]^-$ (An = Th, U; E = O, S, Se, Te; R = $SiMe_3$), to explore these questions. More recently, we have attempted to extend this series to the lanthanide elements. Herein, we will discuss our attempts to synthesize the analogous cerium complexes, $[Ce(E)(NR_2)_3]^-$. Our initial experiments

suggest that the synthetic procedures used to prepare the actinide chalcogenides are not applicable to cerium. However, we have found that judicious modification of our synthetic protocol allows for the isolation of a novel cerium oxo complex, $[Ce(O)(NR_2)_3]^-$. Its synthesis, characterization, and reactivity will be discussed in detail.

NUCL 81

Mediating redox chemistry at the lanthanides using redox-active ligands

*Scott A. Pattenaude, Ezra J. Coughlin, Matthias Zeller, **Suzanne C. Bart**, scbart37@gmail.com. Department of Chemistry, Purdue University, West Lafayette, Indiana, United States*

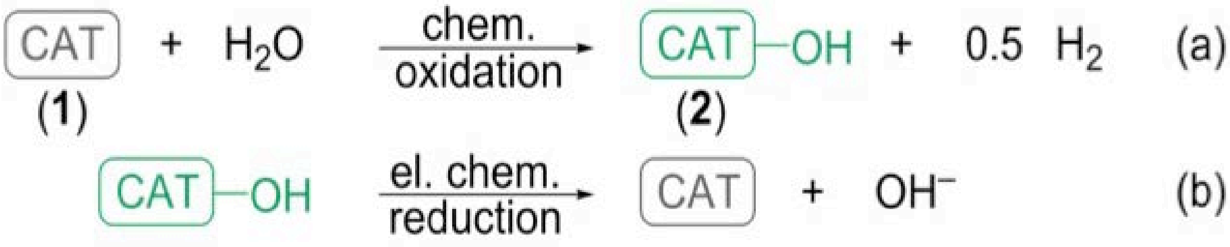
The Lanthanides are typically known for their preference to exist as +3 ions, which precludes them from performing chemical transformations that require redox processes. However, redox active ligands are capable of facilitating redox chemistry at metals that would not otherwise be able to participate in these important reactions. Our group has successfully demonstrated such ligands can mediate redox processes at uranium, imparting transition-metal like reactivity. Recently, we have adapted this strategy to the Lanthanides, showing that performing redox chemistry at the ligand frameworks can serve as a general strategy to perform multi-electron redox reactions. Our most recent studies involving neodymium will be presented, including the synthesis and characterization of new species bearing redox active ligands, as well as their reactivity towards a variety of substrates. Full spectroscopic and structural characterization will also be discussed.

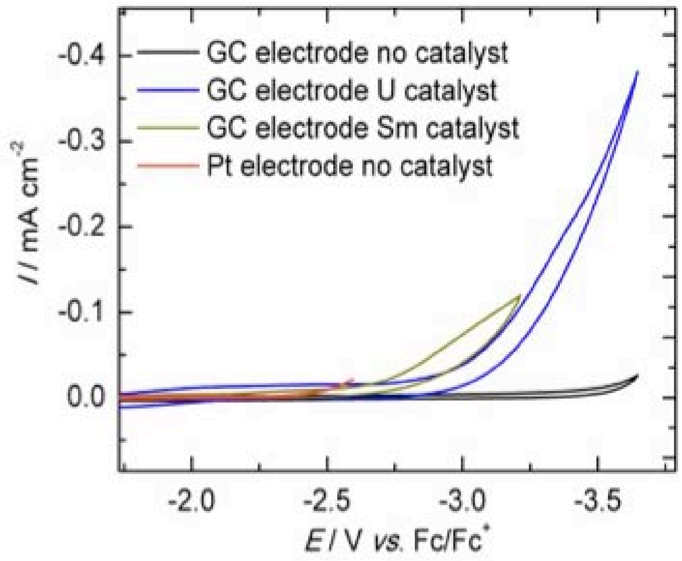
NUCL 82

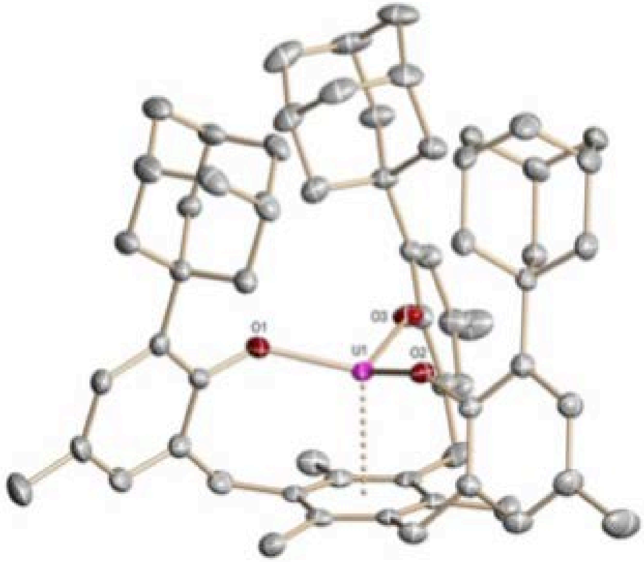
Electrocatalytic production H_2 from H_2O with f-element-based molecular catalysts

***Karsten Meyer**, karsten.meyer@fau.de. Inorganic Chemistry, FAU Erlangen-Nürnberg, Erlangen, Germany*

Research on renewable energies and energy storage, such as H_2 production from H_2O, has become a key challenge for our society. The low efficiency of conventional H_2O electrolysis precludes large-scale applications. Thus, catalysts are desired to make this otherwise convenient strategy more applicable. Due to the high reactivity and oxophilicity of trivalent uranium complexes, as well as the large-scale availability of depleted uranium (^{238}U, DU), uranium complexes are widely discussed as effective and economic catalysts for stable substrates, such as CO_2 and H_2O. In our previous studies of the uranium-monoarene complex $[(^{Ad,Me}ArO)_3mes)U]$ (**1**), unique electrochemical and well defined synthetic behavior were found, rendering **1** a perfect candidate for electrocatalysis. Indeed, trivalent uranium coordination complex **1** was found to be the first molecular uranium catalyst for electrocatalytic H_2 production. Utilization of **1** during H_2O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance of the reaction by 3 orders of magnitude. Isolation of key intermediates and *in situ* EPR experiments allowed to determine the reaction mechanism of H_2O reduction with low valent U(III). This reactivity is now studied in a series of lanthanide complexes $[(^{Ad,Me}ArO)_3mes)Ln]$ (**2–Ln**), which allows for fine-tuning of overpotential and reactivity of the catalyst by choice of the lanthanide ion.







NUCL 83

Evaluation of mixed actinide oxides by laser ablation ICP-MS

*Keri Campbell[2,1], Aaron Unger[1], William M. Kerlin[1], Thomas Hartmann[1], Julie Bertoia[1], Elizabeth Judge[2], Matthew Dirmyer[2], **Ken Czerwinski**[1], krczer@gmail.com. (1) Radiochemistry, University of Nevada Las Vegas, Henderson, Nevada, United States (2) Chemistry Division C-CDE, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

The ability to examine elemental and isotopic ratios of fuels, waste forms, and other solids by direct analysis using laser ablation techniques can greatly reduce analysis costs and time while reducing worker dose. Applying this method to the actinide elements is especially relevant, as these isotopes contain useful information related to nuclear fuel behavior, material origin, and waste form properties. Current methods to evaluate the composition of used fuel include a lengthy process of digestion, separations and often require multiple techniques and sample preparations to determine the elemental and isotopic composition. These techniques also remove all spatial information during the analysis, preventing the collection potentially useful data for detailed analysis.

The goal of this effort is to develop and optimize laser ablation inductively coupled mass spectrometry (LA-ICP-MS) for applications to the analysis of fuel, used fuel, and waste forms. This work focuses on uranium oxide simulated used nuclear fuels starting with binary systems of $(U,Pu)O_2$, $(U,Np)O_2$, $(U,Ce)O_2$ and $(U,Zr)O_2$. Methodology was successful in observing linearity of 0.995 and greater for these systems. This result was achieved by minimizing the particle size distribution of the aerosol and in turn decreases the time-dependent fractionation often observed in LA-ICP-MS.

Actinide matrices and standards were prepared and characterized by physical, thermodynamic, and chemical analysis. The limit of detection, accuracy, and precision of LA-ICP-MS was evaluated using the oxide material. The ablation zone on the material was assessed for physical and chemical changes to determine impact of ablation. The ablation behavior of the elements tested was correlated with physical and thermodynamic properties of the materials. The heat capacity of the materials was measured to determine trends with thermodynamic properties of the desired elements. The limit of detection for ^{239}Pu in a UO_2 matrix was determined to be 0.026 wt. %. The LA-ICP-MS is an excellent technique for determining ^{239}Pu in a UO_2 matrix that will determine burnup rates well below 13 MWd kg^{-1} HM. This technique could be applied to fresh or used fuel to quantify plutonium and neptunium for safeguards, nuclear forensics, and the nuclear fuel cycle.

NUCL 84

Computational study of semiconducting layered technetium chalcogenide compounds

Eunja Kim[4]*, kimej@physics.unlv.edu, Philippe Weck*[2]*, Frederic Poineau*[3]*, Alfred P. Sattelberger*[1]*, Ken Czerwinski*[5]*. (1) Rm A210, Argonne Nat Laboratory, Lemont, Illinois, United States (2) Sandia National Laboratories, Albuquerque, New Mexico, United States (3) UNLV, Las Vegas, Nevada, United States (4) Physics, UNLV, Las Vegas, Nevada, United States (5) UNLV Dept of Chemistry, Las Vegas, Nevada, United States*

Transition-metal dichalcogenides are an important class of inorganic materials exhibiting a wide spectrum of catalytic, electronic, magnetic, and optical properties. Transitionmetal dichalcogenides (TMDs) with layered structures (e.g. MoS_2 or WSe_2) are considered attractive for use in next generation nanoscale field-effect transistor (FETs) devices. Among TMDs, relatively limited knowledge is available on technetium dichalcogenides. The long-lived β−–emitting isotope, 99Tc ($t_{1/2}$ = 2.13 x 10^5 years, β^-=294 keV), is produced in sizable amounts from the nuclear fuel cycle (up to 6% yield from the fission of ^{235}U) and constitutes an important challenge for environmental remediation. The immobilization of Tc as Tc–sulfide compounds has been investigated experimentally. The Tc–chalcogenide system can be important in the fields of nuclear waste management and nuclear medicine. Here, we discuss the structures and properties of layered technetium dichalcogenides TcX_2 (X = S, Se, Te) investigated using density functional theory. The equilibrium structures of TcSe2 and $TcTe_2$, adopting distorted $Cd(OH)_2$-type unit cells similar to TcS_2, are reported for the first time at the atomic level, along with their electronic properties. In contrast to previous X-ray diffraction analyses, calculations reveal that stoichiometric $TcTe_2$ is not isomorphous to the high-temperature monoclinic phase β–$MoTe_2$. The thermal properties of these TcX_2 compounds have also been predicted using phonon frequencies calculated with density functional perturbation theory.

NUCL 85

Computational studies of hydrolysis reactions of cationic and anionic actinide complexes

***David A. Dixon**[2], dadixon@ua.edu, Monica Vasiliu[2], Hayden Arnold[2], Kirk A. Peterson[3], John K. Gibson[1]. (1) Lawrence Berkeley National Laboratory, Emeryville, California, United States (2) Chemistry Dept, Shelby Hall, The University of Alabama, Tuscaloosa, Alabama, United States (3) Washington State University, Pullman, Washington, United States*

There is substantial interest in understanding the reactions of water with complexes containing actinides to better understand their aqueous chemistry. The hydrolysis reactions of AnO_2^+ for An = Pa to Cf as well as for ThO_2 and UO_2^{2+} were studied to examine the role of filling the f shell in the An(V) oxidation state. The potential energy surfaces show that the reaction proceeds initially via a Lewis acid-base interaction followed by a proton transfer step to form the $MO(OH)_2^+$ intermediate which may or may not be symmetric. These calculations were done at the CCSD(T) level with large basis sets. Density functional theory was used to study the reactions of $H_2O + MO(NO_3)_3^-$ and the reactions of HNO_2 with $MO(NO_3)_3^-$ and AnO_2^+.

NUCL 86

Calculating fellow: A theoretical tribute to Bruce Bursten

***David E. Hobart**[1,2], dhobart15@gmail.com. (1) National Security Education Center, Los Alamos National Laboratory, Santa Rosa Beach, Florida, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Bruce E. Bursten received his SB from the University of Chicago, his PhD from the University of Wisconsin-Madison and was an NSF postdoc at Texas A&M. He joined the faculty of Ohio State University as Professor of Chemistry and later as Chair. Bursten then moved to the University of Tennessee, Knoxville as Distinguished Professor of Chemistry and Dean of the College of Arts and Sciences. While President of the ACS he founded the ACS Fellows Program. He is presently Provost, Senior Vice President and Professor of Chemistry at Worcester Polytechnic Institute and Retired Chair of the

Section on Chemistry of the AAAS. He is an internationally recognized authority in the correlation of theoretical and experimental electronic structural data with the bonding and reactivity of heavy element-containing molecules. The presentation will conclude with the latest results on the newly established capability of non-aqueous inert atmosphere actinide electrochemistry at Florida State University.

NUCL 87

Energetic properties of actinide molecular clusters

David A. Dixon*, dadixon@ua.edu, Monica Vasiliu, Zachary Lee. Chemistry Dept, Shelby Hall, The University of Alabama, Tuscaloosa, Alabama, United States*

There is substantial interest in understanding the properties and reactivity of actinide containing molecules, for example their reactions in aqueous solution. The acidities of Th, Pa, U, Np, and Pu for the +III and +IV oxidation states have been calculated with multiple solvation shells with different numbers of water molecules in the first solvation shell. The tetravalent actinides also exhibit extensive hydrolysis and condensation behavior due to their high charge density and acidity and polynuclear species are known to play a significant role in their overall chemistry. Electronic structure calculations of thorium oxide clusters with carboxylate, sulfate and selenate ligands provide new insights into their stability, reactivity, and role as nucleation site precursors. The structures and vibrational frequencies of neutral and anionic actinide fluorides AnF_x where An = Th, Pa, U, Np, Pu, Am, Cm, Bk, and Cf were calculated to determine the maximum formal oxidation state of the actinide. Energetic properties including electron affinities, ionization energies, fluoride affinities, and bond dissociation energies are calculated to provide further insights into periodic trends.

NUCL 88

Layered metal oxide nanosheets as model surfaces for understanding the strong metal-support interaction

Megan Strayer[1], Alyssa S. Rosas[1], Ritesh Uppuluri[1], Jason M. Binz[1], Thomas Senftle[2], Amin Azizi[1], Robert M. Rioux[1], Michael J. Janik[1], Nasim Alem[1], ***Thomas E. Mallouk****[1], tom@chem.psu.edu. (1) Pennsylvania State University, University Park, Pennsylvania, United States (2) Mechanical and Aerospace Engineering, Princeton University , Princeton, New Jersey, United States*

The strong metal-support interaction (SMSI) in catalysis is traditionally explained using models that invoke electron transfer, under catalytic conditions, from metal oxides such as titania and ceria to late transition metal nanoparticles supported on them. We have used oxide nanosheets made by exfoliation of layered Nb, Ta, and Si oxides as crystallographically well-defined, high surface area substrates, to study the nature of chemical interactions at the nanoparticle-support interface. Interfacial bonding energies were measured using isothermal titration calorimetry (ITC) and the dispersion and

stability of nanoparticles were studied using in-situ transmission electron microscopy. ITC measurements show increasing bonding energies for oxide nanoparticles in the order Ag < Cu ≈ Ni ≈ Co < Rh < Ir, on both niobate and silicate nanosheets, as expected from trends in M-O bond energies. The most strongly bonded metals, deposited on niobate surfaces from molecular precursors, can be stabilized as mononuclear species. These trends are corroborated by DFT calculations, which reveal that late transition metals transfer d-electron density from the adsorbed cluster to Nb atoms in the sheets; this mixing is absent in weakly binding metals such as Ag, and in all metals on layered silicates. The large differences between the behavior of nanoparticles on early transition metal oxide and silicate nanosheets highlight the importance of d-orbital interactions in controlling the stability of supported nanoparticles.

NUCL 89

Shortest Th–Th distance from a new type of quadruple bond

*Hanshi Hu, **Nikolas Kaltsoyannis**, nikolas.kaltsoyannis@manchester.ac.uk. School of Chemistry, The University of Manchester, Manchester, United Kingdom*

Compounds featuring unsupported metal–metal bonds between actinide elements remain highly sought after yet confined to inert gas matrix studies. Notwithstanding this paucity, actinide–actinide bonding has been the subject of significant computational effort. In this contribution, density functional theory, CASPT2 and CCSD(T) calculations at both the scalar and spin orbit levels are used to survey the Th–Th bonding in a range of systems of general formula LTh–ThL, where L is one of a range of neutral p block donor ligands. Several of these are found to have very short Th–Th bonds arising from a new type of Th–Th quadruple bond with a previously unreported electronic configuration featuring two unpaired electrons in 6d based δ bonding orbitals. $H_3AsThThAsH_3$ is found to have the shortest Th–Th bond yet reported (2.590 Å). The Th_2 unit is a highly sensitive probe of the L ligand's electron donor/acceptor ability; we can tune the Th–Th bond from quadruple to triple, double and single by judicious choice of L, up to 2.888 Å for singly bonded ONThThNO.

NUCL 90

Actinide-pnictogen chemistry

***Justin R. Walensky**, walenskyj@missouri.edu. Chemistry, University of Missouri, Columbia, Missouri, United States*

The chemistry of the actinides with pnictogens below nitrogen is underdeveloped. The synthesis, characterization, and reactivity of thorium and uranium complexes with phosphorus, arsenic, and antimony will be discussed.

NUCL 91

Accurate solution phase thermochemistry for actinide solvation, complexation, and transport from aqueous to organic phases

***Aurora E. Clark**, auclark@wsu.edu. Washington State Univ, Pullman, Washington, United States*

Accounting for the solution phase environment is an essential aspect of determining accurate thermodynamic cycles that determine the free energy of solvation, complexation, and transport of actinides and their metal-ligand complexes across phase boundaries. In recent work we have developed important new protocols regarding the determination of accurate free energies of solvation of early actinides that displays equal performance irrespective of the oxidation state or overall charge of the ion. The current work extends this cluster-based approach to to develop accurate solution-phase actinide complexation thermodynamics and depictions of the free energy differences for transport across phase boundaries.

NUCL 92

From actinides to transactinides: Peculiarities in electronic structure and properties

***Valeria Pershina**, v.pershina@gsi.de. GSI, Darmstadt, Germany*

When Seaborg introduced his ‘actinide’ concept in 1944, the theory played not the last role in his decision to place newly discovered elements in a second series where the filling of the 5f-shell takes place, similarly to the ‘lanthanide’ series where the filling of the 4f-shell takes place. Later on, together with O. L. Keller, Jr., he suggested an extension of the Periodic Table to even higher Z numbers calling these elements “superactinides.” The first chemical experiments on the elements at the beginning of the 6d-series, Rf and Db, performed in Berkeley and Dubna have shown that these elements are, indeed, members of the new, 6d-series and their properties should be different from those of Th and Pa, respectively. Also, the theory, having provided enormously important information on the electronic structures and properties of the actidies, has shown that the transactinides start a new, 6d series and should belong to the transition-element groups. Thus, e.g., Sg was also found to be different from U in its compounds and to be a homolog of the other group-6 elements. Heavier elements, even though being homologs of the lighter ones in the respective chemical groups, may reveal unusual chemical behavior due to the increasingly important relativistic effects on their electron shells.

In the presentation, important and interesting works on the electronic structures of some actinides and transactinides are overviewed and peculiarities in their electronic structure caused by strong relativistic effects are discussed.

NUCL 93

Roles of 4f and 5f orbitals in bonding: A magnetochemical, crystal field, density functional theory, and multi-reference wavefunction study

***Wayne W. Lukens**[1], wwlukens@lbl.gov, Manfred Speldrich[2], Ping Yang[3], Thomas Duignan[4], Jochen Autschbach[4], Paul Koegerler[2]. (1) MS 70a 1150, Lawrence Berkeley Natl Lab, Berkeley, California, United States (2) Institute for Inorganic Chemistry, RWTH Aachen University, Aachen, Germany (3) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (4) SUNY Buffalo, Buffalo, New York, United States*

In 1989, Bursten, Rhodes and Strittmatter published a series of papers exploring the bonding in tris-cyclopentadienyl actinide complexes (Cp_3M) and their base adducts. At the time, experimental determination of the role of the 5f-orbitals in bonding was not possible, so the results could not be compared with experiment. In this talk, the electronic structures of $4f^3/5f^3$ Cp''_3M and Cp''_3M alkylisocyanide complexes, where Cp” is 1,3-bis-(trimethylsilyl)cyclopentadienyl and M is Nd and U, are explored both experimentally and theoretically with a focus on the splitting of the f orbitals, which provides information about the strengths of the metal-ligand interactions. Experimentally, the complexes and their isocyanide adducts were characterized by electron paramagnetic resonance (EPR) spectroscopy and magnetic susceptibility. f orbital splitting was determined using a crystal field model that was parameterized using a combination of EPR and susceptibility data. The isocyanide derivatives were also studied using density functional theory, resulting in f orbital splitting that is consistent with that determined by crystal field analysis, and by multi-reference wavefunction calculations that largely confirm the electronic structure analysis derived from the crystal-field calculations with one caveat. The results highlight that, contrary to the 4f orbitals, the 5f orbitals are significantly involved in bonding to the isocyanide ligands. The main interaction between isocyanide ligand and the metal center is a sigma-bond, with additional 5f to pi* donation for the uranium complexes. While interaction with the isocyanide pi* orbitals lowers the energies of the $5f_{xz}{}^2$ and $5f_{yz}{}^2$-orbitals, spin-orbit coupling greatly reduces the population of $5f_{xz}{}^2$ and $5f_{yz}{}^2$.

NUCL 94

Insights into the redox chemistry of actinides

***Wibe Dejong**, wadejong@lbl.gov. 50F1650, LBNL, Berkeley, California, United States*

Fundamental insights into the role of 5f electrons in the redox chemistry of actinides is essential for predicting the fate and controlling the behaviour of nuclear materials in the ecosystem, as well as for developing new advanced applications in energy, medicine and forensics. In recent years computational chemistry has become a key pillar of multidisciplinary actinide research, advancing the fundamental understanding of actinide chemistry through strong synergies between experiment and simulations. We will

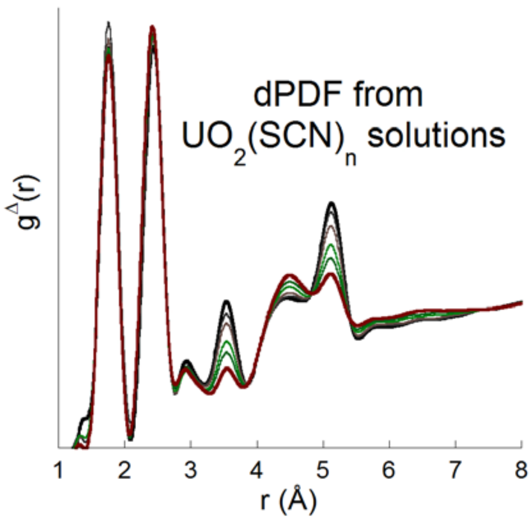
present some recent multidisciplinary gas-phase thermochemistry and spectroscopy efforts focused on understanding the role of metal-ligand interactions on the oxidation states of actinides across the series.

NUCL 95

New insights into metal-ion correlations in solution

***Lynda Soderholm**, ls@anl.gov, S. Skanthakumar. Argonne Natl Lab, Argonne, Illinois, United States*

The first step toward a predictive insight into a dissolved ion’s behavior is a detailed knowledge of its solution speciation, notably all energy-relevant correlations with both counterions and solvent molecules. Underpinning the theoretical as well as experimental hurdles to achieving this goal are the often small energy differences between competing species that ultimately impact a solute’s stability, reactivity, and solubility. From a theoretical standpoint, the cost and time required to describe the environment about a central ion imparts restrictions on the number of ions to include and their explicit interactions. Often choices must be made in the absence of detailed information that can be used to judge the relative importance of the possible contributions. For example, the competition for inner- and outer-sphere coordination environments is often dependent on very small energy differences and equilibria involving a number of species. Particularly challenging are higher-valent ions where electrostatic forces can extend past the central ion’s outer sphere environment. We will discuss our recent approach to providing speciation metrics with the accuracy required to inform such computational efforts. Using high-energy X-ray scattering (HEXS) as a probe of metal ion correlations in solution, and employing a novel approach to data analyses, we can obtain difference pair-distribution functions (dPDF) that can provide accurate inner- and outer-sphere coordination numbers in addition to information about correlations extending well into the solvent. We will discuss selected examples that highlight some of our unexpected findings and some new information that may be helpful to theorists wishing to accurately model and predict the solution chemistry of solute ions in aqueous solutions.



NUCL 96

Updates on uranyl peroxide nanoclusters

Peter C. Burns*, pburns@nd.edu. Univ of Notre Dame, Notre Dame, Indiana, United States*

Uranyl peroxide nanoclusters are a major focus of the Materials Science of Actinides, Energy Frontier Research Center at the University of Notre Dame. Over 100 nanoclusters have been synthesized and tens of them are being fully characterized to improve our knowledge of their behavior. *U60* and *U24P* have been studied most extensively. This presentation will give an update on the solubility of nanoclusters in water, calorimetric studies, radiation effects, and potential formation mechanisms.

NUCL 97

Dissolution of uranium minerals in uranyl peroxide nanocluster forming environments

Haylie L. Lobeck[1]*, hlobeck@nd.edu, Connor J. Parker*[1]*, Sara Boukdad*[1]*, Enrica Balboni*[1]*, Peter C. Burns*[1,2]*. (1) Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States (2) Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States*

Understanding the solubility of actinide material in aqueous environments is important in various aspects of the nuclear fuel cycle, including *in situ* leaching of uranium ore, reprocessing of spent fuel, determining the behavior of radionuclides in geologic repositories, and the transport of actinide contamination at waste storage sites such as Hanford, and at reactor accident sites like Fukushima. Uranyl minerals with low aqueous solubility, such as uranyl phosphates, vanadates, and silicates can be found as alteration products on spent fuel and the precipitation of these phases have been considered as a remediation technique to remove soluble uranium contamination from the environment. Water in contact with these minerals will typically contain less than 100 ppm of U in solution under a broad range of pH conditions. Uranyl peroxide nanoclusters are hollow cage-like structures made up of 16 – 124 uranyl ions connected by peroxide and hydroxyl bridges. They readily assemble at room temperature in aqueous alkaline environments that contain uranyl ions, peroxide, and counter cations such as K^+ or Na^+. Nanoclusters have diameters ranging from 1.5 to 4 nm and can persist in aqueous solution for years. In addition to peroxide, they can incorporate phosphate, pyrophosphate, oxalate, nitrate and transition metals into their structure. Once formed, nanoclusters behave differently in solution than smaller species. Under certain conditions, solutions containing nanoclusters can exceed 170,000 ppm U. The goal of this project is to determine the effect nanocluster forming conditions (alkaline pH containing peroxide) has on the dissolution of nominally insoluble uranyl minerals. Various minerals from the uranyl phosphate, arsenate, silicate, and vanadate groups will be exposed to solutions containing dilute peroxide over a pH range of 7 – 11. After seven days, the solutions will be analyzed with Inductively Coupled Plasma –Optical Emission Spectroscopy for uranium content and Electrospray Ionization –Mass Spectrometry for the characterization of any nanoclusters that form. Preliminary results indicate the formation of uranyl peroxide nanoclusters greatly enhance the dissolution of these uranyl minerals compared to control solutions that lack peroxide or pH adjustments.

NUCL 98

Structural stability of uranyl nanoclusters

Melika Sharifironizi[2], *msharifi@nd.edu, Jie Qiu*[3]*, Jennifer Szymanowski*[1]*, Peter C. Burns*[1]*. (1) Univ of Notre Dame, Notre Dame, Indiana, United States (2) university of Notre Dame, South Bend, Indiana, United States (3) University of Notre Dame, Mishawaka, Indiana, United States*

Naturally occurring nanoparticles are ubiquitous and important in many processes such as weathering and biological processes. Natural water-born nanoparticles can govern the mobility of trace metals in the environment due to their small size and high chemical reactivity. Nanoscale uranyl peroxide cage clusters, which are similar in topology to some transition metal polyoxometalates, are self-assembled structures with uranyl polyhedra linked through peroxide bridges. While peroxide bridges between uranyl polyhedra are necessary to foster curvature, introduction of other functional groups such as oxalate, pyrophosphate and hydroxyl leads to chemically varied nanocluster structures. Charge-balancing alkali ions are located both inside and outside of these negatively charged nanoscale capsules. Due to their unique properties, uranyl peroxide clusters have potential applications in the nuclear fuel cycle. Yet, their thermodynamic properties are poorly studied. In this study, the enthalpy of formation of crystals containing six different uranyl peroxide clusters with different ligands and different numbers of uranyl polyhedra, as well as charge balancing alkali ions, were determined using a high-temperature calorimeter. The roles of the type and the number of alkali

ions as well as the type of ligands in the stability of these structures were studied separately to determine the factors affecting the structural stability of uranyl nanoclusters.

NUCL 99

Sorption mechanism and kinetics of the uranyl peroxide nanocluster (U60) to Ca- and Na-montmorillonite

Luke R. Sadergaski[2]*, lsaderga@nd.edu, Wynn Stoxen*[2]*, Amy E. Hixon*[1]*. (1) Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States (2) Civil and Environmental Engineering and Earth Science, University of Notre Dame, South Bend, Indiana, United States*

In order for nuclear energy to be widely accepted, scientists need to gain a better understanding of how uranium (U) contamination can be tracked and managed in the biosphere and design safe geologic repositories for the long-term storage of nuclear waste. The transport of U contamination has been addressed in part by sorption experiments of UO_2^{2+} to various minerals in many geochemical systems. However, there is an absence of research regarding the behavior of U-based nanoclusters in the environment, which is an important aspect to consider given their high solubility and persistence when dissolved in solution. This study carefully examines the sorption mechanism and kinetics of the uranyl peroxide nanocluster $[UO_2(O_2)(OH)]_{60}^{60-}$ (U60) to Ca- and Na-montmorillonite clay under ambient conditions. The research described here will enhance our molecular-scale understanding of the interactions between polyoxometalate oxyanions, such as U60, and mineral surfaces.

NUCL 100

Uranyl polyrotaxanes: From hydrothermal synthesis to structural diversity

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

For the sake of its great importance in nuclear fuel cycle and environmental safety, actinide chemistry has gained increased attentions from chemists, geologists and materials specialists. More sophisticated knowledge about actinide elements may provide much valuable information and help to achieve improvements in waste treatment and contamination remediation. On the other hand, metal-organic materials with dynamic components, such as mechanically-interlocked rotaxane molecules (MIMs), integrate the attractive feature of flexibility into rigid frameworks as well as broad functionalities. Among plenty of rotaxane-based coordination polymers, transition metal ions and lanthanide ions have been intensively studied. However, polyrotaxanes containing actinide cations, such as uranyl or thorium cations, have been never reported. Hence, we are currently pursuing the preparation of actinide polyrotaxanes from uranyl cation and pseudorotaxanes ligands containing cucurbituril. These efforts

have finally produce a series of uranyl polyrotaxanes with a rich library of structures from one dimension to three dimensions. Moreover, we found that the diversity of topologic structures is in close relationship with the direction role of different uranyl secondary building units.

NUCL 101

Actinide based metal organic framework materials

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

Compared to the transition metal and lanthanide based metal organic frameworks (MOFs), the actinide based MOFs are substantially less explored. The structure and properties of actinide based MOFs can not be simply mimicked/predicted based those analogues of transition metals and lanthanides owing to the uniqueness of actinide ions in bonding and coordination. During the past two years, we have prepared a series of new uranium and thorium based metal organic frameworks that possess distinct structures and properties. Two interesting examples will be presented: one is a unique polycatented uranyl framework that possesses high chemical stability, radiation resistance, and cesium uptake capability; the other is the first hydrolytically stable mesoporous cationic MOF material based on thorium ions with promising anion-exchange properties. These works highlight the bright future of adopting actinide ions in building of unique MOF structure, which may find potential applications in the nuclear industry.

NUCL 102

Effect of processing conditions on lanthanide and actinide oxalate crystal growth mechanisms: Insights from in situ characterization and computational modeling

***Jennifer A. Soltis**[2], jennifer.soltis@pnnl.gov, Michele Conroy[2], William C. Isley[2], Tenisha Meadows[3], Tenisha Meadows[3], Gabriel B. Hall[2], Sayandev Chatterjee[2], Zheming Wang[2], Shawn Kathmann[2], James J. De Yoreo[2], Edgar Buck[2], Gregg J. Lumetta[1]. (2) Pacific Northwest National Laboratory, Richland, Washington, United States (3) Washington State University, Pullman, Washington, United States*

A major goal of nuclear power production is the improvement of efficiency throughout the entire nuclear fuel cycle. This can include fuel reprocessing and recycling, which decreases nuclear waste and reduces the amount of uranium mining needed. Unlike the original low enriched uranium fuel (LEU), mixed oxide fuel (MOX) is composed of both plutonium oxide and uranium oxide. Tight synthetic control is required to produce MOX with the physical and chemical characteristics for optimal fuel performance, however a comprehensive picture of how chemical processing conditions affect MOX synthesis is still lacking. A better understanding of the crystal growth mechanisms involved in producing these materials is important for developing the exacting synthetic control required for mixed oxide nuclear fuels.

Many techniques used to analyze these materials are restricted to dry, ex situ specimens and cannot adequately describe the dynamic processes involved in crystal growth. Two techniques that have rarely been used in nuclear science, cryogenic and fluid cell electron microscopy, are used here to investigate structural intermediates that cannot be observed by any other method. Data from electron microscopy are paired with in situ fluorescence and infrared spectroscopy, X-ray diffraction, atomic-resolution transmission electron microscopy, and computational modeling to help develop a more comprehensive understanding of lanthanide and actinide oxalate crystal growth mechanisms.

NUCL 103

Formation and growth mechanism of U(IV) nanoparticles and colloidal stability in aqueous solutions

***Wansik Cha**, wscha@kaeri.re.kr, Hye-Ryun Cho, Young-Sang Youn, Euo Chang Jung. Nuclear Chemistry Research Division, Korean Atomic Energy Research Institute, Daejeon, Korea (the Republic of)*

Formation of U(IV) nanoparticle (NP) has been of research interest since it is one of key steps in mineralization or immobilization of uranium which can be mediated either by microbes or by abiotic geochemical reactions. Oppositely, colloidal NPs in a groundwater system may also serve as carrier phases influencing radionuclide (RN) migration in subsurface environment. Thus, understanding the evolution pathways and the colloidal stability of NPs is important to predict the migratory behaviors of RNs occurring in anoxic environments of deep geological repository.<br abp="631" />In this study we examined the U(IV) NP formation reactions at different pHs, concentrations and temperatures. The reaction kinetics was spectrophotometrically analyzed by monitoring the consumption of U(OH)<sup abp="632">3+ in the solution under mildly acidic conditions (pH 2~3). The U(IV) NP formation reaction becomes accelerated at higher temperatures. The main outcome of this study is the discovery of the sigmoidal reaction kinetics apparent in an intermediate temperature range (35-50 °C). The observed reaction profiles are well explained by ‘autocatalytic reaction mechanism’. It is proposed that during the initial slow conversion process monomeric or surface oxohydroxo intermediates are created, which also can be called as a nucleation process. Then, faster heterogeneous reactions occur at reactive or catalytic reaction sites of the oxohydroxo complex clusters leading to the growth of primary NPs. TEM image analysis shows that the primary NPs have a few-nm size and uraninite-like crystal structures. Growth mechanisms of primary particles and their clusters will be discussed in detail.<br abp="633" />Additionally, the surface properties of NPs and their colloidal stability are investigated using various analytical techniques including dynamic light scattering analysis, X-ray photoelectron spectroscopy and ATR-FTIR. The zeta potential of U(IV) NP measured during the reaction (pH ~2) has a positive value, approximately +30-40 mV. This indicates that the NP surface is positively charged likely due to partial coordination of hydroxyl ligand, e.g., (U(O)(OH)<sup abp="634">+)<sub

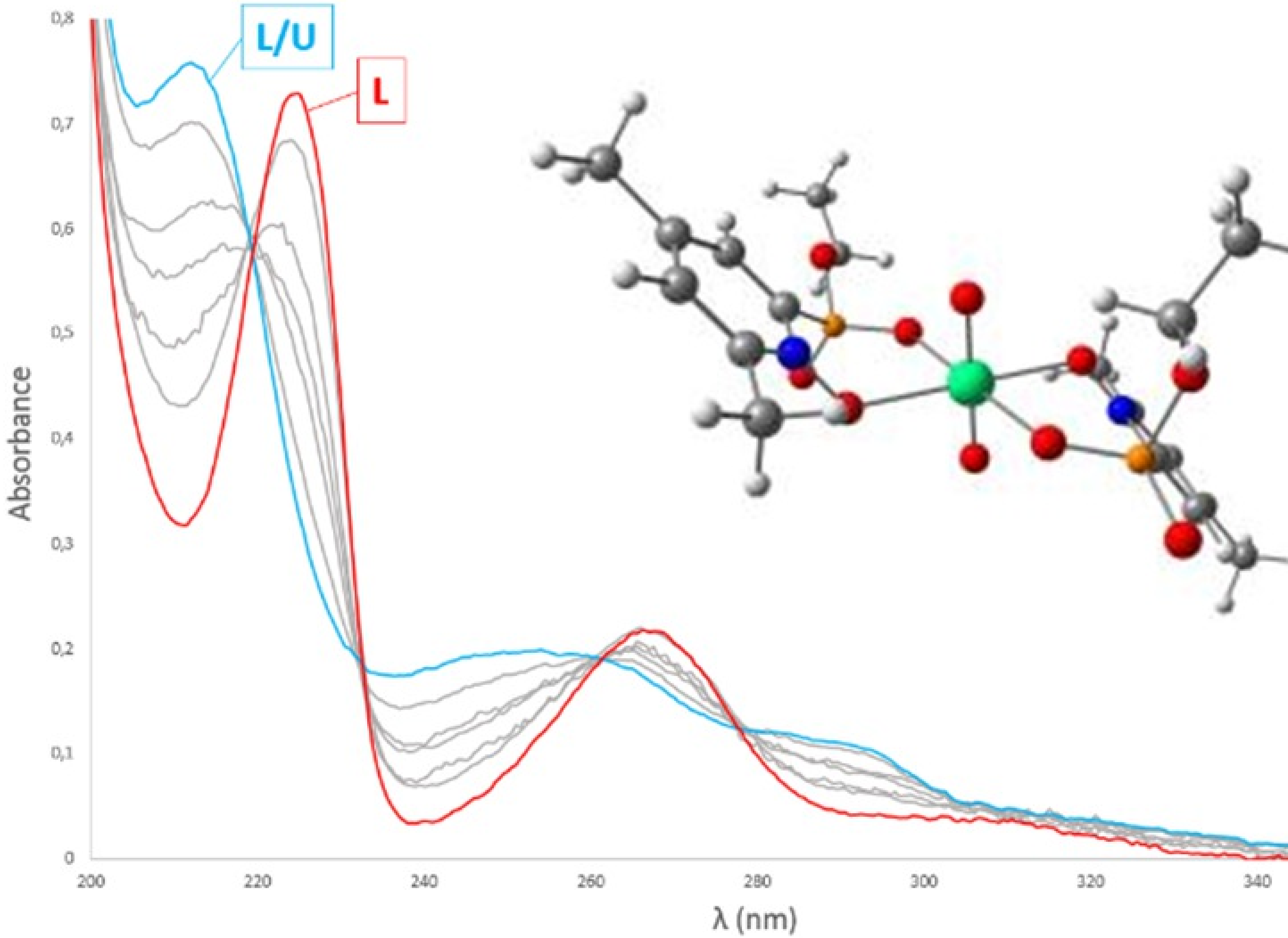
abp="635">n. It is also demonstrated that the organic macromolecules such as polyvinylpyrrolidone and humic acid enhance the colloidal stability of U(IV) NPs even under neutral pH conditions via direct interaction (chemisorption) to the U(IV) NP surface.

NUCL 104

Optimization of novel bifunctional ligand design for uranium extraction

Guillaume Mossand[1]*, guillaume.mossand@gmail.com, Dominique Guillaumont*[1]*, Manuel Miguirditchian*[1]*, Daniel Imbert*[2]*, Marinella Mazzanti*[3]*, Eugen Andreiadis*[1]*. (1) CEA, DEN, DRCP, French Alternative Energies and Atomic Energy Commission, Bagnols-sur-Cèze, France (2) CEA, DRF, INAC, French Alternative Energies and Atomic Energy Commission, Grenoble, France (3) Basic Sciences Department, Polytechnic Federal School of Lausanne, Lausanne, Switzerland*

Uranium is recovered from natural primary and secondary resources by hydrometallurgical processes including ore leaching and purification. Different processes are available for uranium extraction and separation from the associated elements, but the most widely used remains the liquid-liquid extraction. Improving the performance of current processes through the design of more efficient, selective and robust extractants is particularly important.
An approach based on the design of bifunctional extractants combining in the same molecular architecture both cation exchanger and neutral-donor functionalities has led to the development of a new family of ligand molecules containing a pyridine *N*-oxide ring and an acidic phosphonate function, adapted for the liquid-liquid extraction of uranyl (UO_2^{2+}) from highly complexing sulfuric or phosphoric acid solutions.
Several novel molecules have been synthesized using an optimized strategy. The affinity and selectivity of the extractants were evaluated by batch liquid-liquid extraction tests and very high distribution ratios ($D_U > 4200$) of uranium(VI) were measured in the presence of large concentrations of complexing anions such as sulfates. However, the separation factor of U(VI) versus Fe(III) is low.
To establish structure-activity correlations and understand the lack of selectivity of this family in the presence of Fe(III), the molecular environment around U(VI) and Fe(III) cations have been investigated using a combination of experimental (UV-vis and FT-IR spectroscopy, ESI-MS spectrometry) and theoretical approaches. Density functional theory (DFT) calculations coupled to infrared spectroscopy have been performed in order to conclude about the chemical functions contributing to the uranyl coordination environment. The acidity (pK_a) and the complexation constants ($\log\beta$) of these new ligands were calculated using UV spectroscopy. The influence of the molecular design on the efficiency of the molecules to selectively extract U(VI) versus Fe(III) from sulfuric and phosphoric acid solutions was thus established.
The present studies will contribute to a better understanding of the factors influencing the extraction properties and will lead on the longer term to the development of improved uranium extraction processes by organic ligands.



NUCL 105

Cyclic voltammetric studies of unique complexation and solvent effects for the actinide elements

Matthew L. Marsh[1], *mattmarsh0@aol.com, Frankie D. White*[5], *David E. Hobart*[4], *Shane S. Galley*[2], *Thomas E. Albrecht-Schmitt*[3]. *(1) Florida State University, Louisville, Tennessee, United States (2) Chemistry, Florida State University, Tallahassee, Florida, United States (3) Department of Chemistry and Biochemistry, Florida State University , Tallahassee, Florida, United States (4) National Security Education Center, Los Alamos National Laboratory, Santa Rosa Beach, Florida, United States (5) University of South Alabama, Mobile, Alabama, United States*

Large quantities of nuclear waste have accumulated over many years as a result of Cold War defense production and nuclear power plant operation. A major component of

nuclear waste is the actinide elements with half-lives of many thousands of years. Separation of the long-lived actinides from each other and from short-lived fission products is an important step in addressing nuclear waste issues. In this work, redox phenomena are studied with the aid of complexants and non-aqueous solvents to characterize the thermodynamic barriers that exist for performing selective chemistry on the actinides. For example, exploring electrochemical methods to achieve californium(II) in solution is necessary since this element represents a critical break in chemical behavior from its precursors on the periodic table. Such data can be used in the design of an efficient method for the separation of higher and lower valent actinides from curium(III) and lanthanide(III) fission products in nuclear waste.

NUCL 106

Investigation of structure and bonding in transuranium elements utilizing a redox active ligand

Shane S. Galley[1]*, shanesteven182@gmail.com, Scott A. Pattenaude*[2]*, Suzanne C. Bart*[2]*, Thomas E. Albrecht-Schmitt*[1]*. (1) Department of Chemistry and Biochemistry, Florida State University , Tallahassee, Florida, United States (2) Department of Chemistry, Purdue University, West Lafayette, Indiana, United States*

Most coordination chemistry that has been studied with the actinide series has only utilized ligands stable to oxygen and moisture due to the scarcity and radiation hazards associated with these elements. Additionally, the non-aqueous chemistry of the transuranic elements is relatively unexplored and offers a wider platform for exploring methods of deducing electronic structure and information about the actinide-ligand bond. Such information can be very useful for discovering trends in the whole series. In the reported work, a series (U-Cf) of complexes using the redox active ligand 2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxanone (HDOPO) were synthesized in non-aqueous conditions under an inert atmosphere and have been fully characterized with the help of X-ray, optical, magnetic, and computational techniques. Crystallographic data reveal An(DOPO)$_3$ complexes, yet U, Np, and Pu are clearly not in the same oxidation state as Am(III) and Cf(III). Furthermore, the Cf(III) complex disrupts the tris-chelate trend due to radiolysis. It is also shown that the ligand undergoes redox transitions to stabilize the higher oxidation states of the earlier actinides. The results will help contribute toward gaining foundational knowledge of structure and bonding in non-aqueous transuranic chemistry as well as give insight into the participation of *f*-orbitals in bonding

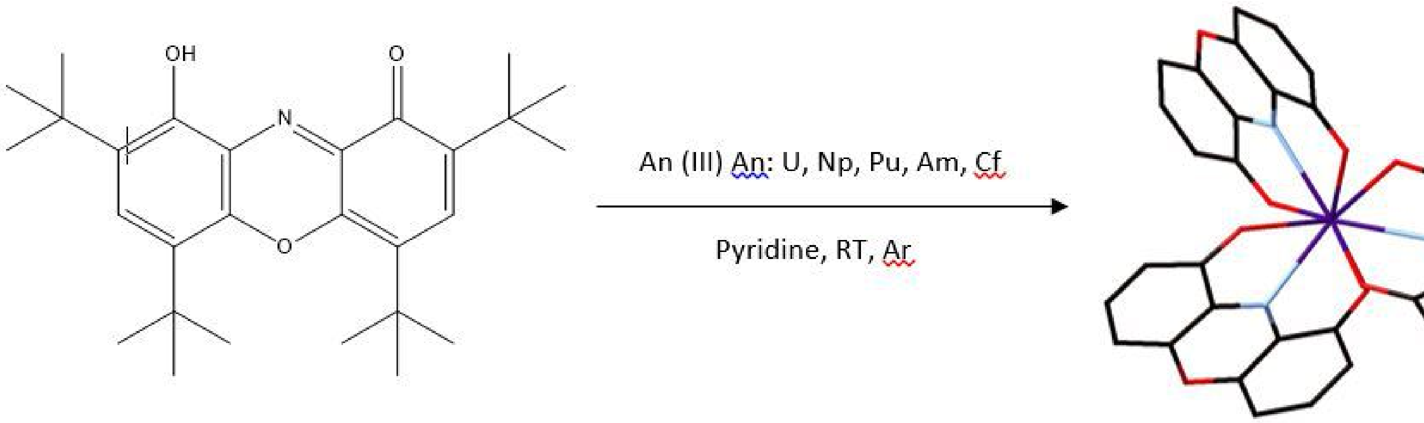


Figure 1: Synthesis of An(DOPO)$_3$ compounds.

NUCL 107

Unraveling the nature of the Am(III)/Eu(III) separation with three structurally similar ligands by changing of bridging groups

***Qunyan Wu**, tongxin8045@163.com. Institute of High Energy Physics, Beijing, China*

With the rapid development of nuclear energy, the reprocessing of spent nuclear fuels has been attracting major concern owing to their chemical and radioactive toxicities, especially for minor actinides (MAs). It still remains a worldwide challenge to separate trivalent An(III) from Ln(III) due to their similar chemical properties. Therefore, designing efficient extractants at the molecular level is of great importance. Our group has synthesized a series of ligands, N,N'-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen, Figure 1) through a hard-soft donor combined strategy, which demonstrates excellent group actinide separation ability, the separation factor of Am(III)/Eu(III) with Et-Tol-DAPhen is about 67. Previous studies have reported that the separator factor of Am(III)/Eu(III) with N,N'-diethyl-N,N'-ditolyl-2,2'-bipyridine-6,6'-dicarboxamide (Et-Tol-BPyDA, L$_b$,) is about 18. In this work, three structurally similar ligands Et-Tol-DAPhen, Et-Tol-BPyDA and N,N'-diethyl-N,N'-ditolyl-pyridine-2,6-dicarboxamide (Et-Tol-BPyDA, L$_c$, Figure 1) were investigated and compared using relativistic density functional theory. The results reveal that the oxygen atoms of the ligands play a major role in the complexation. In contrast, it can be deduced that the nitrogen atoms of the three ligands play an important role for the An(III)/Ln(III) separation. Moreover, molecular orbital analysis indicates that ligand La is a better electron donor compared to ligands Lb and Lc. In addition, the M-O and M-N (M=Am, Eu) bonds have apparent ionic characters, and the Am-N bonds have more covalent character compared to the Eu-N bonds. Thermodynamic analyses suggest that the complexation reaction $[M(NO_3)(H_2O)_6]^{2+} + L + 2NO_3^- = [ML(NO_3)_3] + 6H_2O$ is the most probable for the extraction. This work can provide useful information on achieving efficient actinide separation over the Ln(III) through changing the structural rigidity and hardness or softness of ligands.

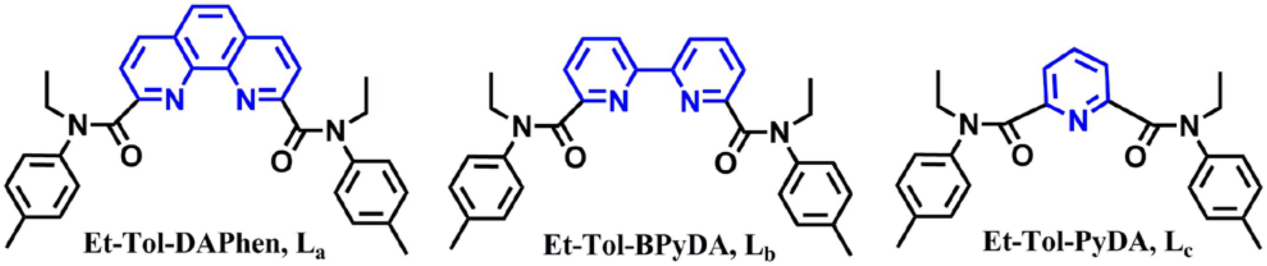


Figure 1. Structures of Et-Tol-DAPhen (L_a), Et-Tol-BPyDA (L_b) and Et-Tol-PyDA (L_c)

NUCL 108

Chemistry of technetium in dilute to concentrated saline systems: Redox processes, solubility and complexation

*Xavier Gaona, **Ezgi Yalcintas**, ezgi.yalcintas@kit.edu, Alexander Baumann, Robert Polly, Marcus Altmaier, Horst Geckeis. Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*

Technetium-99 is one of the main fission products of ^{235}U and ^{239}Pu in nuclear reactors. Due to its long half-life (2.1x10^5 a) and redox-sensitive character, ^{99}Tc is a very relevant radionuclide in the safety assessment of repositories for radioactive waste disposal. Tc(VII) is the prevailing oxidation state under oxidizing and redox-neutral conditions and exists as soluble and mobile TcO_4^-. Tc(IV) forms sparingly soluble hydrous oxides (TcO_2:$x$$H_2O$(s)) under reducing conditions as those expected in deep underground repositories. An appropriate knowledge of the stability fields of Tc redox states, solubility, hydrolysis and complexation behaviour of Tc(IV) in dilute to concentrated saline systems is required for a correct assessment of Tc source term in repositories for radioactive waste disposal. Studies developed within this framework can provide also relevant insights for the understanding of Tc behaviour in legacy sites such as Hanford nuclear tank wastes.

This contribution summarizes recent and on-going research activities at KIT-INE on the solution chemistry of Tc: i. redox chemistry of Tc(VII)/Tc(IV) under acidic to strongly alkaline pH conditions, in dilute to concentrated NaCl and $MgCl_2$ systems, with focus on the definition of the redox boundaries between both oxidation states. The contribution also addresses the impact of nitrate on the redox behaviour of Tc under alkaline conditions; ii. solubility and hydrolysis of Tc(IV) under acidic to strongly alkaline pH conditions, in dilute to concentrated NaCl, KCl, $MgCl_2$ and $CaCl_2$ solutions; and iii. complexation of Tc(IV) with carbonate in dilute to concentrated NaCl–NaOH solutions. The results obtained provide quantitative tools for the assessment of redox processes involving Tc(VII) and Tc(IV) in the absence and presence of nitrate. This work contributes also to an improved thermodynamic description of Tc(IV) in dilute to concentrated saline systems, which can be implemented in geochemical

models/calculations providing further confidence in the safety analysis of repositories for the disposal of radioactive waste.

NUCL 109

Redox behavior of U(VI)/U(IV) and solubility of U(IV) in repository relevant dilute to concentrated solutions in the absence and presence of complexing ligands

Ezgi Yalcintas[2]*, ezgi.yalcintas@kit.edu, Nese Cevirim*[2]*, Xavier Gaona*[2]*, Donald T. Reed*[1]*, Marcus Altmaier*[2]*. (1) Cemrc, Carlsbad, New Mexico, United States (2) Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*

An accurate knowledge of the aquatic chemistry and thermodynamics of actinides is fundamental in the context of nuclear waste disposal. The availability of complete and correct chemical and thermodynamic models represents a key milestone in the development of reliable geochemical model calculations and source-term estimations and, thus, in the safety assessment of repositories for nuclear waste disposal. Uranium contributes with the largest inventory to the radioactive waste. U(VI) is the most stable oxidation state of uranium under anoxic and oxidising conditions, whereas U(IV) prevails in strongly reducing environments, forming the sparingly soluble UO_2(am,hyd) ([U] < 10^{-8} M) in solutions at pH ≥ 5 and in the absence of complexing ligands. The predominance of the latter oxidation state is expected in deep geological repositories, where very reducing conditions are foreseen. The geochemical conditions in the nuclear waste repositories which may provide dilute to concentrated dissolved salts (I =0.1 M–15 M) as well as the strong complexing ligands like CO_3^{2-} and EDTA, can significantly alter the chemical behaviour and, therefore the migration of actinides. In this framework, an appropriate understanding of the redox behaviour of U(VI)/U(IV) as well as solubility and complexation behaviour of U(IV) in dilute to concentrated saline systems is essential for the long term performance assessment calculations. In the present study, the redox behaviour of U(VI)/U(IV) was investigated from oversaturation and undersaturation conditions in dilute to concentrated NaCl (0.1–5.0 M), $MgCl_2$ (0.25–4.5 M) and $CaCl_2$ (0.25–4.5 M) solutions using different reducing chemicals in the presence and absence of complexing ligands. The experiments in the presence of EDTA were performed with variable ligand concentration ($[EDTA]_{tot}$ = 0.001–0.05 M) and ionic strength (I = 0.5–5.0 M) in neutral to alkaline pH conditions. Complexation behaviour of U(IV) was investigated from undersaturation conditions as a function of carbonate concentration (C_{tot} =0.01 M–1.5 M), ionic strength (C_{tot} = 0.1 M–0.3 M, I = 0.5 M–4.0 M ($NaCl–NaHCO_3–Na_2CO_3$)) and OH concentration (C_{tot} = 0.1, 0.01 M ≤ [NaOH] ≤ 0.6 M). The redox boundaries between U(VI)/U(IV) in relevant geological repository conditions were assessed with the intent of extending the chemical, thermodynamic, and activity models for An(IV).

NUCL 110

Complexation of lanthanide and actinide ions with N,N-di-2-ethylhexyl-diglycolamic acid in solvent extraction separation from nitric acid solutions

Guoxin Tian[1,2]*, gtian@ciae.ac.cn, Yan Zhang*[1]*, Suliang Yang*[1]*, Xiaolan Yuan*[1]*. (1) Radiochemistry, China Institute of Atomic Chemistry, Beijing, China (2) Nuclear Chemical Engineering, Harbin Engineering University, Heilongjiang, China*

The separation and complexation of lanthanides and actinides with N,N-di-2-ethylhexyl-diglycol-amic acid (DEHDGA) are investigated in solvent extraction from 0.001-4 M HNO_3. In general, the extraction of Nd(III), U(IV), Pu(IV), and U(VI) decreases with the increasing acid concentration from pH region and reaches the bottom at about 1 M HNO_3, then increases with HNO_3 concentration from 1 to 4 M. For U(VI), only one 1:2 of metal ion to ligand complex are observed, while for Nd(III), at least two complexes, 1:2 and 1:3, are observed in the extraction between 0.01-1 M DEHDGA in branched dodecane and 0.001-4 M HNO_3. With appropriate concentrations of DEHOGA in the organic phase, the extraction of Ln and An ions can be well performed at high acid concentration, 3-4 M HNO_3, and the stripping can be achieved with 1 M HNO_3.

NUCL 111

Effect of elevated temperatures on actinide solubility and speciation–studies performed by KIT-INE within the German project ThermAc

Xavier Gaona, Francesco Endrizzi, Jun-Yeop Lee, ***David Fellhauer****, david.fellhauer@kit.edu, Marcus Altmaier. Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*

The studies of KIT-INE presented in this contribution are developed with the aim of improving the scientific basis for assessing nuclear waste disposal scenarios at elevated temperature conditions. Adequate scientific tools must be available to assess the potentially relevant chemical effects and their impact upon repository safety. Furthermore, this work is contributing to an advanced scientific understanding of general fundamental chemical processes in aqueous media.

Studies are performed within the German ThermAc project, funded by BMBF (coordinator contact: marcus.altmaier@kit.edu). ThermAc is extending the chemical understanding and available thermodynamic database for actinides, long-lived fission products and relevant matrix elements in aquatic systems at elevated temperatures. A clear focus of ThermAc is on long-lived actinides in oxidation states III, V and VI, with selected fission products and important redox controlling matrix elements like Fe also receiving attention. ThermAc mainly addresses the temperature range from ~5°C up to ~90°C, focusing on systems at low or intermediate ionic strength. ThermAc is following an integrated concept with the following strategic components: (a) systematic use of estimation methods for thermodynamic data and model parameters, (b) comprehensive experimental validation of the estimations, (c) fundamental studies for improved process understanding of actinide chemistry at elevated T, and (d) comprehensive critical evaluation of the work performed within (a-c).
Examples of research studies performed by KIT-INE include (i) assessment of the impact of elevated temperatures on the solubility and speciation of U(VI) in dilute to

concentrated NaCl solution - experimental data and modeling, (ii) studies at elevated T on the ternary Ca/Mg-U(VI)-CO_3 systems (iii) solubility phenomena of trivalent actinides at elevated temperatures, and (iv) stability/transformation of solubility limiting solid phases at RT, exposed to elevated T conditions.

NUCL 112

Complexation and phase transfer kinetics of tributyl phosphate degradation products at the liquid:liquid interface during solvent extraction

***Susan Howett**, susan.howett@pnnl.gov, Amanda Casella, Amanda Lines, Sue Clark, Christina Louie, Calvin Delegard, Gregg J. Lumetta, William Karl Pitts, Kaylyn M. McCoy. Pacific Northwest National Lab, Richland, Washington, United States*

The transport of butyl phosphate extractants and actinides across the liquid:liquid interface determines the efficiency and effectiveness of solvent extraction processes. In addition, these species can organize at the phase boundary, sometimes leading to the formation of unwanted interfacial solids. Tributyl phosphate (TBP), an extractant in liquid:liquid reprocessing, undergoes radiolytic degradation, yielding dibutyl (DBP) and monobutyl phosphate (MBP). The solubilities and rates of transfer for these species vary as a function of diluent and process scale.

Kinetic parameters are being measured in real-time by spectroscopic monitoring in a two-phase solvent extraction system. The extraction apparatus is patterned after the Lewis Cell design, which has two stirred phases and a well-defined and controlled interface. The MBP, DBP, and TBP are measured using Raman spectroscopy. Both phases are equipped with the on-line monitoring providing direct, real-time measurement of degradation products and complexes moving from one phase to another within the extraction system.

NUCL 113

Effects of high ionic strength on actinide speciation and oxidation state distribution in subsurface environments

***Donald T. Reed**, dreed@lanl.gov, Michael K. Richmann, Juliet S. Swanson, Timothy Dittrich. Repository Science & Operations, Los Alamos National Laboratory, Carlsbad, New Mexico, United States*

High ionic strength brine systems (typically I> 5 M) represent extreme subsurface environments that can have many impacts on the overall speciation and oxidation state distribution of actinide species. These systems are encountered in many high-level nuclear waste repository scenarios where there may be cyclic drying/heating as a transitional phase of the repository history. More importantly, it is the expected environment for inundation scenarios in salt repository concepts (e.g., WIPP TRU repository).

An overview discussion of the current status of key effects of high ionic strength on actinide speciation will be given. Most high ionic-strength studies relate to process chemistry under highly acidic conditions ([acid] > 3 M). In the geologic repository case, however, high sodium-magnesium-chloride brines can be formed or are encountered under high pH conditions (typically pH 7-13) depending on the prevailing conditions in the repository. A key impact is the loss of ideality due to ion interactions that require empirical modeling approaches (e.g., Pitzer parameter approach) and modified formation constants for complexants. High ionic strength also shifts the relatively importance of the oxidation state distribution relative to low ionic strength systems. This can be demonstrated in shifts in Eh-pH diagrams, the enhanced stability of An(VI) at higher pH, and the stabilization of An(III) under some moderate pH conditions. High ionic strength also impacts the relative stability of nano-structural species that lead to behavioral differences and long-term metastability. This complexity has been most studied in the thorium system but applies to other actinide systems as well. Lastly, high ionic strength chemistry shuts down many microbial effects on actinide speciation. In this context, many microbial effects (e.g., bioreduction, and biodegradation) generally important for long-term containment strategies in low I systems are mitigated by the inability of many microorganisms to survive or function at I > 4 M. Collectively, these high ionic-strength effects can have a pronounced effect on the fate and transport of actinide contaminants in the subsurface and need to be addressed in the performance assessment and long-term safety case.

NUCL 114

Corrosion mechanism of iron in liquid uranium hexafluoride environment

Mickaël Achour[2,1]*, mickael.achour@areva.com, Marc Dubois*[1]*, Laurent Jouffret*[1]*, Ania Selmi*[2]*, Bertrand Morel*[2]*, Sylvie Delpech*[3]*, Sylvie Chatain*[4]*, Laure Martinelli*[4]*, Pierre Bonnet*[1]*. (1) Clermont University, Aubiere, France (2) Service HRP, Site Areva Tricastin, Pierrelatte Cedex, France (3) Institut de Physique Nucléaire, Orsay, France (4) SCCME Laboratoire d'Étude de la Corrosion Non Aqueuse, Commissariat à L'énergie Atomique, Gif sur Yvette, France*

Uranium hexafluoride is used for the enrichment of 235U versus 238U. UF_6 is obtained by fluorination of UF_4 and its high volatility near room temperature makes it compatible with the gaseous centrifugation used for enrichment.
The drawback of UF_6 is his high reactivity with many materials such as metals. It is a strong fluorinating and oxidative agent which can lead to corrosion issues.
From the synthesis to the isotopic separation, the uranium hexafluoride can be solid, liquid or gaseous. The study is focus on the interaction of iron with liquid and gaseous UF_6.
A first approach consisted in thermodynamics study of the U-Fe-F-O system. This led to identify the various stable phases in the experimental conditions.
Fluorination of iron samples were then performed at 80°C under 3 bar of liquid UF_6. In the early stage, UF_6 reacted with iron and formed FeF_2 and UF_x ($4<x<5$). The nucleation took place in some particular sites which could be linked to crystal orientation. This will

be investigated by EBSD. Then the growth and coalescence of those nodules, led to the formation of a continuous FeF_2 layer and uranium fluoride or oxy-fluoride. Fluorination mechanism was investigated by intending to identify the diffusing elements and by determining the chemical reactions taking place. In order to understand these mechanisms some specific experiments (with gold deposit, gaseous UF_6…) were performed and a corrosion mechanism has been proposed.

NUCL 115

Turning on the terminal: Promoting non-covalent interaction with uranyl oxo atoms

Korey Carter[2]*, koreypcarter@gwmail.gwu.edu, Mark Kalaj*[2]*, Robert Surbella*[2]*, Lucas Ducati*[3]*, Jochen Autschbach*[1]*, Christopher L. Cahill*[2]*. (1) SUNY Buffalo, Buffalo, New York, United States (2) The George Washington University, Washington, District of Columbia, United States (3) University of Sao Paulo, Sao Paulo, Brazil*

Harnessing the nominally terminal oxo atoms of the linear uranyl (UO_2^{2+}) cation represents both a significant challenge and opportunity within the field of f-element hybrid materials. We have developed an approach for promoting oxo atom participation in a range of non-covalent interactions through judicious choice of strongly electron donating equatorial ligands and appropriately polarizable halogen-donor atoms. As such, we have generated a family of uranyl hybrid materials based on a combination of 2,5-dihalobenzoic acid and aromatic, chelating N-donor ligands. Delineation of criteria for oxo participation in halogen bonding interactions has been achieved by preparing materials containing 2,5-dichloro-, 2,5-dibromo-, or 2,5-diiodobenzoic acid coupled with 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2':6',2''-terpyridine (terpy), or 4'-chloro-2,2':6',2''-terpyridine (Cl-terpy)), which have been characterized via single crystal X-ray diffraction, Raman, Infrared (IR), and luminescence spectroscopy, as well as via electrostatic surface potential calculations. Raman and IR spectroscopy, and resulting stretching force constant calculations, show a weakening of the U=O bond, when oxo atoms are involved in halogen bonding with the 2,5-diiodobenzoic acid, whereas electrostatic surface potential calculations highlight the importance of halogen polarizability in leading to oxo participation in halogen bonding interactions. Our findings indicate that one route to promote oxo participation in halogen bonding on a consistent basis is the combination of strongly electron donating equatorial ligands paired with benzoic acid groups featuring multiple large, polarizable halogen atoms at the periphery.

NUCL 116

Insight into the uranyl oxyfluoride topologies through the synthesis and crystal structure new oxyfluoride compounds

***Laurent Jouffret**, laurent.jouffret@gmail.com, Jean-Michel Hiltbrunner, Marc Dubois. Institut de Chimie de Clermont - Ferrand, Unversité Clermont Auvergne, Aubière, Auvergne, France*

Before its isotopic enrichment, uranium is chemically treated in order to produce uranium hexafluoride. Depending on the source, this uranium is susceptible to contain impurities that can lead to the formation of secondary mixed phases. Any addition of oxygen in the process will lead to the presence of diverse uranium oxyfluoride compounds. However, while uranium-bearing materials have been extensively studied because of their interesting coordination chemistry and diverse physical-chemical properties very few uranium fluorides and oxyfluorides have been crystallographically characterized and reported in the literature. Most were described after the Manhattan project by Zachariasen and few have been investigated since. Organically templated uranium oxyfluorides have been reported with a wide variety of structures. A large number of these oxyfluorides adopt either mono or bidimensional structures, while only a few exhibit a 3D framework. We will present our work on uranyl (oxi)fluorides at the ICCF and 2 uranyl oxyfluoride structures that will be the starting point for a brief overview of uranyl oxyfluorides topologies.

NUCL 117

Actinide clusters, nanoclusters and cluster-frameworks

*Clement Falaise[2,1], Karoly Kozma[1], Olivier Renier[1], Harrison A. Neal[2], **May D. Nyman**[1], May.Nyman@oregonstate.edu. (1) Oregon State University, Corvallis, Oregon, United States (2) Universite Rennes, Rennes, France*

An(IV) and An(VI) (An=U & Th for this presentation) have very different aqueous, cluster and solid-state chemistries. An(IV) is poorly soluble in water except at low pH, and forms structures featuring 8-9 coordinate polyhedra. The hexanuclear polycation cluster $[An(IV)_6(O,OH)_8(L)_{18}]$ (L=ligand) dominates these solutions conditions. $U(VI)O_2$, on the other hand, forms anionic hollow capsules in acidic to alkaline conditions. The uranyl polyhedra are bridged with peroxide and other bidentate and bridging ligands including pyrophosphate and oxalate. Here we present synthesis, solid-state and solution elucidation of cluster, nanocluster and framework materials of An(IV) and An(VI) chemistries in and from aqueous solutions.

The uranyl peroxide capsules are ideal for X-ray scattering characterization due to the superior scattering power of uranium (Z=92) and the hollow capsule morphologies. We exploit the high-Z in both X-ray total scattering and small-angle X-ray scattering characterization of different cluster topologies. The combination of these techniques proves diagnostic, even in the absence of a crystal structure. Therefore we further exploit X-ray scattering to predict the topology of a cluster for which we cannot (due to poor crystal quality) obtain single-crystal X-ray data. We also demonstrate the role of the hollow capsule topology in identifying these clusters in solution. We synthesized and structurally characterized endohedral clusters in which Bi-O and Pb-O clusters are

enclosed in the uranyl peroxide capsules. These illustrate using capsules to enable dissolution in alkaline pH where solubility and speciation of Bi and Pb is unknown. These clusters also demonstrate the effect of filling the capsule core on the X-ray scattering data.

Finally, we present examples of U(IV) and Th(IV) clusters and their conversion to nanoparticles and framework materials. This too is demonstrated by solid-state structure and solution characterization.

NUCL 118

Influence of alkali metals in dissolving UO_2 to form highly soluble aqueous uranyl peroxide clusters

***Sarah Hickam**, shickam@nd.edu, Peter C. Burns. University of Notre Dame, South Bend, Indiana, United States*

Uranyl peroxide clusters exhibiting rich structural diversity have been recently identified as potential candidates for application in an advanced nuclear fuel cycle. Cations present in these systems, typically alkali metals, are essential components, providing charge balance and stabilization of uranyl peroxide building blocks. Herein, we explore the influence of alkali metals in obtaining high concentrations of uranium in solution. We propose that, in the presence of excess hydrogen peroxide, alkali metal concentration governs the solubility of uranium phases by limiting the concentration of uranyl peroxide cluster species that are formed in solution. This hypothesis is applied to uranium dioxide (UO_2), the typical nuclear fuel form, to achieve high solubility (greater than 400,000 ppm U), rivaling the concentrations of uranium yielded by boiling nitric acid dissolution, though in relatively mild, alkaline pH conditions.

NUCL 119

Uranyl-peroxide nanocapsules: From self-assembly to isomerism

***Pere Miro**, pere.miro@unf.edu. Department of Chemistry, University of North Florida, Jacksonville, Florida, United States*

During the last decade, a new class of self-assembled uranyl-peroxide nanocapsules (UPNs) has rapidly emerged within the polyoxometalate (POM) family. It has been experimentally and computationally demonstrated that their growth is highly influenced by the pH and the alkali cations present in solution. In this communication we will present the first study on the influence of the media on the initial steps of the UPNs growth. Furthermore, we have studied the isomerism of $[(UO_2)_{20}(O_2)_{30}]^{20-}$ (U_{20}) using density functional theory calculations, from which we have derived stability rules applicable all UPNs. We will show the importance of minimizing the number of squares in the overall structure and avoiding square adjacencies as well as to isolate pentagonal faces, similar to fullerenes. These rules are then used to explore the stability of all the

possible isomers for $[(UO_2)_n(O_2)_{1.5n}]^{n-}$ nanocapsules with n=20-60 using classical molecular dynamics in conjunction with a previously developed UPN force field.

NUCL 120

Thermochemistry of neptunium oxides and Np incorporated studtite

Lei Zhang[2]*, lzhang12@nd.edu, Ewa Dzik*[2]*, Jennifer Szymanowski*[2]*, Ginger Sigmon*[2]*, Alexandra Navrotsky*[1]*, Peter C. Burns*[2]*. (1) Chem Eng Mtrls Sci, 4440 Chem Annex, Univ of California, Davis, California, United States (2) Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

Neptunium-237 is of great concern for the long-term geological disposal of spent nuclear fuel because of its long half-life (2.14 Ma) and potential mobility. It can form various compounds with peroxide, sulphate, phosphate, arsenate, etc. The incorporation of neptunium into studtite or metastudtite (important alteration phases of spent UO_2 fuel), in particular, must be considered when accessing its migration in groundwater. Therefore, it is crucial to understand the geochemical stability of Np containing materials. However, there are very limited reported thermodynamic data. We aim to develop high temperature oxide melt drop solution calorimetry at the University of Notre Dame to study the formation enthalpies of neptunium compounds. Neptunium oxides (Np_2O_5 and NpO_2) have been synthesized and characterized for calorimetric study. 5 mg sample powders were made into pellets in a glove box and dropped into the calorimeter containing sodium molybdate solvent at 700 °C. The oxidation enthalpy of $2NpO_2 + 1/2O_2 = Np_2O_5$ at 25 °C is determined to be -7.70 ± 5.86 kJ/mol. This value is in accordance to the literature one of -14.7 ± 10.73 kJ/mol. Meanwhile, thermochemical study of neptunium incorporated studtite or metastudtite is ongoing.

NUCL 121

Plutonium nanocluster formation, structure, and stability

Amy E. Hixon[2]*, ahixon@nd.edu, Ginger Sigmon*[1]*. (1) University of Notre Dame, South Bend, Indiana, United States (2) Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

The aqueous chemistry of Pu(IV) is complex due to its propensity to hydrolyze under all but very acidic solutions and readily form colloids. The structure and assembly of these colloids is highly debated, but is generally believed to be a complex mixture of hydroxides and hydrous oxides. This is unfortunate given the importance of the Pu colloid with respect to plutonium solubility, nuclear waste reprocessing, and environmental fate and transport. Here, we report the synthesis, structure, and stability of a new Pu_{22} oxide cluster and progress towards synthesis of plutonyl peroxide

nanoclusters. Further study of these clusters is expected to shed light on mechanisms of formation and expand our understanding of aqueous plutonium chemistry.

NUCL 122

Developing regional isotopic baselines to trace resource acquisition patterns in the Mesa Verde area of the American Southwest

Amanda L. Werlein[1,2], *awerlein@gmail.com, Virginie Renson*[2], *Joan Coltrain*[3], *Karen Schollmeyer*[4], *John D. Robertson*[1,2], *Jeffrey R. Ferguson*[2]. *(1) Department of Chemistry, University of Missouri, Columbia, Missouri, United States (2) University of Missouri Research Reactor, Columbia, Missouri, United States (3) University of Utah, Salt Lake City, Utah, United States (4) Archaeology Southwest, Tucson, Arizona, United States*

The analysis of strontium and oxygen isotopes in archaeological bone is commonly used to trace human mobility and migrations. In this research, the isotopic approach is being used to reconstruct the changes of human access to large animal resources in the Mesa Verde area between 750-1280 AD. Current work is focused on determining the strontium isotopic variability of the complex geology surrounding the primary study area. Isotopic analyses have been conducted on non-cultural archaeological rodent bones from the surrounding regions, which, due to their limited home ranges, can be used as indicators of the bioavailable strontium isotopic signature of their local environment. While focusing on the strontium analysis we also address oxygen isotopic signatures that provide additional, although more complicated, provenance information.

NUCL 123

Characterization of indigenous Australian ochre by k_0-Neutron Activation Analysis (k_0-NAA) for understanding cultural exchange

Rachel Popelka-Filcoff[1], *rachel.popelkafilcoff@flinders.edu.au, Claire Lenehan*[1], *John Bennett*[2], *Attila Stopic*[2], *Keryn Walshe*[3]. *(1) School of Chemical and Physical Sciences, Flinders University, Adelaide, South Australia, Australia (2) Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales, Australia (3) South Australian Museum, Adelaide, South Australia, Australia*

Ochre is a complex geological material that has several profound cultural uses and meanings worldwide. Despite its importance, there is limited understanding of its fundamental mineralogy, technology, and cultural exchange. Mixtures and applications of pigments present a challenging analytical problem, especially in the context of the need for elemental analysis of mixed pigments on objects in a variety of contexts.
This presentation will describe our recent research into methods to characterize the complexity and diversity of Indigenous Australian ochre pigments. We describe the establishment of an extensive database of ochre from identified sources and archaeological contexts across Australia. Through the use of elemental characterization by k_0-neutron activation analysis (k_0-NAA), we have demonstrated the capability to

identify the chemical “fingerprint” of Australian ochre minerals, including those present in Aboriginal Australian archeological sites. This study complements our recent work using X-ray fluorescence microscopy in developing a toolkit for characterizing ochre and to provide insights into the complex mineralogy and elemental composition of these natural materials.
Our results demonstrate the advantages of using sensitive methods in the analysis of ochre pigments and Australian Aboriginal objects. This presentation will describe the analysis of an extensive NAA data set and understanding archaeological exchange and subsequent cultural interpretation. This study contributes to a more complete understanding not only of Australian ochre but also of Indigenous pigments worldwide.

NUCL 124

^{88}Zr(n,γ)^{89}Zr cross section measurement

__Jennifer Shusterman__[4], shusterman1@llnl.gov, Jacklyn M. Gates[3], Suzanne E. Lapi[5], C. S. Loveless[5], Eric B. Norman[2], Graham Peaslee[6], John D. Robertson[1], Gregory Severin[7], Logan Sutherlin[1], Keenan J. Thomas[4], Mark A. Stoyer[4], Dawn A. Shaughnessy[4], Nicholas D. Scielzo[4]. (1) Univ of Missouri, Columbia, Missouri, United States (2) University of California, Berkeley, Berkeley, California, United States (3) Lawrence Berkeley National Laboratory, Berkeley, California, United States (4) Lawrence Livermore National Laboratory, Livermore, California, United States (5) University of Alabama, Birmingham, Birmingham, Alabama, United States (6) University of Notre Dame, Notre Dame, Indiana, United States (7) Michigan State University, East Lansing, Michigan, United States

Understanding the nuclear-reaction network involving Zr isotopes is important for the stockpile stewardship program. The neutron-capture cross section for the radioactive isotope ^{88}Zr has not been measured and we are working towards filling in this gap in the nuclear data. As part of this project, ^{88}Zr is being produced via two separate methods. First, it was produced at the 88-Inch Cyclotron at Lawrence Berkeley National Laboratory by bombarding a yttrium foil with protons and second, it will be collected using the aqueous isotope-harvesting end station at the National Superconducting Cyclotron Laboratory at Michigan State University. The ^{88}Zr will be purified from its production matrix and made into a target for irradiation at the University of Missouri Research Reactor. After irradiation, the ^{89}Zr reaction product will be detected through γ-ray spectroscopy to determine the thermal neutron-capture cross section. The current status of this project and future plans will be presented.

NUCL 125

Another isomer in Rh102?

Howard A. Shugart, Keenan J. Thomas, __Eric B. Norman__, ebnorman@lbl.gov. Univ California, Berkeley, California, United States

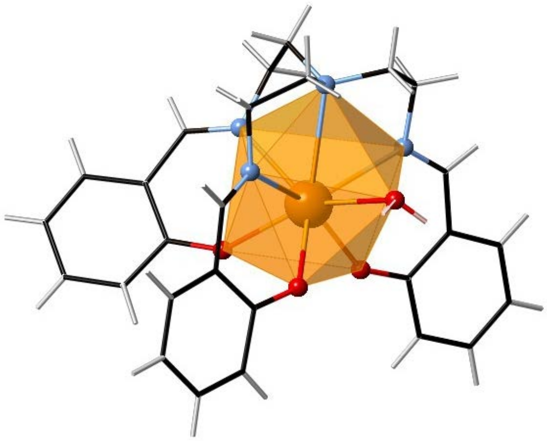
Following the irradiation of a rhodium chloride target with 35-MeV protons from LBNL's 88-Inch Cyclotron, we chemically separated the rhodium and palladium fractions and then counted them separately using high-purity Ge detectors. In the Rh fraction, we clearly see a growth over time in the intensities of several gamma-ray lines attributable to the decay of Rh-102. One possible interpretation of these results is that there exists a previously unknown second isomer in Rh-102. From our measurements, we deduce a half life of this potential new isomer of approximately 46 hours. Puzzles associated with these observations will be discussed.

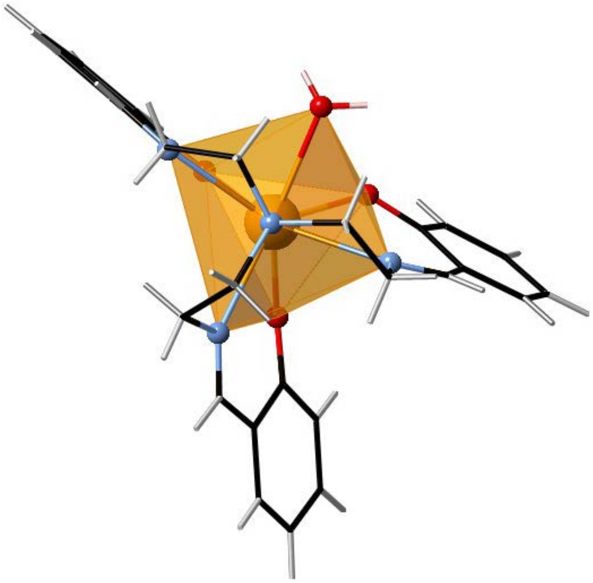
NUCL 126

Unusual coordination of heptadentate tripodal Schiff base lanthanide/actinide complexes

Kevin Seidler, *k.seidler.chem@gmail.com. Chemistry & Biochemistry, Florida State University, Tallahassee, Florida, United States*

Single crystals of the full lanthanide series and americium complexed with 2,2',2''-tris(salicylideneimino)trimethylamine in a 1:1 ratio using a slow diffusion method of methanol and DCM were obtained; single crystal XRD, UV/VIS, and fluorescence spectroscopy experiments were performed. The early lanthanides (La-Nd) as well as americium were 8-coordinate systems in the monoclinic crystal class with $P2_1/n$ space groups. The mid to late lanthanides (Sm-Lu) displayed 7-coordinate geometry in the trigonal crystal class with P-3C1 space groups. The UV/VIS data shows broad charge transfer bands in the near UV region as well as the typical peaks from the respective trivalent metal free ion. This ligand is unique in that the tripodal arms envelop the metal center, causing an unusual 1:1 metal to ligand ratio while maintaining the high order geometry exemplified in the f-elements. Developing unique ligand systems may prove important in selectively separating Ln^{III} from An^{III}, which are both typically found in spent nuclear fuel.





NUCL 127

Utility of MOFs and their derivatives for luminescent sensing and sorption of actinide ions from aqueous solution

Li-Yong Yuan[1], *yuanly@ihep.ac.cn, Nan Zhang*[1], *Zhi-fang Chai*[1,2], *Weiqun Shi*[1]. *(1) Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China (2) School of Radiological & Interdisciplinary Sciences, Soochow University, Suzhou, China*

The renaissance of nuclear energy promotes increasing basic researches on the separation and enrichment of actinide ions. MOFs, assembled from organic linkers and metal ion or cluster nodes, represent a new class of porous solid materials with great potentials for sensing and sorption of actinide ions due to their unique physicochemical properties. We here explored the feasibility of several kinds of MOFs and/or their derivatives as efficient sensor/sorbents of U(VI) and Th(IV), and the results were summarized as: (1) MOF-76 (Tb) exhibits high sensitivity for the detection of U(VI) *via* the host-guest interaction between uranyl cations and the framework, while MOF-76 (Y) shows high performance in U(VI) sorption with a large sorption capacity of more than 300 mg/g at a low pH of ~3.0 and desirable selectivity towards U(VI) over a series of competing metal ions. (2) Amine grafting on the framework of MOFs greatly enhances adsorbability of Cr-MIL-101 towards U(VI) from aqueous solution, and the enhancement dependents on the coverage and flexibility of the grafted amino group. (3) UiO-66 and its amine derivative (UiO-66-NH_2) can be used as stable and low-cost U(VI) sorbents from aqueous solution. The introduction of amino groups into UiO-66, however, does not obviously enhance U(VI) sorption, probably result from the lower activity of aromatic amines, decrease of surface area and formation of intermolecular hydrogen bonds. Besides, very recent efforts by us have focused on the utility of MOFs in the sorption of other actinides such as Th(IV). UiO-66 and its carboxyl derivative (UiO-66-2COOH), and MIL-53 were found to possess excellent adsorbability towards Th(IV) in terms of

large sorption capacities, fast sorption kinetics, desirable selectivity, and good reusability of the sorbent. All these works highlight the vast opportunities of MOFs materials applied in actinides separation from aqueous solution.

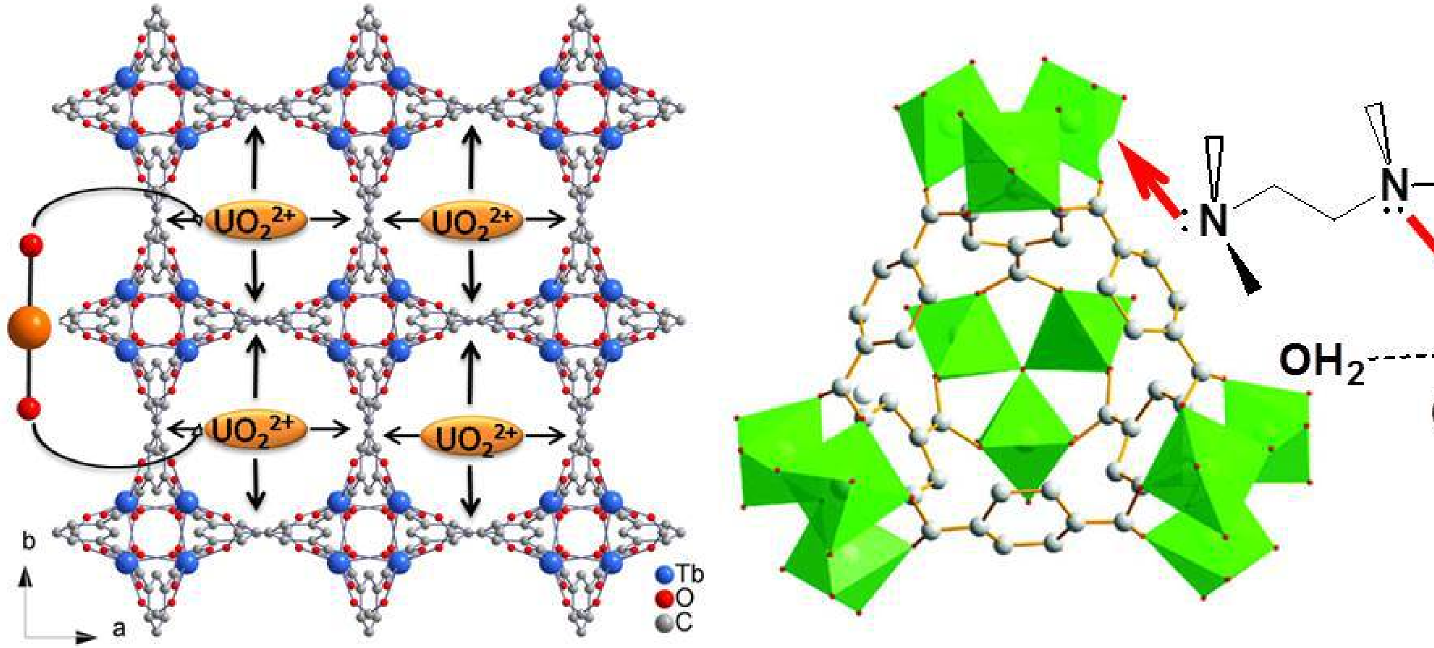


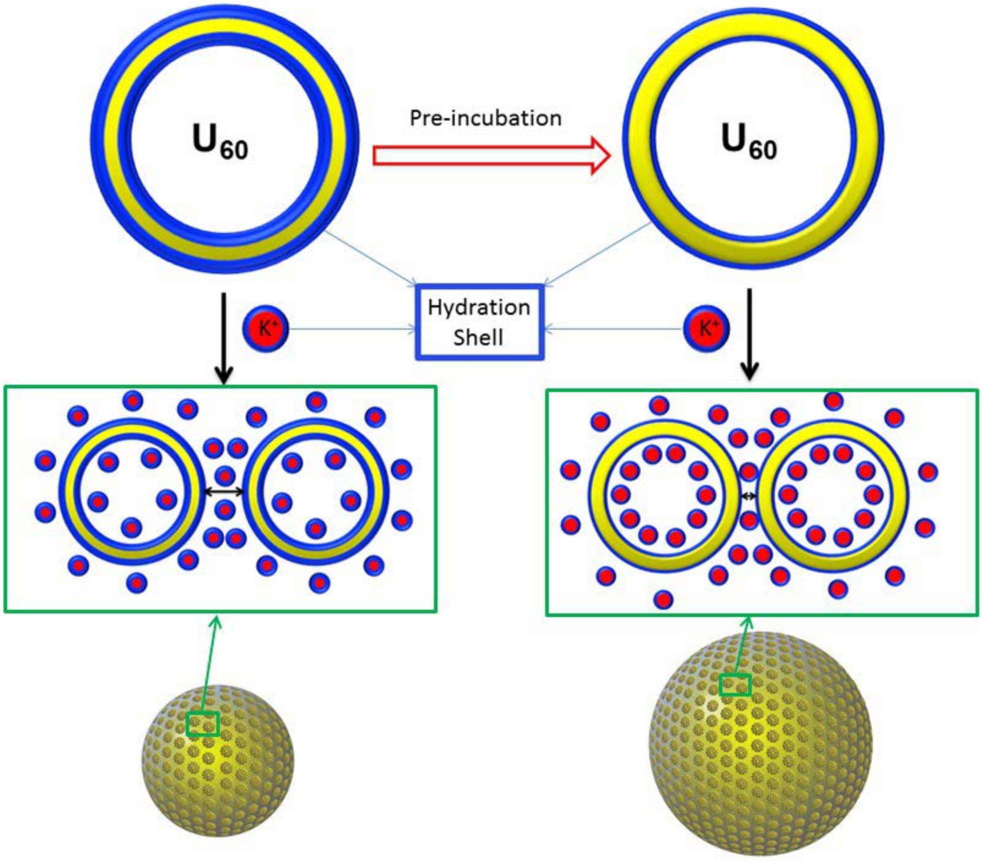
Fig.1 U(VI) sorption in MOF-76 (left), MIL-101derivative (middle), and UiO-66(right)

NUCL 128

Ion selectivity of uranyl peroxide nanocages: An inorganic mimic of K^+ ion channels

Yunyi Gao[3]*, yg27@zips.uakron.edu, Jennifer Szymanowski*[4]*, Xinyu Sun*[5]*, Peter C. Burns*[2]*, Tianbo Liu*[1]*. (1) Department of Polymer Science, The University of Akron, Akron, Ohio, United States (2) Univ of Notre Dame, Notre Dame, Indiana, United States (3) Polymer Science , University of Akron, AKRON, Ohio, United States (4) University of Notre Dame, Notre Dame, Indiana, United States*

We report that $Li_{48+m}K_{12}(OH)_m[UO_2(O_2)(OH)]_{60}(H_2O)_n$ (m≈20 and n≈310) (U_{60}), an actinyl peroxide cage cluster, can precisely select among Na^+ and K^+ ions when heated to certain temperatures, a most essential feature for K^+ selective filters. Additionally, the U_{60} clusters demonstrate several other features in common with K^+ ion channels including passive transport of K^+ ions, a high flux rate, and the dehydration of U_{60} and K^+ ions. These make U_{60}, a pure inorganic cluster, a promising candidate to mimic the function of ion channels in an aqueous environment. Laser light scattering (LLS) and isothermal titration calorimetry (ITC) studies revealed that the tailorable ion selectivity of U_{60} clusters is due to the thermal responsiveness of their hydration shells.



U_{60} clusters demonstrate tunable ion selectivity at different temperatures that can mimic the function of protein ion channels. The adjustable permeability towards different alkali ions is mainly attributed to the thermal responsiveness of U_{60} cluster's hydration shell thickness.

NUCL 129

Possible atomic fuel production through accumulation of specific radioisotopes by fish in offshore Fukushima, Japan

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

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

#1#
The Total Fish Weight % of Okamejei kenojei (English Name: Common-skete; Japanese-Name:KOMON KASUBE) spp. and Sebastes cheni (Japanese rock fish, Japanese sea perch; SHIRO MEBARU) in this sampling in offshore Fukushima-ken,Japan were 26.6824 Weight% and 13.700005 Weight%, respectively; additionally, the fish bodies of Okamejei kenojei spp. and Sebastes cheni had 49.322578 becquerel% and 33.037159 becquerel% of 134Cs, respectively, and had 50.479187becquerel% and 31.779293 becquerel% of 137Cs, respectively. Therefore, Okamejei kenojei spp. has ability to accumulate 1.8485 times of their weight % for 134Cs and 1.92168 times of their weight% for 137Cs. However, Sebastes cheni has the ability to accumulate 2.411 times of their weight% for 134Cs and 2.3195 times of their weight% for 137Cs.
#2#
It is possible to accumulate or separate specific nuclides (134Cs and 137Cs) by combining Sebastes cheni and Kareius bicoloratus (Stone flounder; ISHIGAREI), and Ditrema temmincki temmincki (Surfperch; UMITANAGO) and Cynoglossus joyneri (Red tongue sole; AKASHITA BIRAME).

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

NUCL 130

Thermodynamic studies on the complexation of uranyl ion in ionic liquids

Chao Xu, *suprachao@gmail.com, Jing Chen. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China*

As a novel and functional solvent, ionic liquids have received increasing attentions in nuclear industry for its potential application on the extraction and separation of radioactive metal ions. Despite of a number of studies on the liquid-liquid solvent extraction of metal ions using ionic liquids, studies on the complexation behavior of metal ions in ionic liquids are relatively rare. The present work focuses on the complexation of uranyl ion in ionic liquids. The complexation of uranyl ion with a variety of ligands was studied by means of spectroscopic and thermodynamic techniques. The species of uranyl complexes formed in ionic liquids and the corresponding

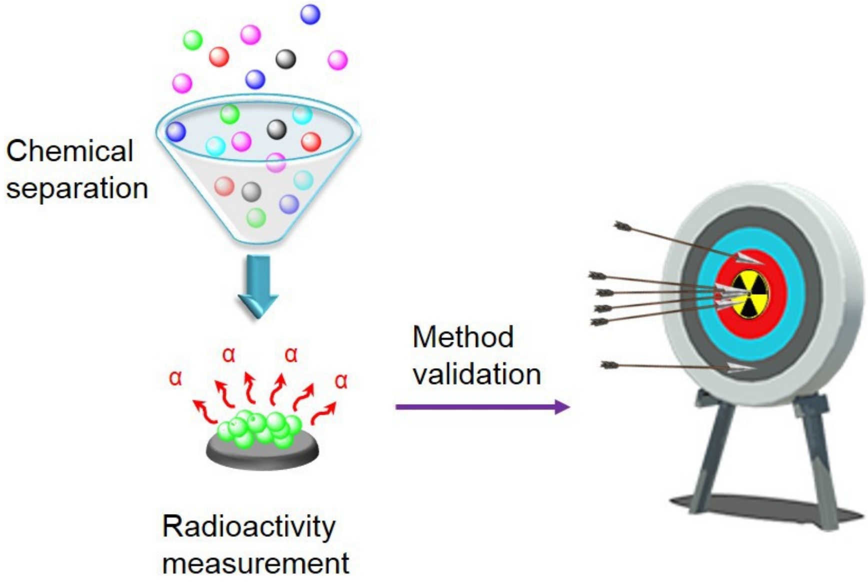
thermodynamic parameters such as conditional stability constants, enthalpy, and entropy have been obtained. The thermodynamic and structural results provide additional insight into the unique solvation environment of ionic liquids and help us further understand experimental behaviors in practical applications such as solvent extraction.

NUCL 131

Determination of radioactivity of uranium and thorium in environmental samples by using fusion and sequential separation method, and its evaluation using key validation parameters

Young Gun Ko*, ygko08@gmail.com, Won Young Kim, Hyuncheol Kim, Wanno Lee, Geun-Sik Choi, Kun Ho Chung, Mun Ja Kang. Environmental Radioactivity Assessment Team, Korea Atomic Energy Research Institute, Daejeon, Korea (the Republic of)*

Monitoring of radioactivity of nuclides in soil is important to reduce hazardous effects to the human health by the uptake and accumulation of the radionuclides because water-soluble radionuclides compounds in the soil migrate into vegetables, which are eaten almost every day, by complex process such as leaching, capillary rise, runoff, sorption, root uptake, and re-suspension. Generally, the radioactivity concentration in environmental samples is low, and many samples should be analyzed for the monitoring of radionuclides in the environment. Therefore, the development of a rapid and precise method for the determination of radioactivity in environmental samples is very important. The fusion method is a very effective way for a rapid and complete sample dissolution, and the sequential separation method helps speed up separation times for the separation of two or more nuclides in samples. In this study, the fusion technique was used to dissolve a soil sample completely, and uranium and thorium were separated by the sequential method. The separated uranium and thorium were analyzed using alpha-particle spectrometry. The developed method was evaluated by assessing the key validation parameters, and demonstrated a satisfactory quality level of the selected criteria of the performance. The developed method is expected to apply to the measurement of the low-level activity concentration of radionuclides in various solid samples with a high level of accuracy.



NUCL 132

Modeling redox coordination chemistry for transuranium elements

Frankie D. White[4], *white.deuce@gmail.com, Matthew L. Marsh*[1]*, Shane S. Galley*[4]*, David E. Hobart*[3]*, Thomas E. Albrecht-Schmitt*[2]*. (1) Florida State University, Louisville, Tennessee, United States (2) Department of Chemistry and Biochemistry, Florida State University , Tallahassee, Florida, United States (3) National Security Education Center, Los Alamos National Laboratory, Santa Rosa Beach, Florida, United States (4) Chemistry, Florida State University, Tallahassee, Florida, United States*

The oxidation state of an element is a fundamental property for understanding the type of chemistry an element will possess. Although the trivalent oxidation state predominantly exists throughout the 4*f* block, the divalent state can be obtained with a strong reducing agent. In the actinide series, the An(III) oxidation state is only readily observed from americium to mendelevium. Because the lanthanides also prefer the trivalent state, they serve as excellent surrogates for modeling the An(III) → An(II) reduction chemistry of coordination compounds. Air-free and non-aqueous electrochemistry has allowed the reduction potential of *f*-block elements to be observed in various reducing environments to determine suitable reaction conditions for these transuranics. In particular, the modeling of divalent americium and californium coordination compounds are explored to gain a better understanding of the structure and bonding in these later actinides.

NUCL 133

Preparation of alumina microspheres by internal gelation method

Cristina Padilla-Cintron*, cpadilla@tutanota.com, Jeffrey Katalenich. Pacific Northwest National Laboratory, Richland, Washington, United States*

Plutonium-238 (Pu-238) oxide is the favored material for thermoelectric power generation due to its high power density, long half-life, and low shielding requirements. An alternative, solution-based method for Pu-238 processing is internal gelation via sol-gel techniques. Sol-gel methodology lends to monodisperse and uniform microspheres that can be pressed into a pellet. A recent study has suggested that Al_2O_3 may be a preferred $^{238}PuO_2$ pellet surrogate, rather than CeO_2, due to its thermal properties. In the present study, attempts were made to determine optimum process parameters, particularly the quantity of organic additives urea and hexamethylenetetramine present in the sol-gel feed solution. Good broth ratios were observed with aluminum concentrations ranging from 2.335 to 2.170 M in the temperature range of 82-84 °C. The latest results on microspheres production using an optimal formulation will be presented.

NUCL 134

Characterization of lanthanide chlorides for nuclear forensics

Shayan Shahbazi*, shayanshahbazi@gmail.com, John Auxier. Nuclear Engineering, University of Tennessee, Knoxville, Knoxville, Tennessee, United States*

In an effort to meet the growing demand for more rapid separation methods, this work reports the development and thermodynamic characterizations of lanthanide chlorides as a vehicle for the rapid separation of nuclear fission products. These compounds can be rapidly separated from each other via gas phase chromatographic separations due to differences in adsorption enthalpy. Because adsorption and sublimation thermodynamics are linearly correlated, there is considerable motivation to determine sublimation enthalpies to improve the ability to predict separations effectiveness. A method using thermogravimetric analysis (TGA) is employed in this study on thirteen lanthanide chlorides. Sublimation enthalpies are determined using the Langmuir method involving isothermal jump heating. An empirical correlation is used to estimate adsorption enthalpies of lanthanide complexes on a quartz column from the sublimation data. TGA-MS and melting point analysis are used to confirm sublimation as well as confirm the stability of the compound through the sublimation region. Further characterization of the lanthanide halide is necessary due to a possible side reaction involving lanthanide oxychloride formation upon heating.

NUCL 135

Synthesis of Bis-Triazinyl Pyridine (BTPs) ligands for ^{15}N ESEEM experiments in actinide and lanthanide complexes

David Dan*[1], dd15g@my.fsu.edu, 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

N-donor ligands such as BTPs have shown selectivity for actinide complexation in the presence of lanthanides, but the reasons for this selectivity are still unclear. The ease of synthesis and low cost of BTPs make them ideal targets for use in lanthanide–actinide metal separations. NMR experiments have shown that the 5*f* elements bond more covalently than the 4*f* elements to BTPs[1]. ^{15}N ESEEM experiments would be able to further expand the knowledge of how BTP ligands bind to 4f/5f elements. This new understanding of actinides and lanthanides could lead to better designed ligands for the separation of actinides and lanthanides in nuclear waste streams.

NUCL 136

PDF analysis of uranyl clusters from aqueous solutions

Karoly Kozma, *kozmak@oregonstate.edu, Clement Falaise, Harrison A. Neal, May D. Nyman. Oregon State University, Corvallis, Oregon, United States*

Uranium is the heaviest naturally occurring element, therefore conducive to characterization by X-ray techniques including small, wide and total angle X-ray scattering. In this study we implemented a laboratory instrument for X-ray total scattering on solution samples containing various uranyl-oxo clusters. These compounds are of interest since the discovery of first uranyl peroxide clusters in 2005. Despite having the same building blocks for these clusters -uranyl ion, peroxide and hydroxide anions (and sometimes phosphates and oxalate)- the variety of the discovered clusters is rich in both topology and size. We collected X-ray scattering curves on these solutions in which the clusters contain 22, 28, 32 and 60 uranyl polyhedral, denoted U_{24}, U_{28}, U_{32} and U_{60}, respectively. The raw data were analyzed to obtain the atomic pair distribution function (PDF) of these samples in order to exploit atomic-level structural information in aqueous solution. These studies provide information about the atomic pair separations as well as the particle size in aqueous state, which makes it a very powerful supplementary technique for investigation of solutions. Our findings show that the local structure depends on the topology of the cluster: tetragonal, pentagonal and hexagonal faces of building units creates different environment in the local structure, however this feature slightly differs with the overall size of the cluster. We have also coupled small and wide angle X-ray scattering (SWAXS) with this technique to describe overall cluster size. Uranyl peroxide clusters also have particularly informative and characteristic SWAXS curves due to their capsule-like topology. With this information in hand, we are endeavoring to predict the building units through local structure and the overall particle size of an unknown or a new species in solution, for which we are unable to obtain structural data via single-crystal X-ray diffraction.

NUCL 137

Ordered mesoporous carbons functionalized for actinide and lanthanide separations chemistry

Kyle Kluherz[3], *tigery@skybeam.com, Gauri Deodhar*[3]*, Erin Bertelsen*[3]*, Jenifer Braley*[1]*, Brian G. Trewyn*[2]*. (1) Chemistry Geochemistry/Nuclear Engineering, Colorado School of Mines, Golden, Colorado, United States (2) Dept Chem Geochem, 152 Coolbaugh Hall, Colorado School of Mines, Golden, Colorado, United States (3) Chemistry, Colorardo School of Mines, Golden, Colorado, United States*

Ordered mesoporous carbons (OMCs) have shown great promise for a number of applications, including catalysis, electrochemistry, selective sequestration, drug delivery, and separations chemistry. This versatility is based on their high surface area, regular ordered pores, tunable pore size and structure, physical durability and low reactivity, diverse potential surface functionalization, and adaptable synthesis routes. Furthermore, their durability in an oxidizing environment, such as that produced by radioactive decay, and ability to protect internal functional groups make them particularly well-suited to radiochemistry applications. We have been developing OMCs for the separations of actinides from solution through the use of surface-attached tropolone and bis-2-ethylhexyl phosphoric acid (HDEHP) functional groups. The ultimate goal of this research is to gain a fundamental understanding of the material properties, allowing synthesis of novel materials to replace the decades-old separations methods currently used in the radiochemistry industry. Such materials could allow for on-site post-detonation identification of fission products, allowing for faster and more effective nuclear forensics analysis. We have been synthesizing MCN materials from MSN-10 and SBA-15 type silica using a multi-step hard templating approach, and functionalizing them with tropolone, HDEHP, and other ligands using a previously reported lithiation method. We are also performing computational investigations of these materials in order to better understanding the exact nature of the lithiation reaction, allowing us to further improve our functionalization methods.

NUCL 138

Soft N-, S-, and mixed donor site ligands for selective separation of actinides from lanthanides

Megan Twomey[1,2]*, mtwom001@fiu.edu,* ***Ingrid Lehman-Andino***[1]*, ingrid.lehman@gmail.com, Logesh Mathivathanan*[1]*, Raphael G. Raptis*[1]*, Konstantinos Kavallieratos*[1]*. (1) Department of Chemistry & Biochemistry, Florida International University, Miami, Florida, United States (2) Applied Research Center, Florida International University, Miami, Florida, United States*

Nuclear energy has the potential to greatly increase the world’s clean energy supply, but currently presents a serious drawback in how the used fuel is handled. A critical issue in the nuclear fuel cycle is the separation of actinides (An) from lanthanides (Ln) in spent material. The minor An, generated, especially ^{241}Am, are strong heat emitters and limit the capacity of geologic repositories. Removal of the minor An can help reduce

long-term toxicity and storage time from thousands of years to just a few hundred years. The separation of An from Ln *via* selective complexation and solvent extraction has presented major difficulties due to similarities in their ionic radii and identical oxidation states. The presence of An 5f electrons give the An(III) a somewhat “softer” character relative to Ln(III), and presents a strategy for separation, by using properly placed soft binding sites. Recently, there have been extensive efforts to incorporate ligands with softer N and S sites to increase An/Ln separation selectivity. In this work, we present novel organic ligand frameworks with soft N-, S- and mixed donor sites for selective An separation from Ln. These ligands incorporate soft thioamide groups, which are not widely studied, and soft N-containing frameworks derived from 1,10-phenanthroline, diphenylpyridine, and tripodal pyrazoles. Preliminary studies indicate coordination of N^2,N^6-diphenylpyridine-2,6-bis(carbothioamide) with $Ce(NO_3)_3$ as evident by an increase in the 380 nm fluorescence emission (l_{exc} = 233 nm) of the ligand (6.2×10^{-5} M) upon addition of the metal solution (2.5×10^{-4} M). The characterization of ligands and their metal complexes by NMR, FT-IR, fluorescence spectroscopy, and X-ray crystallography will be discussed.

NUCL 139

Electrochemical reduction of aqueous uranium

Brandon Stevenson, *brandnstevensn@gmail.com, Jonathan Scaggs, Dale D. Russell. Chemistry, Boise State University, Boise, Idaho, United States*

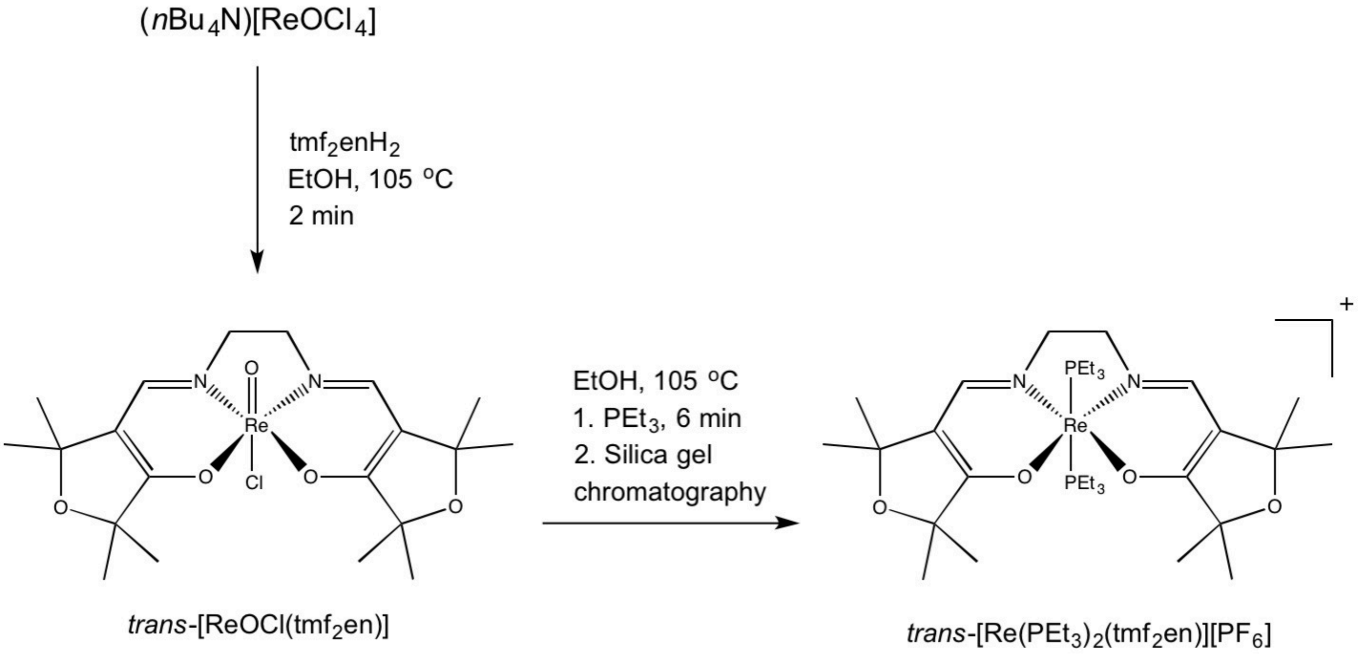
Nuclear power generation will continue to have a role in the United States total energy production in the forseeable future, and whether or not that role continues, the legacy waste from nuclear power generation will need to be remediated. Long term storage options are no longer seriously considered. The Purex and other processes for removing uranium and plutonium from aqueous wastes are very successful and most of the remaining radioactivity of the wastes is due to americium and curium (minor actinides, "MAs"). Their removal is complicated by similarity in size, charge, surface charge density, and reactivity to the lanthanides which are also present and which can prevent the transmutation of these MA isotopes to stable elements. Therefore the long term goal of this project is to develop an extraction method for the elements americium and curium. This project will use a ligand designed by Idaho National Laboratory (a polyfluoridated dithiophosphinic acid) to selectively extract minor actinides from a mixture containing the lanthanides as well. The hypothesis is that the minor actinides favor more covalency in coordination (i.e. softer donor atoms), while the lanthanides favor more ionicity in the coordination sphere. A trend in donor preference is expected across the actinide series, from actinium through curium, from greater ionicity of the coordination bond, to greater covalency. To demonstrate such a trend it is desirable to include as many elements in the series as we can. Therefore we will use thorium and uranium in addition to the MA's. These two elements favor higher oxidation states than the MAs therefore they must be reduced to include them in the series, so that charge is not a differentiator in the strength of the ligand-metal bond. The reduction of uranium in aqueous solution has proven to be challenging. We seek to characterize the reduction of uranium using a specially designed electrochemical cell in which U(III) can be generated electrochemically. Studying the thermodynamics and kinetics of the reduction process will enable us to define a protocol for generation and stabilization of the uranium(III) ion in acidic aqueous solution. Progress in reduction of uranium(VI) to uranium(III) will be reported.

NUCL 140

Re (III and V) Schiff base complexes as potential therapeutic agents

Jakob E. Baumeister, *jebhx4@mail.missouri.edu, Charles Barnes, Silvia S. Jurisson. Chemistry, University of Missouri, Columbia, Missouri, United States*

Technetium-99m (^{99m}Tc) continues to dominate diagnostic nuclear medicine owing to its ideal nuclear properties and availability from generator systems. Recent attention has been given to rhenium-186 (^{186}Re) compounds as therapeutic analogues to ^{99m}Tc agents. The ^{99m}Tc-"Q-series" (*trans*-[^{99m}Tc^{III}(PR$_3$)$_2$(N$_2$O$_2$-Schiff base)]$^+$) has shown utility as SPECT imaging agents for myocardial perfusion and multi-drug resistant tumors. Development of a Re-"Q-series" has been studied with limited success and few examples of Re(III)-"Q compounds". This is due in part to the slow reactivity of Re and its stability in high oxidation states. One strategy to counteract this slow reactivity is the use of microwave chemistry. We report here the microwave assisted synthesis of ^{99m}Tc-Q12 analogs based on Re. ^{99m}Tc-Q12 is complexed by the tetradentate Schiff base ligand 4,4'-((1*E*,1'*E*)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2,2,5,5-tetramethyl-2,5-dihydrofuran-3-ol) (tmf$_2$enH$_2$). Several Re(III and V)-tmf$_2$en complexes were synthesized by microwave irradiation. All compounds were characterized using standard spectroscopic techniques, and single crystal X-ray diffraction. Reaction of (*n*-Bu$_4$N)[ReOCl$_4$] with tmf$_2$enH$_2$ yields *trans*-[Re^{V}OCl(tmf$_2$en)]. The *trans* chloride is readily exchanged to form mononuclear and di-nuclear Re(V)-tmf$_2$en complexes. Reduction of *trans*-[Re^{V}OCl(tmf$_2$en)] by triethylphosphine yields the cationic *trans*-[Re^{III}(PEt$_3$)$_2$(tmf$_2$en)]$^+$ species. The phosphine identity was varied to study the steric and redox properties of Re(III)-tmf$_2$en complexes. This work demonstrates the first Re analogues to ^{99m}Tc(III)-Q12 with potential application as therapeutic agents. Research is ongoing to extend this chemistry to ^{186}Re at the tracer level. It is expected Re will demonstrate different reactivity at the dilute concentrations experienced *in vivo*.



Synthesis of *trans*-[Re(PEt$_3$)$_2$(tmf$_2$en)][PF$_6$]

NUCL 141

Radiolabeling of a trithiol-bombesin ligand with ^{77}As and ^{72}as for use as radiopharmaceuticals

Michael Phipps[1], *mpd32@mail.missouri.edu, Yutian Feng*[1], *Fabio Gallazzi*[2], *Alan Ketring*[3], *Silvia S. Jurisson*[1]. *(1) Chemistry, University of Missouri, Columbia, Missouri, United States (2) Structural Biology Core, University of Missouri, Columbia, Missouri, United States (3) Research Reactor Center, University of Missouri, Columbia, Missouri, United States*

Arsenic-72 (^{72}As) and ^{77}As have nuclear properties suitable for use in radiopharmaceuticals. ^{72}As is a positron emitter making it useful in positron emission tomography (PET) imaging. ^{77}As is a beta emitter whose emissions have appropriate energy to treat cancer. This makes the two isotopes a perfect pair for diagnosis and targeted radiotherapy, since they are the same element. ^{77}As is produced by neutron irradiation of ^{76}Ge to form ^{77}Ge, which decays to ^{77}As. The ^{77}As is separated from a neutron irradiated ^{76}GeO$_2$ target using silica gel column chromatography to yield no carrier added ^{77}As. The ^{77}As is eluted in oxidation state +5 as [^{77}As]arsenate. Trithiol ligands have been shown to form stable ^{77}As(III) complexes in high radiochemical yield. For translation to use in targeted radiotherapy, a bombesin peptide was incorporated into a trithiol ligand as a bifunctional chelate. Bombesin (BBN) is a peptide with high affinity for the gastrin releasing peptide receptor, which is highly expressed on several cancers including prostate, small cell lung and breast cancers. A trithiocyanate protected trithiol ligand was conjugated to the bombesin (BBN) peptide following standard procedures used in peptide synthesis. This Trithiol-BBN precursor was

deprotected with tris(2-carboxyethyl)phosphine (TCEP) to generate the Trithiol-BBN ligand. Radiolabeling of the Trithiol-BBN ligand required reduction of ^{77}As(V) to ^{77}As(III); ammonium mercaptoacetate (NH_4SR) was used as the reducing agent to yield $^{77}As(SR)_3$, which was then reacted with the Trithiol-BBN to yield the desired ^{77}As-Trithiol-BBN complex in greater than 95% yield. Verification of complex formation was done by comparison with the non-radioactive standard ^{75}As-Trithiol-BBN using reversed-phase HPLC. The non-radioactive standard had been characterized by LC-MS. The stability of the ^{77}As-Trithiol-BBN was investigated following purification. The addition of ascorbic acid was necessary to minimize radiolysis.

NUCL 142

Application of inductively coupled plasma mass spectroscopy and enriched tungsten isotopes to nuclear fusion research

***Jonah Duran*[2]*, jduran2@vols.utk.edu, David C. Donovan[2], Chris Eley[2], Anurag Maan[2], John D. Auxier[1], Seungsup Lee[2], Shawn Zamperini[2], Ezekial Unterberg[3], Dmitry Rudakov[4], Peter Stangeby[5], William Wampler[6]. (1) Department of Nuclear Engineering , Institute for Nuclear Security , Jefferson City, Tennessee, United States (2) Nuclear Engineering, University of Tennessee Knoxville, Knoxville, Tennessee, United States (3) Oak Ridge National Lab, Oak Ridge, Tennessee, United States (4) University of California, San Diego, La Jolla, San Diego, California, United States (5) University of Toronto Institute for Aerospace Studies, Toronto, Ontario, Canada (6) Sandia National Lab, Albuquerque, New Mexico, United States*

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) was used to measure isotopic ratios of deposited tungsten (W) on graphite collector probes inserted into the nuclear fusion experiment, DIII-D. Tungsten is very important to the fusion community because it will be used to make the highest heat flux region of the inner wall (divertor) of the largest fusion experiment in the world, ITER. However, the plasma-material interactions will gradually erode the W surface and release W impurities into the fusion plasma. These impurities can cause prohibitively large radiative power losses, so it is essential to understand and minimize impurity production and transport in the plasma. During the DIII-D Metal Tile Campaign, two toroidal rings of W-coated TZM inserts were installed in the divertor. The rest of the inner wall is covered in graphite tiles. The inner ring was coated in natural-W and the outer ring was coated with 93.5% isotopically enriched W-182. The unique “isotopic fingerprint” of the enriched W-182 ring enabled the eroded W to act as “tracer particles”. Graphite collector probes were inserted into the edge plasma during operations to sample impurities. ICP-MS analysis of the collector probes has yielded isotopic ratios of the deposited W, which have been used with the Stable Isotope Mixing Model (SIMM) to estimate the relative contribution of W from each of the divertor rings that contributed to the total W deposition on the probe. ICP-MS analysis required dissolving the graphite substrate and leaching the W into an aqueous solution. Modified acid digestion techniques have been explored to enhance the recovery rate of W. Samples were dissolved in a solution of deionized water with ultra-high purity hydrofluoric and nitric acids. W becomes more stable to hydrolysis

when complexed with fluorine ions. Microwave acid digestion vessels were utilized to catalyze the digestion process. The resulting samples were then diluted and analyzed with the use of the OptiMass 9500 ICP-TOFMS. The use of W tracer particles and isotopic analysis of the collector probes has provided important information about how various plasma operating configurations affect impurity production from the divertor and transport to other regions of the device. This presentation will discuss the methods developed for the ICP-MS analysis of isotopically enriched W on the graphite collector probes and preliminary findings from the DIII-D Metal Tile Campaign.

NUCL 143

Actinide-carbon bond activation in gas-phase organoactinide complexes

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

Gas-phase organoactinyl anion complexes $[AnO_2(R)(O_2CR)_2]^-$ (An = U, Np, Pu; R = $CCCH_3$, *cyclo*-C_6F_5, etc.) are synthesized by CO_2 elimination from carboxylates, $[AnO_2(O_2CR)_3]^-$, which are prepared by electrospray ionization. It has previously been demonstrated that the An-C bonds in these organoactinyls hydrolyze upon reaction with water to yield hydroxides in which the An-C bond is replaced by an An-OH bond concomitant with generation of neutral HR. We are employing the reactive character of An-C bonds in attempts to access other types of actinide chemistry. Potential targets include reactions with CH_3X (X=F, Cl, Br I), to yield An-X bonds and induce C-C coupling, and with CH_3ChH (Ch=O, S, Se, Te), to yield An-ChH and/or An-$ChCH_3$ bonds concomitant with formation of C-C and/or C-H bonds. Although the thermodynamics of such processes might be substantially favorable, there may insurmountable kinetic barriers to such bimolecular reactions carried out under low-energy conditions in a quadrupole ion trap. For reactions that do proceed, the comparative reactivities of U-C, Np-C and Pu-C bonds are of interest for assessing chemical variations across the actinide series, and particularly for evaluating fundamental aspects of actinide chemistry that can be addressed by complementary computational approaches.

NUCL 144

Characterizing actinide speciation using electrospray ionization mass spectrometry

Teresa Eaton*, tmne7633@gmail.com, Jiwen Jian, John K. Gibson. Lawrence Berkeley National Laboratory, Emeryville, California, United States*

Developing and refining actinide separation strategies are crucial for reducing the hazards and costs of processing and storing radioactive waste. Electrospray ionization quadruople ion trap mass spectrometry (ESI-QIT/MS) can be used to probe the selectivity of potential separation ligands, and the structures and bonding of ligand-actinide ion complexes in the gas phase. Comparing ESI-QIT/MS results to those from complementary techniques, including structural, thermodynamic and spectroscopic studies in condensed phases, and computational studies of gas-phase species, provides a useful approach for relating solution and gas-phase behavior, and for revealing fundamental ion-ligand binding properties. Various complexants, including elementary model ligands such as 1,4,8,11-tetrathiacyclotetradecane, acetamide oxime, and acetate derivatives, are used to investigate speciation and selectivity towards uranium, transuranic actinides, and lanthanides.

NUCL 145

Utilizing Diffusion Ordered Spectroscopy (DOSY) to probe organic phases in liquid-liquid solvent extraction systems

Ashleigh Kimberlin, *ashleigh.kimberlin@wsu.edu, Kenneth L. Nash. Washington State University, Pullman, Washington, United States*

There are a variety of solvent extraction based separation processes under investigation for advanced nuclear fuel cycle development, particularly processes to remove lanthanides from the minor trivalent actinides. A principle defining feature for any new extraction system is the optimization of movement of the target species across the liquid-liquid boundary and into the bulk organic phase. Suitable extractant molecules share the properties of conventional surfactant molecules: a polar “head” for interfacial activity and a greasy “tail” for organic phase compatibility. Such “amphiphilic” molecules display a tendency to mask their bipolar behavior by hiding (via head-to-head interactions in the lipophilic medium) as hydrogen bonded dimers or reverse micelles in the nonpolar organic phase. Their movements and organization of these molecules (and their metal complexes) is of significant interest but challenging to probe. Most methods used to characterize these interactions rely on optical spectroscopy or indirect methods like freezing point depression or vapor pressure osmometry. NMR spectroscopy is a versatile technique that can be used to directly probe organic phases and the interactions occurring in situ without many of the limitations of other techniques. Diffusion Ordered Spectroscopy (DOSY) is an advanced NMR technique used to determine the diffusion coefficients of species by tracking an NMR active nucleus. The diffusion coefficient can be used to infer the size of species in solution. Recent research at WSU has focused on using DOSY to investigate the self-aggregation of extractants along with their interactions with phase modifiers, water, acids, and extracted lanthanide complexes. The results obtained from DOSY are comparable to small angle neutron scattering and the relative ubiquity of NMR makes DOSY a far more accessible technique to smaller institutions. The nondestructive nature of DOSY makes it a versatile tool in organic extractant development and characterization. In this report,

recent results featuring the application of DOSY to the characterization of extractants of interest in nuclear separations (and their metal complexes) will be discussed.

NUCL 146

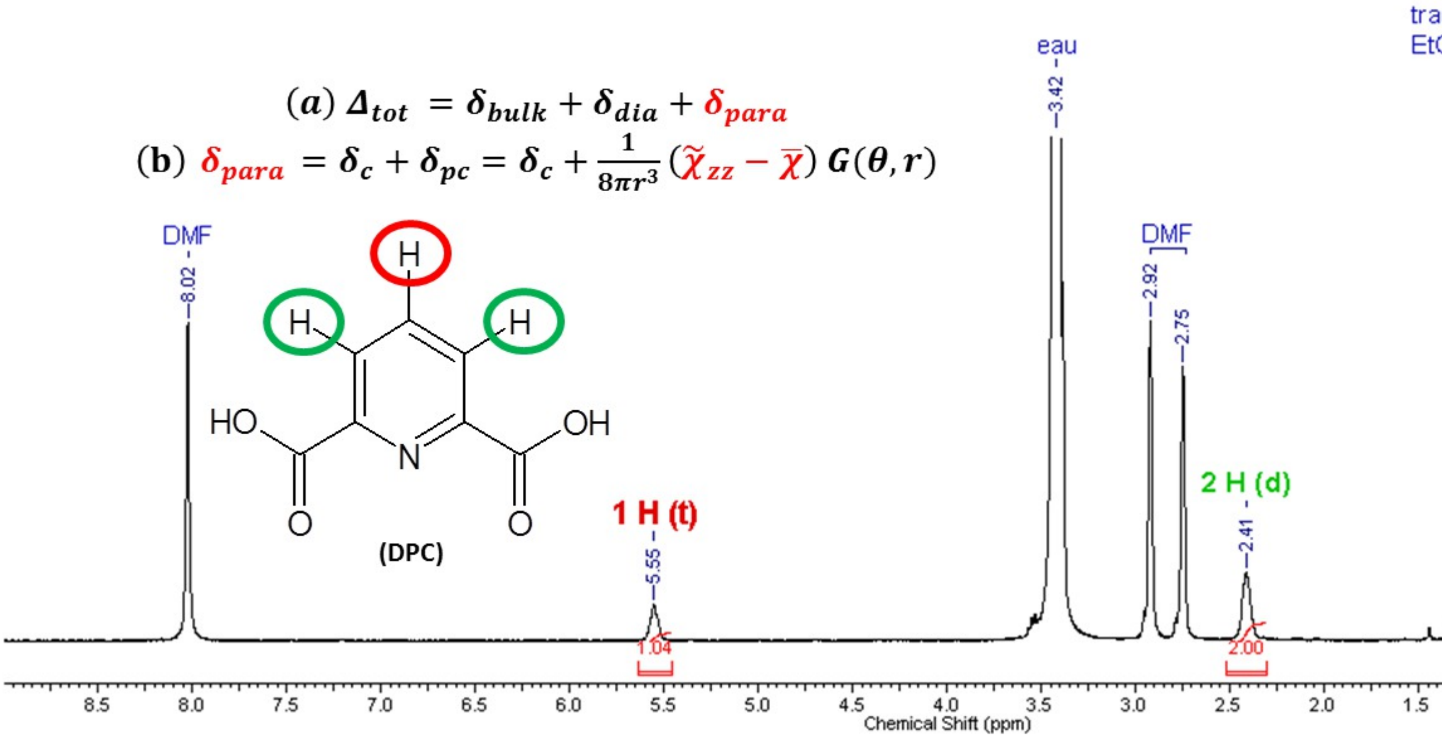
Study of actinide cations in solution through their paramagnetic behavior

Marie-Claire ILLY[1], *marie-claire.illy@orange.Fr, Matthieu Autillo*[1], *Laetitia Guerin*[1], *Dominique Guillaumont*[1], *Eric Colineau*[2], *Philippe Moisy*[3], *Hélène Bolvin*[4], *Claude Berthon*[1]. *(1) DEN/MAR/DRCP/SMCS/LILA, CEA Marcoule, Bagnols-sur-Ceze, Gard, France (2) Actinide Research Unit, EU - JRC - ITU, Karlsruhe, Germany (3) DEN/MAR/DRCP, CEA Marcoule, Bagnols-sur-Ceze, Gard, France (4) Laboratoire de Physique et de Chimie Quantiques, Université Toulouse 3, Toulouse, France*

NMR spectroscopy is one of the most relevant and widespread techniques that provides structural information for solid or liquid samples. It can be applied in many fields from small molecule analysis in organic chemistry to large molecule protein analysis in biology. Recently, with the advent of “nuclearized” spectrometers, it has proven useful in nuclear chemistry as well. The presence of an actinide cation, with 5f electrons, generates a modification of the NMR spectrum i.e. a broadening and/or a shift of the chemical shift, which is characteristic of the cation paramagnetism. The structure of the complex in solution can then be deduced by the ^{1}H NMR spectrum. The total experimental shift (Δ_{tot}) depends on the paramagnetic shift (δ_{para}) whose equation can be solved by magnetic susceptibility measurements (equations a and b).

Quantification of the paramagnetic contribution involves measurement of magnetic susceptibilities, accessible by NMR spectroscopy, and determination of two parameters that depends on the electronic configuration of the metallic cation. Bleaney and Golding have determined and calculated these constants for lanthanide cations. For actinide cations (U, Np, Pu), they are unknown but first molar magnetic susceptibilities have been determined (equation b) for the free ion and the An – dipicolinate (DPC) complex.

For a better and more complete understanding of the magnetic behavior of 5f electrons, the present study is focused on the comparison between experiment and theory. Two areas of study are undertaken. First, a magnetic susceptibilities study of actinide (IV and VI) complexes in concentrated hydrochloric and nitric acid solutions (up to 9 M) were performed to complete literature data. Second, a study of the influence of the change in ligand symmetry, specifically from DPC to the DOTA ligand, for actinides (III and IV) are ongoing.



^{1}H NMR Spectrum of $\mathrm{Np^{VI}O_2(DPC)_2Li_2}$

NUCL 147

Method comparison for the determination of Pitzer parameters for Tc(VII), Re(VII), and V(V) in aqueous systems

*Cecilia Eiroa Lledo, **Gannon Parker**, parkergannon@gmail.com, Donald E. Wall, Nathalie Wall. Washington State University, Pullman, Washington, United States*

It is necessary to build models that accurately predict chemical behavior in solutions containing low to high salt concentrations. Ionic interaction models allow for the prediction of electrolyte behavior in their environment. The Pitzer model takes into account the ionic strength dependence on ion interactions using a virial expression, which unlike other models is still valid at high ionic strengths. The Pitzer parameters of common salts and metals have been reported extensively in literature since the 1970s, but reported values vary widely for some specific compounds. The mathematically and experimentally methods employed to find these parameters have biases associated with them. The purpose of this work is to understand whether the literature value divergences are due to a method bias or to experimental error. This research provides experimental data for the comparison between Pitzer parameters determined using liquid-liquid extraction methods and those based on solution molal volume variations. The metals of interest for this study are technetium(VII), rhenium(VII) and vanadium(V).

NUCL 148

Elucidating bonding preference in tetrakis(imido)urinate (VI) dianions

Jing Xie[2]*, xiejingsilent925@gmail.com, Nickolas H. Anderson*[1]*, Debmalya Ray*[2]*, Matthias Zeller*[3]*, Suzanne C. Bart*[1]*, Laura Gagliardi*[2]*. (1) Department of Chemistry, Purdue University, West Lafayette, Indiana, United States (2) Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, United States (3) Youngstown State University, Youngstown, Ohio, United States*

Actinyl species, $[AnO_2]^{2+}$, and their nitrogen analogue, $[An(NR)_2]^{2+}$, are characterized by their two strong *trans*-An-element multiple bonds. Here we report these robust bonds can be significantly weakened by increasing the number of multiple bonds to uranium, as demonstrated by a family of uranium(VI) dianions bearing four U-N multiple bonds, $[M]_2[U(NR)_4]$. The uranium(VI) tetrakis(imido) species, $[M]_2[U(NDIPP)_4]$, where DIPP = 2,6-diisopropylphenyl, and M = Li, Na, K, Rb, and Cs, have been synthesized and the nature of the bonds in these species has been characterized by quantum chemical calculations.
Density functional theory (DFT) calculations have been carried out. Molecular orbital analyses show that the U-N bonds are composed of two covalent bonds of predominantly U 5*f*, U 6*d*, and N 2*p* orbitals, with strong competition for the limited number of uranium-based orbitals due to the sharing among all four strongly π-donating imido ligands, see Fig. 1. Natural bond order (NBO), quantum theory atom in molecule (QTAIM), and complete active space self-consistent field (CASSCF) approaches have been employed to analyze the bonding characters. DFT calculations proved that the most stable structure of $[M]_2[U(NDIPP)_4]$ family is the observed pseudo-C_{2v} see-saw structures, as compared to the ideal square-planar and tetrahedral structures. To understand the driving force for the see-saw structures, a family of tetrakis(oxo) and tetrakis(imido) dianionic complexes (UO_4^{2-}, $U(NH)_4^{2-}$, $U(NMe)_4^{2-}$, $U(NPh)_4^{2-}$, and $U(NDIPP)_4^{2-}$) and their corresponding neutral complexes (Na_2UO_4, $Na_2U(NPh)_4$) were analyzed. Structural information support that the geometry of $[M]_2[U(NDIPP)_4]$ family is driven by cation-coordination and sterics rather than electronic factors.

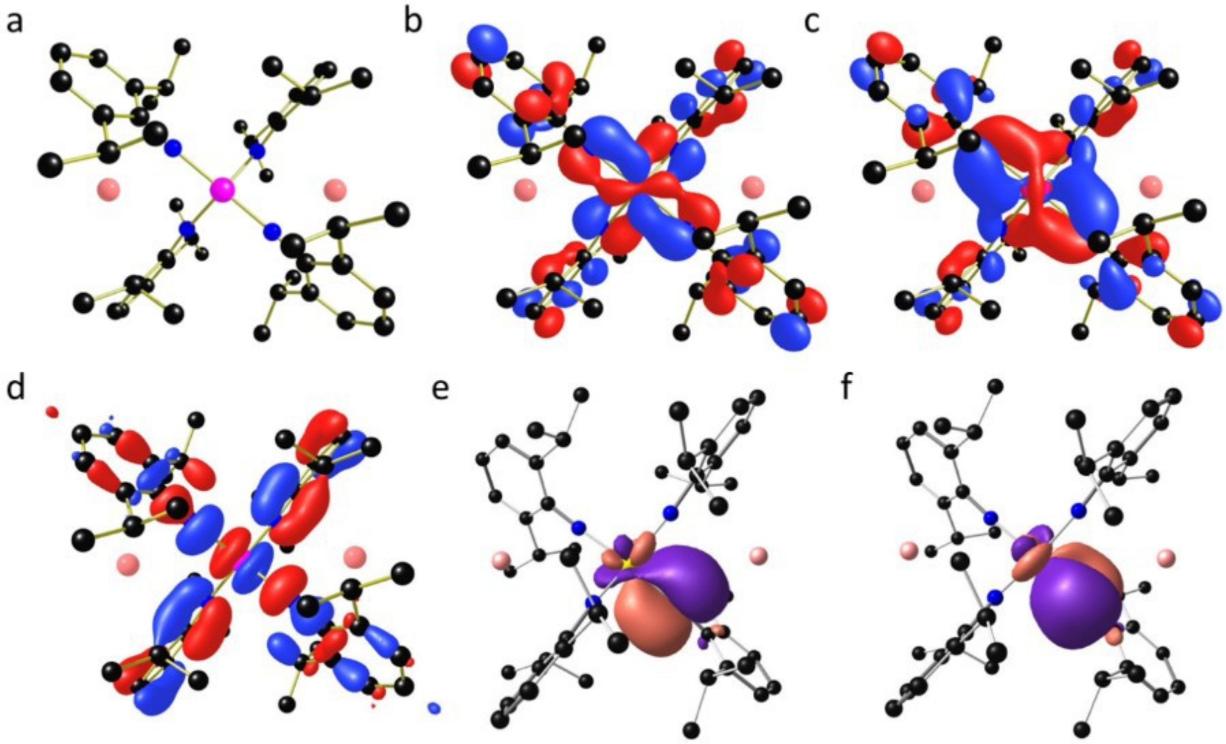


Figure 1. Molecular orbitals (b-c) and natural bond orbitals (e-f) of $Rb_2[U(NDIPP)_4]$

NUCL 149

Radiochemical, elemental, and isotopic analysis of epsilon phase material from irradiated fuel

Kristi L. Pellegrini[2], *kristi.lynn.66@gmail.com, Chuck Soderquist*[2]*, Richard A. Clark*[2]*, Jon M. Schwantes*[1]*. (1) Pacific Northwest Natl Labs, Richland, Washington, United States (2) Pacific Northwest National Laboratory, Richland, Washington, United States*

Epsilon phase material, which is produced during irradiation of oxide fuels, has many implications for the nuclear fuel cycle including fuel performance and post-irradiation processing. Although the presence of the material has been known since the 1960's, much is still unknown about the formation and transport of epsilon metal inclusions in oxides fuels. The material is considered a five metal phase composed of molybdenum, technetium, ruthenium, rhodium, and palladium in a hexagonal close packed arrangement and forms inclusions within the oxide fuel. To gain further insight into these mechanisms, epsilon phase material is currently being studied *in situ* and separated from irradiated fuel. Insoluble in both the hot nitric acid and carbonate peroxide fuel dissolution process, the noble metal phase can easily be separated from the bulk fuel. Material separated from three uranium oxide fuels—ATM-105, ATM-106, and ATM-109, each representing distinct burnups—using the carbonate peroxide fuel dissolution process were subsequently dissolved using a potassium nitrate/potassium hydroxide

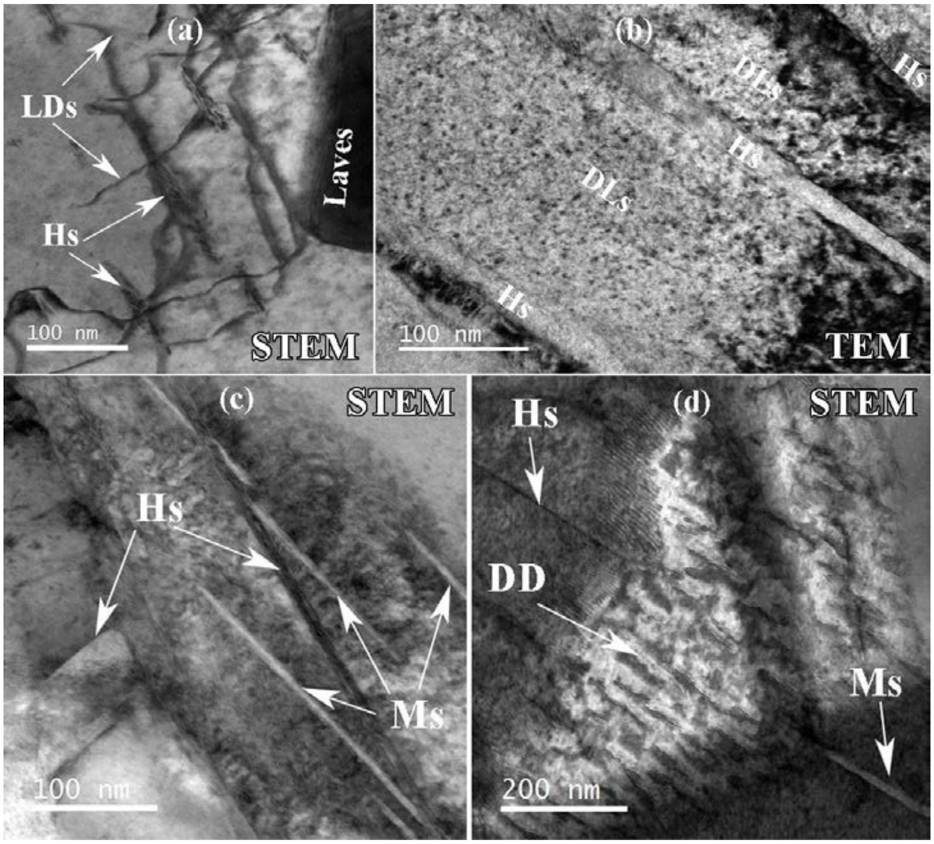
fusion and fully characterized. We present the radiologic, elemental, and isotopic characterization of the separated epsilon phase material.

NUCL 150

Microstructural examination of neutron irradiated base metal and TIG-welded zircaloy-4

Chinthaka Silva, *silvagw@ornl.gov, Keith Leonard, Chris Bryan. Materials Science & Technology, Oak Ridge National Lab, Oak Ridge, Tennessee, United States*

Zircaloy-4 is a structural material for nuclear reactors, especially light water reactors, where it has been used as fuel cladding, pressure tubes, fuel spacer grids, and etc. It possesses high mechanical strength and a considerable amount of ductility. In water-cooled nuclear reactors, however, the zircaloy-4 can be attacked by hydrogen, which is formed as a result of Zr reacting with water. If the hydrogen level is greater than the solubility limit in Zircaloy-4, it can form hydrides (ZrH_{2-x}). This in turn could result in deleterious effects such as embrittlement, decrease in fracture toughness, delayed hydride cracking, and becoming susceptible for corrosion. While Zircaloy-4 has been studied mostly for light water reactor conditions, interest on the material's behavior at lower irradiation temperatures has also shown by various companies and research institutions. In this present study, the focus has been made on the microstructural characteristics of Zircaloy-4 in its base metal (BM) and tungsten inert gas (TIG) welded forms as a function of hydride concentrations and at low-temperature (80 – 100 °C) neutron irradiation conditions. This microstructural evaluation was performed in explaining low ductility observed in the samples.



Bright field TEM and STEM images of (a) nonhydrided, 1.40x10^{20} n/cm^2 BM, (b) 170 wppm H, 1.17x10^{20} n/cm^2 TIG-welded, (c) nonhydrided 1.17x10^{20} n/cm^2 TIG-welded, (d) 170 wppm H, 1.17x10^{20} n/cm^2 TIG-welded Zircaloy-4. LDs, Hs, DLs, DD, and Ms stands for line dislocations, hydrides, dislocation loops, dislocation density, and martensites, respectively. Plate-like hydrides within grains are mainly observed in BM samples. Welded samples contained grain-boundary needle-shaped hydrides and martensite precipitates. Line dislocation channeling is disrupted by the presence of hydride and martensite precipitates.

NUCL 151

Using technetium’s volatility to decontaminate barrier material

***William R. Wilmarth**, bill.wilmarth@srnl.doe.gov, Lawrence Oji, Michael Restivo, Mark Duignan. E&CPT, Savannah River National Laboratory, Martinez, Georgia, United States*

The Department of Energy’s Office of Environmental Management is faced with challenges of dismantling large gaseous diffusion cascades at the Paducah Gaseous Diffusion Plant that have been contaminated with technetium in unknown chemical forms. These cascades will be disassembled and the technetium-contaminated parts will be size reduced to be disposed of at an offsite low-level waste burial facility. Since the technetium entered the cascade as a volatile fluoride, testing is being examined to determine the volatility of the existing compounds and chemical synthesis to achieve a

volatile species which would effectively in situ decontaminates the large scale equipment. This opens options for alternative disposal that could be far less expensive and reduce worker exposure to the technetium while conducting the job on an accelerated schedule. The results of initial testing with flowing air, partial vacuum and flowing steam thermal treatments will be presented as well as a discussion of future work.

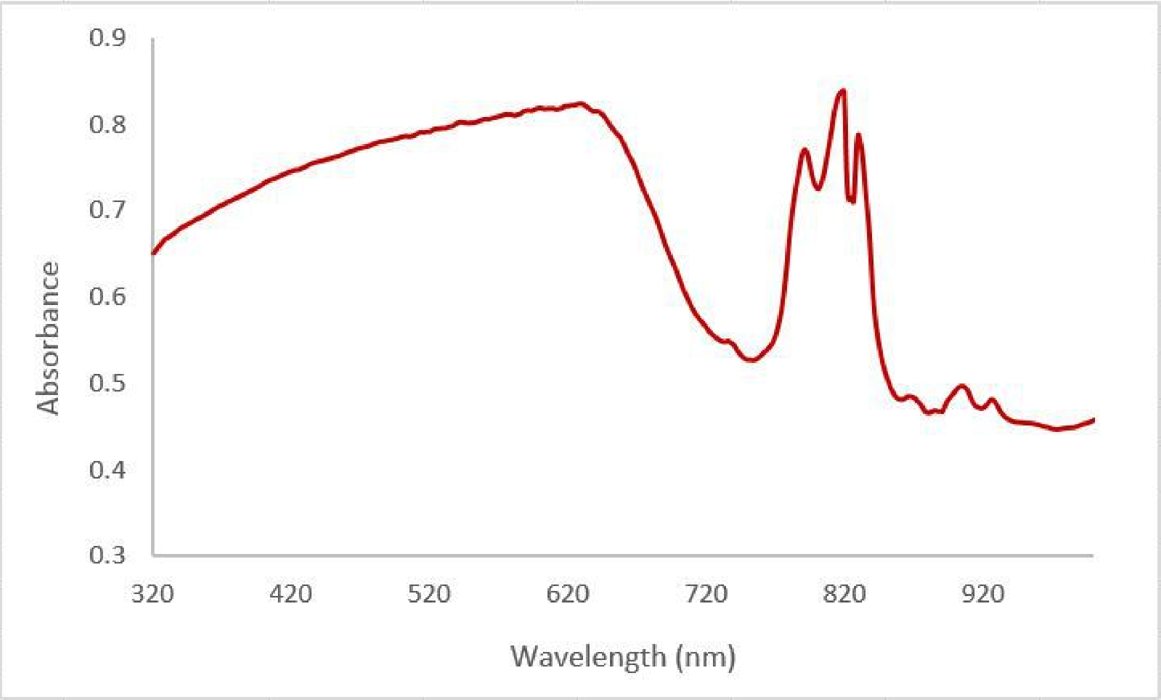
NUCL 152

Semiconductivity in plutonium and americium chromates and molybdates: Evidence for energy-degeneracy-driven covalency

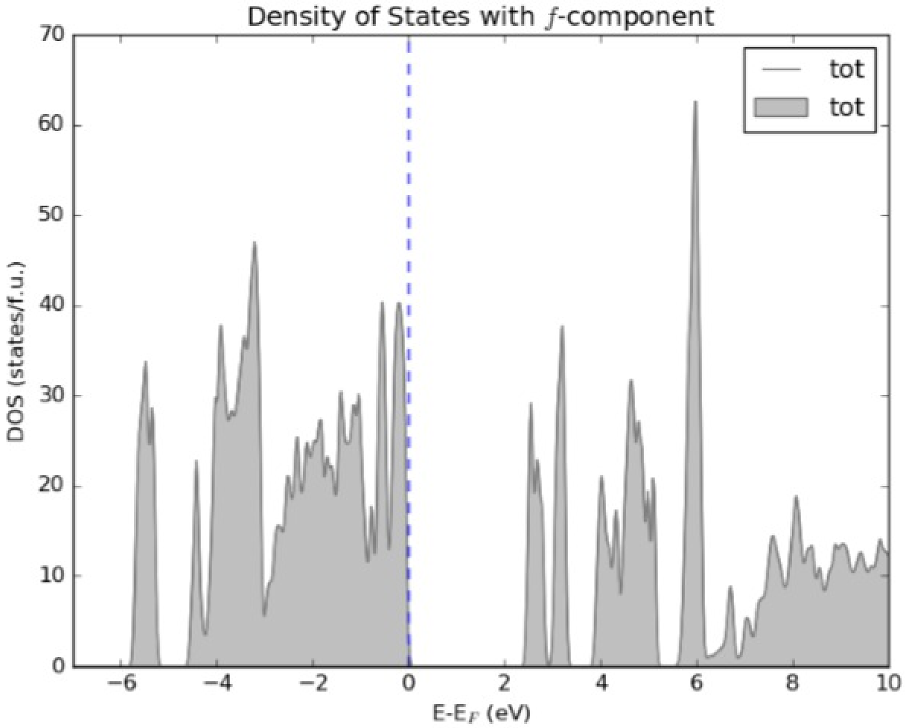
***Ali Arico**, aaa08c@my.fsu.edu. Chemistry, Florida State University, Tallahassee, Florida, United States*

The need to discover unique bonding tendencies in the heavier actinides (Pu-Cf) grows more urgently every day, as this knowledge is necessary for separating these elements in spent nuclear fuel. One way our group investigates this is to employ different inorganic ligand systems in synthesis that can potentially access the 5*f*-orbitals. Ligands with high hyperpolarizabilities are attractive in this regard due to their flexible electron cloud; it is important that the bonds of the ligand are strongly polarizable in order to induce a more covalent interaction with the actinide metal. Based on second-harmonic generation measurements as well as second hyperpolarizability calculations, the Group VI transition metal-oxygen bonds have significant bond polarization suitable for our investigation of inorganic actinide compounds.

$CsPu_3Mo_6O_{24}(H_2O)$, $CsAm(CrO_4)_2$, and their lanthanide analogues have been prepared. The former actinide compounds are black or dark red semiconductors, whereas the latter are gold or orange insulators. The trivalent americium compound deviates from the structural and spectroscopic trends observed across the 4*f* chromates; there is a shift from monoclinic structure types in the lanthanide compounds to triclinic for Am, and the charge-transfer features in the lanthanide UV-Vis-NIR spectra are not nearly as broad as that of the americium compound. Band structure calculations give further information on how the 5*f* and 6*d* electrons are participating in bonding with the chromate ligand in $CsAm(CrO_4)_2$.



UV-Vis-NIR for $CsAm(CrO_4)_2$



Density of States for $CsAm(CrO_4)_2$

NUCL 153

Recent progress on the development of pyroprocessing techniques for TMSR in SINAP

***Yu Gong**, gongyu@sinap.ac.cn, Qingnuan Li. Department of Radiochemistry, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, China*

Molten Salt Reactor (MSR) is one of the candidate reactors that can be operated based on thorium uranium fuel cycle, in which fertile 232Th can be converted to fissile 233U mediated by 233Pa. However, formation and accumulation of neutron poisons such as 233Pa and fission products require reprocessing of the fuel such that the neutron economy of reactor core can be maintained. Due to the poor solubility and high radioactivity of liquid used fluoride fuels, pyroprocessing is more appropriate for the reprocessing of the liquid fuels from MSR. In this talk, the R&D of several pyroprocessing techniques in Shanghai Institute of Applied Physics (SINAP) in recent years including fluoride volatility, low pressure distillation and fluoride based electrolysis will be presented. A flowsheet aiming at recycling UF4, ThF4 and fluoride molten salt by using pyroprocessing techniques is proposed as well.

NUCL 154

Pyroprocessing of spent nuclear fuels: Theoretical calculations and multiscale molecular simulations of solute behavior in molten salts

***Xuejiao Li**[1], 996448355@qq.com, Liuming Yan[2], Jia Song[2], Shuping Shi[2], Baohua Yue[2]. (1) Department of Physics, Shanghai University, Shanghai, China (2) Department of Chemistry, Shanghai University, Shanghai, China*

Theoretical calculations and multiscale molecular simulations are applied to the study of solute behavior in pyroprocessing of spent fuels, including classic molecular dynamics (MD) and first principles molecular dynamics (FPMD) simulations of structural, energetic and transport properties of actinide elements in molten salts, first principles calculations of redox potentials of metal ions in molten salts, and first principles calculations in combination of recursive fitting of force field parameters for actinide molten salts and liquid actinide alloy. The radial distribution functions, probability distribution of coordination numbers, dynamic fluctuation of coordination structure, self-diffusion coefficients and ionic conductivity in actinide molten mixtures are evaluated and compared with experimental and other simulation results. In addition, polarizable force field model and embedded atom model are developed, respectively, for actinide molten mixtures and liquid U-Zr alloy.

The MD and FPMD simulations reveal that the 6-fold coordination structure of U^{3+} dominates in molten LiCl-KCl-UCl_3 mixture and high temperature is conducive to the formation of low coordinated structure. Besides, a computational strategy for the evaluation of redox potentials of solute elements in molten salts is developed based on ensemble average of FPMD simulations, and the calculated redox potentials agree

satisfactorily with experimental values (**Figure 1**). For liquid U-Zr alloy, the mixed volume of U and Zr increases compared to the component elements, and the mixing of U and Zr is energetically unfavorable with positive mixing enthalpy. These achievements are essentially important for the development of pyroprocessing techniques of spent fuels by providing fundamental physical chemistry data.

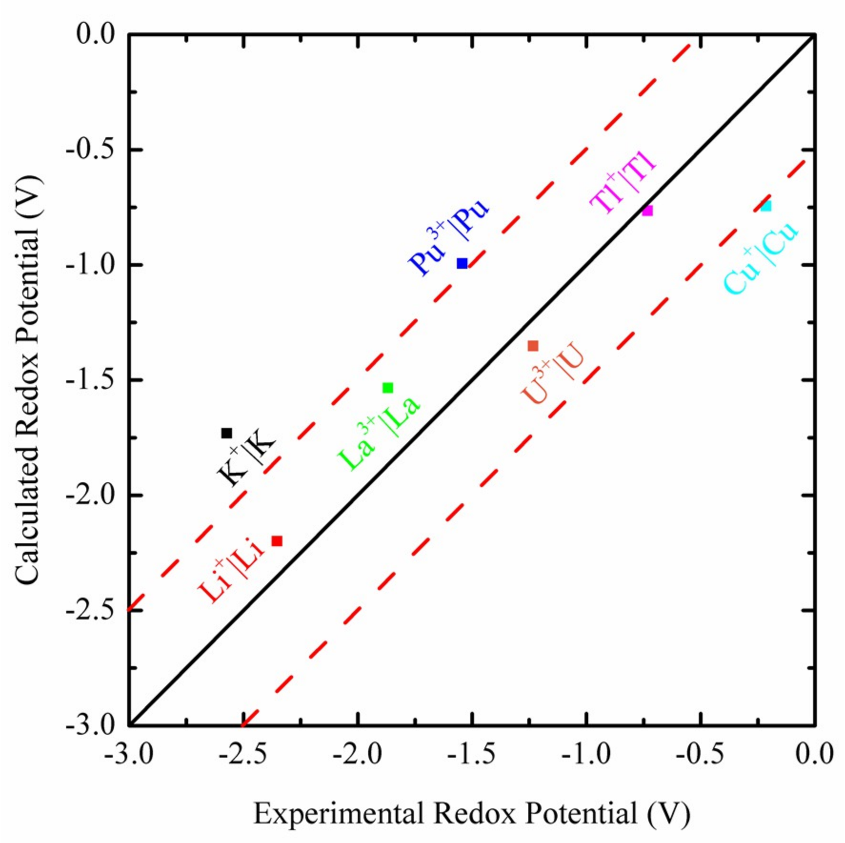


Figure 1 Redox potentials of related solute elements in LiCl-KCl eutectic

NUCL 155

Speciation of uranium in condensing laser ablation plasmas

David Weisz[2], *weiszdg@berkeley.edu, Jonathan C. Crowhurst*[2]*, Harry Radousky*[1]*, Tim Rose*[2]*, Wigbert Siekhaus*[2]*, Batikan Koroglu*[2]*, Michael Armstrong*[1]*, Elissaios Stavrou*[2]*, Joseph M. Zaug*[2]*, Magdi Azer*[3]*, Mikhail Finko*[3]*, Davide Curreli*[3]*. (1) Lawrence Livermore National Lab, Livermore, California, United States (2) Lawrence Livermore National Laboratory, Livermore, California, United States (3) University of Illinois Urbana-Champaign, Champaign, Illinois, United States*

The fractionation of UO_x and other metal oxide species as they condense in nuclear fireball environments remains an unconstrained parameter important to improving post-detonation debris formation models. The goal of this study is to quantify vapor-phase

uranium speciation during plasma condensation for the purposes of improving these models. To do this, the change in emission spectra of selected diatomic metal oxides (*i.e.* AlO, FeO, MgO, and TiO) in varying atmospheres at plasma temperatures (~1 eV), were compared to the emission spectra of uranium metal and UO_2 under the same parameters. To generate plasma conditions, a 1064 nm Nd:YAG was used to ablate pure metals of Al, Mg, Ti, Fe, and U, as well as UO_2, with 5 ns pulses (<50 mJ). Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) were used for *ex situ* analysis of ablation products collected at various points in the ablation plume. Further, we are exploring whether ^{18}O-enriched gas may produce isotopically-substituted molecules that exhibit peak shifts in their emission spectra. Together, these data provide insight into the formation conditions of metal oxides (including UO_x) during plasma condensation, and will serve as input parameters to a kinetics-based, semi-empirical computational model of uranium fractionation.

NUCL 156

Design and efficient synthesis of a bifunctional octadentate ligand for PET imaging with ^{89}Zr

Mahmoud A. Abdalrahman[1], *mahmouduwc@gmail.com, Roy P. Planalp*[2]*. (1) Chemistry, University of New Hampshire, Durham, New Hampshire, United States (2) Dept of Chemistry Parsons Hall, University of New Hampshire, Durham, New Hampshire, United States*

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

NUCL 157

Contamination and decontamination of steel components

Adam Lang[1,2], *adam.lang@manchester.ac.uk, Dirk Engelberg*[2]*, Paul Coffey*[3]*, Philip Martin*[3]*, Nicholas Smith*[4]*, Alex Jenkins*[5]*, Gareth Law*[1]*. (1) Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Manchester, United Kingdom (2) Corrosion and Protection Centre, School of Materials, The University of Manchester, Manchester, United Kingdom (3) School of Chemical Engineering and*

Analytical Science, The University of Manchester, Manchester, United Kingdom (4) Chadwick House, National Nuclear Laboratories Ltd, Warrington, United Kingdom (5) Decontamination Centre of Expertise, Sellafield Ltd, Cumbria, United Kingdom

The incorporation of radioactive species into nuclear plant stainless steel is a key decommissioning challenge that generates large volumes of waste over a plant's lifetime. Characterisation of the chemical processes that underpin contamination is essential in consideration of developing cost effective decontamination treatments, as are in-situ measurement techniques that allow assessment of contamination. The availability of reliable information regarding safe and efficient decommissioning programmes is in turn critical in the management of the world's nuclear legacy. To address these issues, contamination experiments to simulate the nitric acid-based reprocessing streams of the PUREX (Plutonium Uranium Redox Extraction) process, and alkaline spent fuel storage ponds were investigated. Solution and surface spectroscopic measurements were performed to characterise the sorption behavior of stable analogues of two high yield fission products, ^{90}Sr and ^{137}Cs, on AISI Type 304 stainless steel. Laser Induced Breakdown Spectroscopy (LIBS) was investigated as a standoff contamination assessment technique. Fission product accumulation was modelled to a second order kinetic fit that considers chemisorption, typically to a hydrous metal oxide surface, as rate controlling. This reflects complexation to the passivating surface chromium oxide film, and as determined by depth elemental analysis, effectively inhibits contaminant migration into the bulk material. This process is observed to be independent of solution composition. The manifestation of contamination as a surface phenomenon suggests that decontamination strategies should be orientated towards detachment of the Cr_2O_3 layer from the parent steel material, simultaneously removing any bound radioactive constituents. This approach would offer superior results to chemical based techniques, which would require an energy intensive input to overcome the strong chemical interaction between the fission products and steel surface. LIBS was found to be an adequate technique for measurement of Sr sorbed to steel but Cs could not be detected at the concentrations used in this experimentation.

NUCL 158

Automated clean chemistry for bulk analysis of environmental swipe samples

Shalina C. Bottorff[1], *Shalina.Bottorff@gmail.com, Kayron N. Tevepaugh*[1], *Debra A. Bostick*[1], *Cole R. Hexel*[1], *Hwan Kim*[2], *Paul Field*[2], *Brian W. Ticknor*[1]. *(1) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (2) Elemental Scientific Inc., Omaha, Nebraska, United States*

To shorten lengthy and costly manual chemical purification procedures, sample preparation methods for mass spectrometry are being automated using commercial-off-the-shelf (COTS) equipment. This addresses a serious need in the nuclear safeguards community to debottleneck the separation of U and Pu in environmental samples—currently performed by overburdened chemists—with a method that allows unattended,

overnight operation. In collaboration with Elemental Scientific Inc., the prepFAST-MC2 was designed based on current COTS equipment that was modified for U/Pu separations utilizing Eichrom™ resins. Initial verification of individual and combined columns yielded small elution volumes, consistent elution profiles, ample separation, and good recovery without cross-contamination of the eluent. Optimization of the packing and unpacking methods led to a reduction in the variability of the packed resin from >15% to <5% daily. The reproducibility of the automated system was tested with multiple samples containing 30ng U and 15pg Pu, which were separated in a series with alternating reagent blanks. Washout of both the resin and sample from the columns was evidenced by low blank values. Analysis of the isotope ratios for U and Pu provided values well within data quality limits for the IAEA. Additionally, system process blanks spiked with 233-U and 244-Pu tracers were separated after the system was moved outside of a clean room and yielded levels equivalent to clean room blanks, confirming that the system can produce high quality results without the need for expensive clean room infrastructure. Comparison of the amount of personnel time necessary for successful manual vs. automated chemical separations showed a significant decrease in hands-on time from 9.8 h to 35 min for 7 samples, respectively. This documented time savings and reduced labor translates to significant cost savings per sample. Overall, the system will enable faster sample reporting times with reduced costs by limiting personnel hours dedicated to the chemical separation.

NUCL 159

Characterizing mixed ligand f-element complexes for better An(III)/Ln(III) separations

***Ian M. Hobbs**[2], hobbian@isu.edu, Kenneth L. Nash[1]. (1) Washington State University, Pullman, Washington, United States (2) Chemistry, Washington State University, Pullman, Washington, United States*

Seaborg and coworkers established in the 1950s that the most effective approach to accomplishing a Ln(III)/An(III) group separation was to introduce donor atoms softer than oxygen, specifically Cl^-, into a low selectivity separation platform like Dowex 50 cation exchange resin. This soft-donor effect was attributed to the slightly stronger covalent contribution in the bonding of actinides to such ligands. A decade later, Weaver and Kappelmann developed the TALSPEAK concept, based on the introduction of multiple N-donor holdback reagents, like DTPA (diethylenetriamine pentaacetic acid) to accomplish a similar separation. Though the chemistry of TALSPEAK is more complex than the soft donor-cation exchange separation, it did enable a potentially high throughput countercurrent solvent extraction approach to An(III)/Ln(III) separations with high separation factors. Because the covalency effect is relatively weak (7-8% increased bonding affinity for An(III) over similarly-sized Ln(III)), the adoption of reagents with more N-donor atoms increases separation efficiency. However, the octadentate DTPA suffers from some issues arising from the comparatively slow complexation/decomplexation kinetics of complex molecules. In the Advanced TALSPEAK system, the primary aqueous holdback reagent is HEDTA ((2-

hyroxyethyl)ethylenediaminetriacetic acid), a pentadentate aminopolycarboxylate ligand, with three water molecules completing the cation coordination environment. The $Ln(HEDTA)(OH_2)_3$ aqueous complex leaves room for the addition of a secondary soft donor ligand, for example iminodiacetic acid. In this report, selected results of an investigation of the thermodynamics and kinetics of such ternary complexes and their impact on Advanced TALSPEAK separations will be described.

NUCL 160

Studies of the impact of the diluent on interfacial properties of the advanced TALSPEAK/ALSEP extractant HEH[EHP]

Devon E. Dodd[2], *devon.dodd@wsu.edu, Kenneth L. Nash*[1]. *(1) Washington State University, Pullman, Washington, United States (2) Chemistry, Washington State University, Pullman, Washington, United States*

In the development of solvent extraction-based separation processes, the most effective route to success is the trail blazed through detailed knowledge of the chemistry in both the bulk aqueous and organic phases with some degree of understanding of the transitions that most often occur in the interface to selectively transform the water–miscible into the lipophilic. In the separation of metal ions, understanding of the aqueous chemistry is often rather good, the organic phase speciation defined by stoichiometry-probing slope analysis experiments (rather than being built from first principles), and the interface is simulated in a thought experiment, as it is singly experimentally probed with difficulty. It is well known that altering the solvent composition by changing the diluent or introducing a phase modifier has a significant impact on the partitioning of Ln^{3+} by 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (HEH[EHP] – the extractant in the Advanced TALSPEAK and ALSEP processes for actinide/lanthanide separations) from nitric acid media. Common phase modifiers (*n*-octanol, tributyl phosphate) are interfacially active species, acting similarly to the extractant, structuring the phase boundary while also increasing hydrophobicity of solute molecules. However, diluents and phase modifiers also account for bulk organic phase compatibility of the lipophilic species. The interfacial competition between extractant and phase modifier and their behavior in various diluent environments are currently poorly understood (but under investigation). With the objective of creating a more complete model for the partitioning of Ln^{3+} by HEH[EHP], the interfacial region of selected biphasic systems has been examined by measuring the surface tension of solvent-water interfaces in a range of solvent conditions. Complemented by a significant number of Eu^{3+} partitioning studies, these observations aim to advance knowledge of solvent extraction separation science.

NUCL 161

Liquid phase chemistry study of indium and thallium for a future investigation of element 113

Merinda F. Volia[1,2], *merinda.volia@tamu.edu, Evgeny Tereshatov*[2], *Maria Boltoeva*[3,4], *Charles M. Folden*[2]. *(1) Nuclear Engineering, Texas A&M University, College Station, Texas, United States (2) Cyclotron Institute, Texas A&M University, College Station, Texas, United States (3) IPHC, Universite de Strasbourg, Strasbourg, France (4) CNRS, Strasbourg, France*

A study of the liquid phase chemistry of indium and thallium, the two closest homologs of the “super-heavy” element 113 (abbreviated as E113), was conducted by the liquid-liquid extraction (LLE) technique. This study is aimed to provide a basis for the future investigation of E113 chemistry. E113, whose discovery was recently officially accepted by the International Union of Pure and Applied Chemistry (IUPAC), has a very low production rate and a very short half-life ($t_{1/2} < 20$ s). Therefore, the study of E113 homologs requires a chemical system that is highly selective and has rapid reaction kinetics. In this work, ionic liquids (ILs) were chosen as the solvents for LLE due to their tunability properties, which are found to be useful for the effective and selective extraction of metallic species. Indium and thallium transfer from hydrochloric acid (HCl) media into several imidazolium- and pyrrolidinium-based ILs with bis(trifluoromethanesulfonyl)imide and bis(fluorosulfonyl)imide anions were investigated. The results showed that the extraction efficiency of Tl(I) and In(III) into these ILs are lower than that of Tl(III), with the latter being extracted as the anionic species TlX_z^{3-z} (X = Cl^- or Br^-). At lower acid concentrations, the increase in the length of the alkyl chain of the ILs decreases the extraction efficiency of Tl(I), while the opposite trend was observed for Tl(III) extraction. The study was extended to the extraction of indium and thallium from HCl media into menthol-based deep eutectic solvents (DESs). Preliminary results indicate that effective separation of indium and thallium is possible by carefully controlling the pH of the HCl solution. The effect of adding an extractant on the extraction efficiency of IL and DES LLE systems was also investigated. This talk will discuss the latest results on all of these topics and their potential application to study the chemistry of E113.

NUCL 162

Environmental technetium chemistry: Sulfide treatment of iron-containing minerals

Kimberly Reinig[1], ***Nicole Moore***[3,2], *nmoore2@nd.edu, Silvia S. Jurisson*[2], *Timothy Phelps*[1]. *(1) University of Missouri, Columbia, Missouri, United States (2) Chemistry, University of Missouri, Columbia, Missouri, United States (3) CEEES, University of Notre Dame, Mishawaka, Indiana, United States*

Technetium-99 has become an environmental concern at Department of Energy nuclear waste sites, such as Hanford, WA, due to the Manhattan Project. ^{99}Tc is the focus of this research because it is generally present in its most stable form, pertechnetate (TcO_4^-), which is soluble and mobile. The half-life of ^{99}Tc is approximately 2.13×10^5 years, making the threat to the water tables even more challenging because the radionuclide is so long-lived.

Immobilization is the main solution to this ^{99}Tc threat. Initially, the focus was to study the interactions between hydrogen sulfide (H_2S) and pertechnetate and potentially apply it as an immobilization technique. The result, however, proved to be less stable than other options, such as interactions with iron sulfide. Research has shown that the interaction between Fe-bearing minerals and SH^- can create a reactive surface of FeS that may be used to immobilize and precipitate TcO_4^-.
The FeS-TcO_4^- reaction was investigated under different conditions to determine the parameters under which the iron sulfide most effectively immobilizes pertechnetate. Different oxidation states of iron were investigated by evaluating different minerals goethite, hematite, and magnetite. This furthers the understanding of the FeS-TcO_4^- reaction and contributes to finding the most efficient way to eliminate this threat to the environment.

NUCL 163

Investigation into the stability and ion-exchange processes of the metatorbernite-metazeunerite solid solution

Joanna Kulaszewska, *j.kulaszewska@lboro.ac.uk, Caroline Kirk, Dimitrios Kosmidis. Chemistry, Loughborough University, Loughborough, United Kingdom*

Uranyl phosphates, such as metatorbernite ($Cu(UO_2)_2(PO_4)_2.8H_2O$), are known for their low solubility at circum-neutral pH. They are important in the control of uranium mobility, and even being considered as materials for remediation of contamination in groundwater. Metatorbernite has been reported to be present at the abandoned mine site of South Terras in Cornwall, UK. Also known to be present is the related mineral phase – metazeunerite ($Cu(UO_2)_2(AsO_4)_2.8H_2O$). Our analysis of samples taken from spoil heaps at the South Terras site, have found the presence of mineral phases which can be thought of as members of a metatorbernite-metazeunerite solid solution. We have synthesised members of the solid solution with the aim to investigate their long-term stability in the natural environment, as well as their potential as materials for remediation of contaminated land and/or radiochemical waste.

Synthesis of single phase metatorbernite and metazeunerite analogues was successfully carried out. Investigations into solid solution formation between these two end member phases was then carried out. Powder XRD data collected on the resulting samples indicted that new, single phase compounds were formed.

Stability of the solid solution phases in 0.5 mol dm^{-3} bicarbonate solutions ($XHCO_3$, X=NH_4, Na, K) was found to be composition dependent with the more As-rich phases either undergoing ion exchange, (e.g. Cu(II) is partially exchanged for $NH4^+$) or, when in the presence of $NaHCO_3$ or $KHCO_3$, undergoing dissolution and releasing As and U into the solution.

A proposal to carry out advanced synchrotron experiments on I11 at the Diamond Light Source in Oxfordshire was successful. These experiments will involve carrying out *in-*

situ monitoring of the processes occurring after addition of the bicarbonate solution to targeted solid solution member phases.

NUCL 164

Europium sorption to aluminum (hydr)oxide minerals

Patricia Kay[1], *pkay@nd.edu, Teresa Baumer*[2], *Amy E. Hixon*[2]. *(1) Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana, United States (2) Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

Geologic repositories are accepted as the best long-term disposal and storage solution for high-level nuclear waste. Due to the long half-lives of several actinides (^{242}Pu ($t_{1/2}$ = 3.5×10^5 years), these materials remain present in the environment for many years and pose threats to human and environmental health. Therefore, it is necessary to understand how these materials move and behave so they may be safely stored out to 1 million years, as required by law.

In this research project, the interaction between europium and aluminum (hydr)oxide mineral phases was studied through a series of batch-sorption experiments in order to analyze sorption trends and predict sorption behavior. These experiments were designed to test the partitioning of the europium between the aqueous and solid phases over the pH range 3 to 10 and as a function of mineral concentration, europium concentration, and ionic strength. Europium, which has an oxidation state of +III, was studied as an analog to the +III oxidation state of plutonium, which can exist at four different oxidation states (+III, +IV, +V, +IV). Aluminum (hydr)oxides contain key surface termination sites found in the clay materials which will be used to backfill nuclear waste storage repositories. The four minerals chosen—corundum (α-Al_2O_3), γ-alumina (γ-Al_2O_3), gibbsite ($Al(OH)_3$), and bayerite (α-$Al(OH)_3$)— have distinct structures and acidities based on ratios of oxygen and aluminum at the surface.

Current debate in the scientific community centers around how minerals with similar chemical compositions, but different surface terminations and surface acidities, have an influence sorption behavior. Results show that at low europium concentrations, sorption behavior is similar in the presence of corundum, γ-alumina, and gibbsite with slight preference to bayerite. At higher europium concentrations, all minerals follow the same sorption pattern, which is shifted to a higher pH value.

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Alkali ion bridge complexation between uranium nanoclusters and mineral surfaces

Wynn Stoxen[3], *wstoxen@nd.edu, Luke R. Sadergaski*[2], *Jennifer Szymanowski*[3], *Amy E. Hixon*[1]. *(1) Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States (2) Civil and Environmental Engineering and Earth Science, University of Notre Dame, South Bend, Indiana, United States (3) Civil* *and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

Uranyl peroxide nanoclusters ($([UO_2(O_2)(OH)]_{60})^{60-}$ play a potential role in the subsurface fate and transport of uranium contamination. Understanding the interactions of these nanoclusters with abundant subsurface minerals and the mechanisms by which they interact is crucial for public and environmental safety. This study examines mineral-nanocluster interactions driven by bridged surface complexes formed by Li, Na, K and Cs alkali metals. Previous experimentation has shown that nanoclusters are not removed from solutions containing silica (SiO_2) and are removed slowly in the presence of iron and alumina minerals (α-Fe_2O_3 and Al_2O_3). We hypothesize that K^+ ions are moving from the interior of the uranyl peroxide nanoclusters to form bridge complexes with these minerals. By adding differing alkali cations to the reactions of nanoclusters and minerals, the presence of bridge complexation, and the extent to which it occurs, will be determined.

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Determination of thermodynamic parameters associated with Tc(IV) sulfate complexation

Gannon Parker, *parkergannon@gmail.com, Donald E. Wall, Nathalie Wall. Washington State University, Pullman, Washington, United States*

Much information is currently missing in the field of technetium chemistry. The goal of our research is to determine thermodynamic and kinetic parameters for the complexation of Tc(IV) with a series of ligands. This particular work shows the quantification of stability constants for the complexation of Tc(IV) by sulfate using a liquid-liquid extraction (LLE) method. Experiments were carried out over a wide range of ionic strengths (0.1 - 1 m) for extrapolation to zero ionic strength, using the Specific ion Interaction Theory (SIT). Values for enthalpy and entropy of the complexation reactions were determined by conducting these LLE experiments over a range of temperatures.

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Stability of uranyl peroxide nanoclusters under hydrothermal conditions

John R. FitzPatrick[1]*, john.r.fitzpatrick.98@nd.edu, Haylie L. Lobeck*[1]*, Sara Mana*[1]*, Peter C. Burns*[1,2]*. (1) Civil & Environmental Engineering and Earth Sciences, University of Notre Dame, Granger, Indiana, United States (2) Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States*

The focus of this research is to investigate the properties of uranyl peroxide cage clusters under hydrothermal conditions and their possible applications in the nuclear fuel cycle. The nuclear fuel cycle is the series of industrial processes that use uranium in nuclear power reactors to produce electricity. Inside the reactor, temperatures can reach above 400 degrees Celsius, where storage pools for spent fuel average around 90 degrees Celsius.

Uranyl peroxide nanoclusters are spherical, cage-like clusters of uranyl ions bound together by peroxide and hydroxyl bridges. Uranyl peroxide nanoclusters are synthesized by combining a uranyl solution, hydrogen peroxide, a base, and counter cations such as Li^+ or K^+. To date, over 120 unique nanoclusters have been synthesized that vary in size and shape, and these can incorporate different bridging ligands, such as oxalate and pyrophosphate. Nanoclusters behave differently than simple uranyl species in solution, making it important to investigate their properties.

Nanoclusters with varying size, shape, and bridging ligands will be synthesized and dissolved in 18 MW water. The aqueous cluster solutions will then be slowly heated to 180 degrees Celsius in a sapphire tube while *in situ* Raman Spectroscopy is performed every 30 minutes. The stability of the clusters will be monitored by the persistence of the –yl oxygen and peroxide symmetric stretching bands in the Raman spectra. Once the system has cooled, the final solution and any precipitate formed will be analyzed for remaining clusters in solution in addition to other phases that possibly formed during heating with ICP-OES, ESI-MS, and PXRD.