NUCL 1

Studies of the thermodynamics of actinide reactions: A tribute to Heino Nitsche

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Studies of the thermodynamics of actinide reactions have played a central role in the discovery of the actindes and elucidation of their bonding interactions. As a contemporary, friend, and colleague of Professor Heino Nitsche, the author of this abstract (like Professor Nitsche) benefitted considerably from the tremendous contributions of our scientific forebears. In the spriit of a tribute to Heino, this presentation will focus on the role and impact of actinide thermodynamic data on the advancement of actinide science.

NUCL 2

Treatment of contaminated water at Fukushima

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The failure of the primary containment in three of the Fukushima Dai-ichi reactors resulted in a cooling loop for these facilities that includes the reactor buildings, turbine buildings and the central radioactive waste processing facility. Due to the site hydrogeology, there is an intrusion of up to 400 T/day of additional water into the process loop through the basements of these buildings. Since the accident, this has led to the capture of 400,000 T of process water that is contaminated with various radionuclides. This paper will provide an overview of the strategy, the separation processes, and the facilities that have been installed and operated to treat the contaminated water. Examples of the separation processes used at the Fukushima site include coprecipitation, filtration, adsorption and ion exchange.

NUCL 3

Thermodynamics and predicting actinide behavior in repository science

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The thermodynamic properties of actinide phases and aqueous species are a critical need in predicting the solubility of actinides and correspondingly their long-term migration in a geologic repository. Many of these data are tabulated in compendia such as the NEA blue books and these well-regarded data sets are extensively used in

repository science. There are, however, data gaps for room-temperature low ionic strength actinide data and these gaps are exacerbated when higher temperatures and high ionic strengths are also considered. There are also key and critical subsurface processes, e.g. radiolysis and microbial effects, which are not readily described by the traditional way that thermodynamic data are used.

Herein we will provide a critical assessment of the data gaps for key actinide systems. The most important actinides with respect to long-term repository performance are U, Np, Am and Pu, with plutonium usually predominant. Since these actinides are all multivalent under the wide range of subsurface conditions that are germane to repository concepts, there is much overlap in their behavior and in many cases oxidation-state analogies can be used to investigate actinide species when redox stability is problematic or used to estimate the thermodynamic data needed. Extensive data for lower-valent plutonium and neptunium, which are predominant in salt repository concepts, particularly at high ionic strength and elevated temperature, do not exist and we continue to rely on analogs to support the repository safety case.

Recent experimental results to address the missing data gaps from our ongoing studies to establish actinide behavior in TRU and HLW salt repository concepts will also be presented. The effects of temperature and ionic strength on Np(V) and Np(IV) spectroscopy will be presented. Increased in uranium solubility observed as a function of initial phase (U_3O_8 and $UO_2(OH)_2$) and temperature in sodium chloride systems will be summarized. Data on the formation and stability of Pu(III) phases in brine illustrate the potential importance of this oxidation state of plutonium in iron-rich systems. Lastly the potential role of microbial activity as a kinetic pathway to the formation of thermodynamically-stable actinide phases will be discussed. These experimental data discussed in the context of the data gaps and actinide trends that are key/important to a salt-based repository concept.

NUCL 4

Spatially resolved characterization techniques for next generation nuclear forensics signature development

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In response to the need created from the February 14th 2014 contamination event at the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico, Pacific Northwest National Laboratory has established an operational set of unique analytical techniques designed to nondestructively interrogate individual radioactive particles within heterogeneous materials. This suite of microscopic techniques situated within radiological laboratories includes micro-florescence, 865 and 1064 nm excitation wavelength micro-Raman, micro X-Ray Fluorescence (m-XRF) and Attenuated Total Reflectance Fourier Transform Inferred (ATR-FTIR) Spectroscopies. Together these techniques have provided Department of Energy’s Technical Assessment Team investigating the WIPP incident with a “needle in the haystack” ability to identify reaction residues of the

excursion event that led to the release of radioactive contamination. Beyond the WIPP investigation, however, these and other microscopic methods being stood up in our Nuclear Hazards Category Level II Radiochemical Processing Laboratory at PNNL, coupled with best in class computational tools, represent a window into the future of nuclear forensic analyses. State of the art instrumentation like a dual beam Focused Ion Beam (FIB), coming online in early 2015, will provide 3-D imaging capability of individual particles and micron level sectioning and fabrication of “sealed sources” from highly radioactive materials that can be ported to low-level and potentially non-radiological facilities for further analyses. Such instruments will provide the analytical support needed for lab-scale nuclear process R&D in the future. Novel computational tools also being developed, like Phase Field models, provide the theoretical construct to test and evaluate our predictive understanding of microscopic morphological features from scaled nuclear processes. Examples of optical and electron microscopic techniques as applied to the field of nuclear forensics and chemical process reconstruction from heterogeneous materials will be discussed.

NUCL 5

Investigation of silica-grafted CMPO-modified calix[4]arenes for radionuclide separations

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Within the past two decades, calixarenes have been examined for their properties in effecting the separation of radionuclides for a variety of purposes. The cavity inside these calixarenes as well as the opportunities for attaching functional groups to the calixarene’s upper and lower rims have proven useful for separating elements possessing similar chemistry and oxidation states but slightly different radii, such as the lanthanides, americium, and curium. This has most commonly been done in the context of a liquid extraction system. In this study, four carbamoylmethylphosphine oxide (CMPO) ligands, shown to be selective for extracting trivalent f-block elements, were attached to the upper rim of a calix[4]arene which was anchored via the lower rim to a porous silica support. Preliminary testing was undertaken to determine the ideal pH and ionic strength to promote the sorption of europium on this solid-supported calixarene system. This study builds on previous work by investigating europium sorption to the overall material and the possibility of enhancing selectivity by virtue of interactions with the silica support or the anchored calix[4]arene site.

Although this work was in its early stages in July 2014, it would have been impossible to

foster the necessary collaboration or skillset for this project without Professor Heino Nitsche. Heino brought a highly unique blend of radiochemistry prowess, camaraderie, humor, and intensity to the lab each day. I would like to highlight the silica-grafted CMPO calix[4]arenes, just one of the contributions his work has made toward solid-supported systems for radiochemical separations, as well as discuss the impact that his mentorship has made upon the next generation of radio and nuclear chemists.

NUCL 6

Interactions of plutonium and ordered mesoporous materials

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The large tunable interface provided by ordered mesoporous solids may be advantageous in applications involving separation, sequestration, or detection of actinides in solution. However, the fundamental chemical interactions of actinides with the materials must be understood before applications can be implemented. The primary focus of my work with Professor Heino Nitsche was investigation of the adsorption and redox reactions of plutonium with ordered mesoporous silica and carbon based materials. The interactions were studied by batch contact, Pu L_{III} edge X-ray absorption spectroscopy, and electron microscopy techniques. The sorption and redox behavior of Pu with organically-modified mesoporous silica is variable, and completely dependent on the identity and accessibility of the ligands grafted to the surface. In contrast, unfunctionalized porous carbons behave as reducing agents towards Pu, with profound effects on the sorption reactions of Pu with carbon-based materials.

NUCL 7

FIONA: A new mass analyzer for superheavy elements

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Six new superheavy elements (Z = 112 - 118) and over fifty new transactinide isotopes ($Z \geq 104$) have been synthesized in compound nuclear fusion reactions using ^{48}Ca on actinide targets in the last decade. These superheavy elements (SHE) are short-lived, with their resulting decay chains ending in spontaneous fission before reaching a known mass region. At the Lawrence Berkeley National Laboratory (LBNL), we use the 88"-cyclotron to produce heavy ion beams and the Berkeley Gas-Filled Separator (BGS) to produce and separate the SHE of interest from transfer reactions products and unreacted beam. Unfortunately, the BGS's high beam suppression comes at the cost of mass resolution and detection is limited by close proximity to the target and beamstop. Ongoing upgrades to the BGS, including beam thermalization and fast ion transport, will allow us to couple a dedicated mass analyzer to the BGS. Known as FIONA (Facility for Identification Of Nuclide *A*), the analyzer is a novel mass separator based on an unbalanced Wien velocity filter. It has been designed for 100% transmission with an expected mass resolution of 2000 $A/\Delta A$. In addition to determining the mass of a given SHE, these upgrades increase sensitivity by drastically lowering background counts. I present the current progress in commissioning the FIONA mass analyzer and the future directions of the project, including the first direct mass measurement of a superheavy element. This work was performed under the supervision of my advisor, Prof. Heino Nitsche.

NUCL 8

Solid-phase extractants for sequestration and separation of actinides and lanthanides

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Separation systems for the lanthanides and actinides are necessary for treatment of used nuclear fuel and legacy defense waste, processing irradiated target materials, and analyzing forensic samples. We are focused on solid-liquid separations because they involve no organic diluent, thus minimizing the production of hazardous mixed wastes. We have developed solid-phase extractants based on organically-modified mesoporous silica for the separation of actinides and lanthanides. A diglycolamide ligand was grafted to ordered mesoporous silica microspheres to create a novel high-capacity extraction resin. The chemical interactions of this material with a selection of lanthanides and actinides in acidic media have been studied. The material characterization, results from batch uptake experiments, solid-state NMR and infrared spectroscopies will be presented.

NUCL 9

DTRA basic research for combating weapons of mass destruction

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The Defense Threat Reduction Agency safeguards the United States and its allies from weapons of mass destruction (WMD) by providing capabilities to reduce, eliminate, and counter the threat and mitigate its effects. DTRA accomplishes its mission by investing in basic research efforts at universities, national labs and DoD service labs to better counter threats posed by WMD. We also facilitate productive relationships with other scientific organizations and seek to identify promising research efforts overseas. Through the Basic Research program, DTRA recruits and trains scientists and engineers to develop a talented workforce for the future.

Basic research is directed towards greater knowledge or understanding of phenomena without regard to specific applications. The DTRA Basic Research Program pursues efforts within and across disciplines such as chemical science, computer/network science, materials science, mathematics, nuclear science, and physics. The presentation will describe the DTRA Basic Research Broad Agency Announcements, research “Thrust Areas,” proposal solicitation processes, and technical areas or subjects of interest.

NUCL 10

Scientific contributions of Heino Nitsche to actinide and transactinide chemistry

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The individual fields encompassed by nuclear chemistry and technology are manifold, cross- cutting the classical disciplines of chemistry, nuclear physics, and nuclear engineering. The scientific contributions of Heino Nitsche to these fields cover areas as diverse as environmental actinide and radiochemistry to the production and chemistry of the heaviest elements. In a career spanning more than 30 years, Heino made seminal contributions to the fields of actinide environmental chemistry including thermodynamic descriptions of actinide solubility, speciation, and the extension of these studies to understanding the exceptionally complex chemistry of actinide adsorption complexes and redox transformations on mineral and microbial surfaces. Heino enthusiastically embraced the application and development of advanced spectroscopic and analytical methodologies for the study of and advancement of actinide chemistry. Studies on a variety of aspects of the transactinide elements became a part of Heino’s scientific portfolio after his transition to the Lawrence Berkeley National Laboratory, and the University of California, Berkeley. The synthesis in nuclear fusion reactions and the study of their nuclear structure and decay formed one focus, with another one being on the chemical properties of the heaviest elements studied in atom-at-a-time experiments in Berkeley as well as in accelerator centers around the world. Importantly, Heino devoted significant efforts to the advancement of nuclear and radiochemistry,

strengthening the education and training of the next-generation workforce in nuclear and radiochemistry, and supporting many scientists and students during the course of his career. Heino's contributions as a chemist, collaborator, and enthusiastic critic, to the fields of actinide and transactinide chemistry will be highlighted.

NUCL 11

Heavy element studies at Berkeley

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When Heino Nitsche returned to Berkeley in 1998, he took on responsibility as leader for the Heavy Element Nuclear and Radiochemistry Group, peforming experiments at the 88-Inch Cyclotron. At that time, the first experiments with the Berkeley Gas-filled Separator were about to begin. Heino directed the design and construction of the cryogenic gas-phase chemistry apparatus that was used after preseparation with the Berkeley Gas-filled Separator to measure the adsorption enthalpy of volatile OsO_4. This device became the model for next generation devices used for atom-at-a-time chemistry of Elements 108, 112, and 114. We carried out many studies of heavy element production systematics, including "hot fusion" between actinide targets and light projectiles (from ^{22}Ne through ^{30}Si) and "cold fusion" using shell-stabilized Pb and Bi targets with heavier projectiles (^{48}Ca through ^{64}Ni). During Heino's last years, we built on the knowledge gained in these reaction studies to access the nuclear structure of isotopes from ^{254}No through ^{261}Sg, and finally to produce and study superheavy elements.

NUCL 12

Impact of [Ca_2 UO_2 (CO_3)$_3$]aq.-complex formation on environmental behavior of uranium

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The increasing input of uranium into the bio-sphere by uranium mining and milling, and industrial processes like production of cement, fossil fuels, and fertilizers has led to the realization of the importance of the environmental chemistry of that element. Knowledge about the uranium speciation especially in aqueous systems is one of the basic parameter to predict its availibility, distribution, and mobility in bio- and geo-systems. The much simpler laboratory systems often contain significantly less constituents than environmental aqueous systems and may therefore not completely represent the speciation in natural compartments. The [Ca_2 UO_2 (CO_3)$_3$]aq.-complex e.g. was found

in uranium mining related waters for the first time /1/.
Newest results about the spectroscopic identification of that complex in commercial mineral waters, pore waters, and natural body-fluids will be reported. These findings are discussed in the context of relevant thermodynamic calculations.

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NUCL 13

Molecular scale investigations towards actinide retention at mineral surfaces

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Mobility of radionuclides in different nuclear waste repository barrier systems is strongly determined by solubility and mineral-water interface reactions. Classical batch type experiments, spectroscopic and quantum chemistry studies provide complementary and detailed insight into a multitude of different solid-liquid interaction mechanisms on a molecular scale. Beside classical surface sorption phenomena, surface induced redox reactions and surface incorporation determine the fate of actinide and long-lived fission products. Reactions may either contribute to enhanced mobilization in case of radionuclide interaction with mobile colloidal species or strong retention if sorption onto mineral surfaces is considered.

The present contribution discusses recent investigations related:
- to radionuclide reactions with container corrosion products in the near field of a nuclear waste repository,
- the impact of enhanced salinity on actinide sorption on various mineral surfaces as well as
- the role of surface sorption on actinide redox state and
- kinetic aspects of colloid-mediated actinide transport reactions.

NUCL 14

Applications of molten salts in nuclear technology

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Molten salts have applications in nuclear technology because they have a high resistance to radiation, possess a high thermal stability and have good retention capacity of volatile fission products. For these reasons they are studied as solvents for separation processes, and as fuel and/or coolant in innovative reactors. Molten salt separation techniques are studied in the frame of future advanced nuclear energy systems that are characterised by effective fuel utilization for sustainability and waste minimization through recycling and transmutation of actinides in dedicated reactors. The fuels used in the advanced reactor systems are likely to be significantly different from the present commercial fuels and their processing by hydrometallurgical methods might not be suitable. Therefore, different pyrochemical separation techniques using high temperature and radiation resistant molten salt solvents are developed [1]. Apart from basic research on the electrochemical methods for nuclear fuel processing, the technology has been tested at JRC-ITU in the METAPHIX project [2], an experimental demonstration of a closed metal fuel cycle, including fabrication, irradiation, and post-irradiation examination. In the molten salt reactor (MSR) a liquid mixture of metal fluorides is used as a fuel and coolant. The MSR belongs to the group of six reactor concepts considered within the GenIV international forum and can be used to burn higher actinides or as a breeder based fuel cycle. To identify the optimal composition of the fuel salt and to perform the safety assessment of the reactor a fundamental knowledge of the physico-chemical properties of the molten fluoride salts must be developed. In this context systematic experimental studies of binary and ternary salt mixtures are ongoing at JRC-ITU focusing on key properties such as heat capacity, solubility of actinides in the fuel solvent, melting temperature, phase diagram data and vapour pressure. The results from these measurements are used to establish a comprehensive thermodynamic database which is an essential tool to predict the chemical behaviour of the fuel salt during normal operation and accident conditions.

References:

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NUCL 15

Advances in the production and chemistry of the heaviest elements

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Prof. Heino Nitsche has been the guest editor of the thematic issue 2013 (Febuary) on Nuclear Chemistry in the highly cited journal Chemical Reviews. Together with my colleague Valeria Pershina from superheavy element theory we have contributed an extensive review on the topic of superheavy element production and chemistry [1]. In my contribution to the Seaborg Award Symposium in Honor of Heino Nitsche I would like to highlight the latest developments in the field and put those in perspective to the many accomplishments of Heino Nitsche to nuclear chemistry and especially superheavy element research. His service to the community and his efforts to promote our field were of great value and exemplary.

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NUCL 16

Laser-induced spectroscopy of actinides: From simple metal systems to species in living cells

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Application of laser-induced methods allow the direct determination of uranium speciation at extremely low concentrations. First tunable solid state laser in an actinide chemistry lab was installed in 1993 in Dresden-Rossendorf under Heino Nitsche's directorship. Later the installation of the first fs-laser system allowed us to study the interaction of organic compounds with actinides.

U(VI) released anthropogenically, e.g. through mining activities, can be accumulated for instance in plants and consequently can enter further parts of the food chain. Uranium as a redox-active heavy metal can cause also various redox imbalances in plant cells. Recently we have shown that uranium can be taken up by plant cells. Fractionation studies showed that the uranium was present in nearly all cell compartments.

One of the major remaining questions concerns to the ways of uranium uptake. Recently published work proposed that the uranium uptake is influenced by the iron uptake. As it is known that the iron uptake occurs via reduction of the iron(III) into iron(II), we conclude that uranium uptake should also by accompanied by a redox process.

The evaluation of Laser-Induced Photoacoustic Spectra (LIPAS) in the wavelength range 620 nm to 680 nm gave evidence for the formation of both reduced oxidation states in the media studied. The uranium(V) is assigned to an absorption at around 637 nm, while uranium(IV) absorbs light at ~660 nm.

NUCL 17

Toward A and Z identification of superheavy elements

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Over the last 15 years, a collaboration working at Flerov Laboratory for Nuclear Reactions [FLNR] has reported the discovery of six new superheavy elements (SHE) with proton number Z=113-118 [1]. Despite knowing about SHE for more than a decade, several important questions about these nuclei remain unanswered, including what are the atomic numbers and masses of these nuclei. At Lawrence Berkeley National Laboratory (LBNL), we have begun to investigate this question using a two-pronged approach:

In an experiment aimed at identifying the atomic number of a SHE through the observation of characteristic K X-rays with the α decay of a SHE, we bombarded ^{243}Am with beams of ^{48}Ca in April – June 2013. Forty-three decay chains matching those reported for ^{288}115 were produced during a five-week long experiment LBNL. The element 115 evaporation residues were separated with the Berkeley Gas-filled Separator [2] and implanted into the Corner-Cube-Clover (C3) detector. The C3 detector is designed for the detection of *g*-rays in prompt coincidence with the *a*-decay of heavy elements (i.e. element 115 and its daughters). A similar experiment at GSI involving the LUND/GSI/LBL collaboration reported 22 correlated decay chains assigned to ^{288}115 [3]. Results from the combined data set will be presented

To obtain mass numbers of SHE, we have designed a new mass analyzer FIONA, which will couple to the BGS. FIONA will i) provide a mass separation (M/ΔM) of ~500 and ii) transport nuclear reaction products to a shielded detector station on the tens of milliseconds timescale. A small-scale test setup of FIONA has been built and results of commissioning will be presented here.

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NUCL 18

Chronology of $^{239/240}$Pu and of ^{236}U in the Miaergou glacier from eastern Tien Shan, China

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A 57.6 m long ice core was drilled in 2005 to bedrock at the eastern-most glacier of the Tien Shan mountains ranging from Kirgistan to China [1].The core ranges back to about 1851 [2]. This site is interesting since it is a possible collecting location of nuclear debris from the Chinese (Lop Nor) and/or former Soviet (Semipalatinsk) test sites. Indeed using b- counting increased activity was observed between 7 m and 12 m depth [1]. Isotope ratios between ^{239}Pu and ^{240}Pu are a fingerprint of the emission source and can be measured very accurately even from ultra-trace amounts of plutonium stored in glacier ice cores using accelerator mass spectrometry (AMS). In addition, recently also ^{236}U has become a widely used tracer for environmental studies but its deposition rate chronology is still poorly known. This nuclide can also be determined via AMS. Results from ^{239}Pu, ^{240}Pu and ^{236}U were determined with the compact 0.5 MV TANDY accelerator at ETH Zürich for the ice core section between 8 m and 15 m depth. This

section corresponds to the period between about 1940 and 1970. Each sample was 1 m in length for the first and two last samples (with background activity from b-counting) and 0.5 m in length for all other samples (with increased b-activity). The covered time ranges were about 4 years for the 1m segments and 2 years for the 0.5 m segments, respectively.
The measured concentration pattern showed a pronounced double peak with higher concentrations in the pre-moratorium period (maximum at about 1958) compared to the post-moratorium period (maximum at about 1963). The ^{240}Pu to ^{239}Pu ratios varied between 0.18 and 0.21 – except for one possible outlier with 0.27. These values are typical for global fallout and do not yield evidence for local sources from Lop Nor or Semipalatinsk. The ratios (at/at) for ^{236}U to ^{239}Pu were between 0.15 and 0.52 (average 0.32) with rather large uncertainties due to some analytical problems in the separation of plutonium. These values agree with recently measured values in ice cores from Antarctica that range between 0.18 and 1.4 [3]. Some measured values in sea and river water samples were between 1.0 and 12.0 [4].

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NUCL 19

Energy dependence of fission product yields from ^{235}U, ^{238}U and ^{239}Pu for incident neutron energies between 0.5 and 14.8 MeV

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Under a joint collaboration between TUNL-LANL-LLNL, a set of absolute fission product yield measurements have 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 2 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,

4.6 and 14.8 MeV. These results are contrasted to previous measurements and theoretical estimates.
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NUCL 20

Measurement of fission product yields and nuclear reaction cross sections using mono-energetic neutrons from a dense plasma focus

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The relative yields of fission products are a useful post-detonation diagnostic of a nuclear device. The relative yields can be used to infer the nuclear fuel and whether or not the device had a thermonuclear component. The activation of materials by high-energy neutrons can also provide nuclear forensic evidence. There is need for reaction cross sections to support this forensic activity. The Dense Plasma Focus, DPF, is a nuclear fusion device that can provide neutrons at energies of 2.45 to 3.05 MeV and 14.1 to14.7 MeV. The NSTEC DPF facilities provide 50 to 100 nanosecond pulses of neutrons with a yield of 1E12 for DD fusion and 1E13 for DT fusion. These neutron sources are providing new data for fission product yields and nuclear reactions. The fission product measurements will be placed in the context of the two fission mode hypothesis.

NUCL 21

Fission product chain yields from fission spectrum irradiations at NCERC

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Fission product chain yields measured using the fission spectrum critical assemblies at the National Criticality Experiments Research Center (NCERC) at the Nevada National Security Site (NNSS) are presented. Irradiations of 93% enriched ^{235}U (HEU) and depleted ^{238}U (DU) targets were performed on both the COMET/ZEUS and Flattop assemblies. The fission products were elementally separated by radiochemistry, and measured using high-precision beta counting. The observed fission product chain yields show that several of the isotopic species vary with the effective energy inducing fission in the assemblies. The observed fission product chain yields are consistent with

historical measurements, and support the two-mode fission hypothesis of Ford and Norris.

NUCL 22

SPIDER: New instrument for fission mass yield measurements

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The SPIDER (SPectrometer for Ion DEtermination in fission Research) instrument has been recently developed at the Los Alamos Neutron Science Center (LANSCE) to measure products from neutron-induced fission of actinides. The independent fission product yields will be measured with high resolution as a function of incident neutron energy, product mass, charge, and total kinetic energy. The independent yields measured by SPIDER will provide important insights into diagnostics of nuclear applications. Device yields and neutron environments are two areas that would benefit from the high resolution independent mass yields provided by SPIDER. First results of fission yields measured with SPIDER will be presented.
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NUCL 23

Relative fission product yield determination in varying neutron environments

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Fission product yield data sets are one of the most important and fundamental compilations of basic information in the nuclear industry. This data has a wide range of applications which include nuclear fuel burnup and nonproliferation safeguards. Current data sets present a wide range of uncertainty and demands for improved accuracy of fission product data are prevalent throughout the industry. Relative fission yields constitute a major fraction of the reported yield data and reduce the number of required absolute measurements. R-values are a double ratio of fission product yields where the numerator is the ratio of a given fission product yield to a standard isotope from a given fissile fuel and neutron energy. The denominator is the ratio of the same two fission products in the thermal fission of 235U. R-values are sensitive to the neutron environment of the fissile fuel and particularly useful when separation methods are used. Radiochemical separations of fission products reduce interferences, facilitate the

measurement of low level radionuclides, and are instrumental in the analysis of low-yielding symmetrical fission products. It is especially useful in the measurement of the valley nuclides and those on the extreme wings of the mass yield curve, including lanthanides, where absolute yields have high errors. Early measurements have been made with thermalized neutrons within sampling positions in the US Geological Survey TRIGA Reactor (GSTR) at the Denver Federal Center in Lakewood, CO. These studies have focused on identifying sources of error in radioanalytical separations and detection and removing or reducing them in order to measure relative fission product yield with minimal error.

NUCL 24

Synthesis of rapid separation targets by hydrothermal methods

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In nuclear forensics, it is important to be able to analyze the fission products of a device to determine

its origin and constitution. In order for this analysis to occur, standards of these fission products must

be obtained. The goal of this work is to synthesize porous metal organic framework (MOF) structures

with an actinide metal center. These can be used in the production of nuclides. The synthesis and

characterization of MOFs is presented. Methods to improve uranium containing MOF synthesis is

discussed.

NUCL 25

Thermochromatographic separations of volatile rare earth compounds for nuclear forensics analysis

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A growing focus of nuclear and radiochemistry is in the area of post-detonation material analysis from both a synthesis and chemical standpoint. It is the focus of this work to concentrate on chemical analysis, particularly with regard to rapid separation of entrenched fission oxides, principally rare earth oxides. The focus of this work is to highlight recent efforts to use thermochromatography to perform separations of rare earth oxides. Prior to separations, the oxides are dissolved in acid then treated with a variety of ligands, including 1,1,1,5,5,5-hexalfuoroacetylacetone (Hfac), 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod) and 2,2,6,6-tetramethyl-3,5-heptanedione (Hdpm). The resulting compounds are easily volatilized, allowing for gas-phase separation which will permit rapid separation over conventional liquid-liquid or column methods. In order to perform these separations, a gas chromatography (GC) system has been connected to an inductively coupled plasma mass spectrometry time-of-flight mass spectrometer (ICP-TOF-MS) to be used as the detector. The GC will be used to heat and separate the compounds, and the ICP-TOF-MS will be used to detect the resulting fragments. As a result, the metal ions and the time of arrival can be simultaneously determined. Additionally, the isotopic information of the metal ions can be validated to allow for rapid comparison to the results of other nuclear forensics techniques, including gamma-ray analysis, thermal ionization mass spectrometry, and x-ray fluorescence. The initial results have shown the time required for these samples is less than 8 hours, including the dissolution and compound preparation, while the actual separations require less than 10 minutes to obtain elemental and isotopic composition. The results of the separations using the three aforementioned ligands will be discussed in terms of resolution and thermodynamic parameters. It is the focus of this work to introduce another technique to the nuclear forensics community that will allow for rapid separations and subsequent elemental and isotopic analysis.

NUCL 26

Synthesis and characterization of Ln[fod]$_x$ and Ln[dpm]$_{x\ c}$ompounds for the development of rapid gas-phase separation methods

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In the aftermath of a nuclear event, a prompt identification of weapon characteristics is essential for determining the origin and composition of the detonated device. Deterministic procedures aimed at procuring such information are presently limited to lengthy aqueous chemical separation techniques that provide temporally undesirable results. A method of transitioning from aqueous to gas-phase separation techniques requires chemical manipulation to modify fission and activation products into easily volatilized complexes. Subsequently, these complexes can be easily separated in a gas chromatography mass spectrometer (GC-MS) for separation method optimization. In this approach, two ligands, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (hfod) and 2,2,6,6-tetramethyl-3,5-heptanedione (hdpm), have been employed to form lanthanide compounds (common fission products) for utilization in rapid gas-phase separation techniques. The synthesis of $Ln[fod]_x$ and $Ln[dpm]_x$ complexes will be discussed in detail, including procedure stages and percent yield efficiency fluxes amongst the lanthanides. Additionally, characterization of these complexes including elemental analysis, melting point data, detailed chemical structure, Nuclear Magnetic Resonance (NMR), Powder X-Ray Diffraction (PXRD), Single-Crystal X-Ray Diffraction (SCXRD), and Fourier Transform Infrared Spectroscopy (FT-IR) will be discussed. Resulting synthesis efficiency and perceptible trends are identified and will be compared between the Hfod and Hdpm ligands.

NUCL 27

Determination of decontamination factor for various radioisotopes during the PUREX process of irradiated DUO_2

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Nuclear proliferation is a growing concern and due to this increasing threat, nuclear forensics capabilities are being developed at Texas A&M University with sponsorship from the Department of Homeland Security. We are currently using computational and experimental methods to determine the isotopic characteristics of weapons-grade plutonium that could be produced in foreign nuclear reactors.

The uranium samples for this project were irradiated at the High Flux Isotope Reactor (HFIR) of Oak Ridge National Laboratory. After chemical processing of the irradiated uranium samples, the isotopic concentrations (and ratios) of selected fission products and actinides were measured and the burnup of nuclear material was determined. Our objective was to determine the differences in fission products and actinides characteristics for uranium samples irradiated in different type of nuclear reactors (thermal and fast reactors). This paper will present the experimental part of this research. These operations were performed inside a glove box to analyze trace elements and isotopes present in the each and every step of industrial PUREX chemical reprocess by alpha and gamma spectroscopy and other analytical tools. The weapon grade plutonium separated from other actinides and fission products such as Cs, Ce and Sm was determined by ICP-MS to match with the computational results.

NUCL 28

Source facility determination based on PUREX process trace metal signatures

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Nuclear forensics uses techniques such as material fingerprinting to identify and eliminate illicit sources of nuclear material. The purpose of this project is to determine which trace metals are good candidates for PUREX (**P**lutonium and **U**ranium **R**edox **EX**traction) process signatures based on solvent extraction experiments under PUREX conditions. A radiotracer method was developed where the activities of radioisotopes of 15 elements in the aqueous and organic phases of a batch extraction were used to calculate a distribution coefficient for each. The USGS TRIGA reactor located at the Denver Federal Center was used as a neutron source in the production of these radioisotopes. The distribution of these elements, representing the major trace metal impurities found in spent nuclear fuel, were quantified using gamma and beta spectroscopy. Radioisotopes of each element in the extraction system were supplemented by nonradioactive isotopes to simulate the chemical composition of a PUREX feedstream. Distribution coefficients found under idealized PUREX process conditions are presented and used to identify possible signatures. Future work will introduce perturbations to the batch extraction PUREX conditions which are representative of possible variations between facilities.

NUCL 29

Actinide sorption to aluminum (hydr)oxides: Influence of sorption site acidity

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The presence of the actinide elements in the geosphere poses a long-term environmental concern due to the toxicity and long half-lives of several isotopes. Therefore, understanding the mechanisms responsible for enhancing or retarding the mobility of the actinides in the environment is important for risk management. The environmental fate and transport of the actinides is particularly influenced by interfacial reactions such as adsorption and reduction.

The acid-base properties and hydration/dehydration mechanisms of corundum (α-Al_2O_3), γ-alumina (γ-Al_2O_3), and gibbsite (γ-$Al(OH)_3$) were previously studied. The results showed that surface acidity follows the trend corundum > gibbsite > γ-alumina. This is presumably related to a difference in surface sorption sites $\equiv AlOH$, $\equiv Al_2OH$, and $\equiv Al(OH)_2$, where the greater proportion of aluminum at the surface leads to higher surface acidity. Therefore, metals that act as Lewis acids should preferentially sorb to γ-alumina. However, the relationship between sorption affinity and surface acidity has not been explicity established. The objective of this work was to examine actinide interactions with aluminum (hydr)oxide minerals with the intent of being able to characterize binary actinide-mineral systems based on fundmental thermodynamics.

Batch sorption experiments were used to monitor the amount of Eu(III), Th(IV), Np(V), and U(VI) sorbed to corundum, gibbsite, and γ-alumina as a function of time, pH, and ionic strength. In addition, high-resolution transmission electron microscopy (HRTEM) imaging was used to identify possible surface precipitates and monitor for morphological changes in the solid phases. Batch sorption data and HRTEM observations were used to develop preliminary surface-complexation models describing actinide sorption to aluminum (hydr)oxide mineral phases.

This research supports the eventual investigation of plutonium sorption to aluminum (hydr)oxide minerals where, based on previoius research, surface-mediated reduction and strong inner-sphere surface complexation is expected.

NUCL 30

Pu transport mechanisms in the environment: Field evidence, conceptual models, and experimental data

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The migration of plutonium in groundwater (e.g. Mayak, RU, Nevada National Security Site (formerly Nevada Test Site), USA, and Hanford Site, USA) and surface water (e.g. Rocky Flats, USA, Little Forest Burial Ground, AU) has been documented at various locations in the world. In nearly all cases, colloid-facilitated Pu transport has been identified as the dominant mechanism leading to this migration. Importantly, Pu concentrations downgradient from contaminated sites have been consistently low. Both solubility constraints and colloid stability limits likely minimize the migration potential of Pu. Nevertheless, development of a credible conceptual model has been hampered by the lack of experimental data. The single most important process controlling Pu migration in groundwater is Pu stability and desorption from migrating colloids.

To elucidate the mechanisms controlling Pu transport, we have investigated Pu desorption rates from montmorillonite and other mineral colloids under controlled laboratory conditions. These data suggest that Pu desorption rates are slow enough that colloid-facilitated transport of adsorbed Pu is possible at the field scale (km distances and decade timescales). Organic matter surface coatings on mineral surfaces could further decrease desorption rates and enhance colloid-facilitated transport. However, these data also suggest that Pu concentrations and transport distances will be inherently limited and very sensitive to the desorption rates and flow velocities expected in the field.

One important alternative conceptual model that may be relevant at the NNSS and under hydrothermal repository conditions is Pu incorporation into secondary mineral colloids during rock alteration processes. This co-precipitation phenomenon could yield a truly irreversible association of Pu with colloids. This has been investigated through

long-term hydrothermal alteration experiments. The results suggest that Pu co-precipitation with secondary phases could yield a “permanent” Pu association with migrating colloids in which colloid filtration rates, and not desorption rates, will limit transport distances at the field scale.

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NUCL 31

Separating uranyl nanoclusters using ultrafiltration membranes

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Uranyl peroxide cage clusters form upon addition of peroxide to an aqueous solution of uranyl nitrate and adjusting the pH with base. These clusters are unique in actinide chemistry in that they form an extensive family of nanoscale capsules that have several potential applications. Two of these, designated U60 and U24P, are the subject of the current study. U60 consists of sixty uranyl peroxide hydroxide polyhedra that are linked into a fullerene topology that is identical to C60. U24P contains four-membered rings of uranyl ions bridged through peroxide that are linked into the capsule through pyrophosphate units. We are interested in methods to separate clusters in aqueous solution on the basis of their size or mass. In the current study, filtration of cluster species was used to separate U60 cage clusters from U24P cage clusters by taking advantage of the difference in their sizes. The U60 and U24P clusters were synthesized separately and mixed together in a feed solution. Electrospray ionization mass spectrometry (ESI-MS) and small-angle X-ray scattering (SAXS) confirmed the presence of both of the clusters in the original feed solution before filtration. A Millipore Amicon stirred cell along with flat sheet ultrafiltration membranes with reported molecular weight cutoffs of 8, 10, 12-14, and 20 kDa (based on polyethylene glycol and dextran standards) were used to execute filtration experiments. Using ESI-MS and SAXS to analyze the solution that permeates through the membrane, preliminary filtration experiments indicate that microporous membranes with a molecular weight cutoff of 12-14 kDa are capable of achieving a size-selective separation of U60 and U24P. This method of separation can also be used in studying time-resolved growth data of co-growth nanoclusters such as U60 and U24.

NUCL 32

Superheavy element discovery and chemistry program at LLNL

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The heavy element group at Lawrence Livermore National Laboratory (LLNL) has had a long tradition of nuclear and radiochemistry dating back to the 1950’s. Some of the most exciting work has taken place in the last decade (in collaboration with the Flerov Laboratory of Nuclear Reactions in Dubna, Russia) with the discovery of six new elements - 113, 114, 115, 116, 117, and 118. By pushing the boundaries of the periodic table, we can start to answer some of the most fundamental questions of nuclear science, such as the locations of the next “magic numbers” of protons and neutrons, and the possibility of an “Island of Stability” where nuclides would have lifetimes much longer than those currently observed in the heaviest elements. We have already seen evidence of extra-stability in the heaviest nuclides, which leads to half-lives that are long enough for us to perform chemistry on these isotopes one atom at a time. Work is underway on developing an automated chemical system that will be used for studying chemical properties of elements 104 and 105. New chemical separations are being studied that can be deployed using a multi-column automated system. These experiments will provide the ground work for performing aqueous chemistry later on even heavier elements such as element 114 where the chemical properties are completely unknown. In this overview the discovery of these new elements and the chemical experiments in progress will be discussed. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NUCL 33

Biotransformation of plutonium

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One of the major environmental concerns is the migration of plutonium (Pu) released from nuclear- weapon tests, accidents at nuclear power plants, and from the disposal of radioactive waste. Microorganisms, ubiquitous in the environment, also have a high capacity to sorb and bind actinides on their surfaces, and so might affect the movement of Pu. We have studied the interaction of Pu with microorganisms. Pu as Pu(IV) is preferably sorbed to bacterial cells in the mixture of *Bacillus subtilis* and kaolinite, and that Pu(VI) is reduced to Pu(V) and then to Pu(IV) during the interaction with the mixture. Adsorption of Pu(IV)-desferrioxamine B (DFO) on bacteria indicate that Pu(IV) is dissociated by contact with cells, after which Pu(IV) is adsorbed, and that pH dependence of adsorption density of Pu(IV) on cells is dominated by the stability of Pu(IV)-DFO complexes. Study on reduction of Pu(IV) in the presence of citric acid at pH 7.0 suggested that Pu(IV) is reduced to Pu(III) by the activity of sulphate reducing bacteria. Th(IV) as an alternative of Pu(IV) is adsorbed by biogenic MnO_2 and fungus hyphae immediately after contact, followed by the release from MO_2 by the association with organic ligands released from fungal cells. These facts indicate that microorganisms change chemical states of Pu during migration in environments.

NUCL 34

Plutonium hydrolysis and condensation

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Tetravalent-metal ions (M^{IV}) as solutes in aqueous systems present a chemistry complicated by hydrolysis and condensation reactions, often realized as unpredictable solution behavior and amorphous, ill-defined precipitates. The type and degree of metal-ion condensation is known to be influenced by several factors, notably concentration, pH, and temperature, all of which can be externally controlled for study. Also reported to influence condensation is a metal-ion's hardness or Bronsted acidity, with harder ions, such as hexavalent Mo^{VI} and W^{VI}, forming well defined oxo-brigded clusters, known collectively as polyoxometalates. In contrast, tetravalent ions, exemplified by M^{IV} = Th, Pu, Zr, and Hf, are generally known to form ill-defined amorphous precipitates. Of particular note is Pu^{IV}, which has an ionic radius, and hence hardness, intermediate within the tetravalent series. Its hydrolysis/condensation reactions are well studied because of their roles in aqueous solution chemistry, including solvent extraction techniques used in chemical separations and reprocessing as well as in geological fate and transport modeling of Pu as an environmental contaminant. We report our recent work on the structures of M^{IV} condensation products studied in solution and in the solid state. High-energy X-ray scattering (HEXS) provides quantitative information about metal-ion correlations in solution and how they change as a function of temperature, acidity, choice of anion and anion concentration. These studies are complemented by the structures determined by X-ray diffraction of single-crystal precipitates. Taken

together, our results are providing detailed information about condensation products, highlighting the importance of the anion in directing correlations and impacting precipitation. We will discuss observed trends, with an emphasis on the unusual behavior of Pu within this series of M^{IV} ions and their potential to provide predictive insights into how to manage, control, and predict this chemistry. This work was performed at Argonne National Laboratory, operated by UChicagoArgonne LLC, and supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Heavy Element Chemistry Program, under contract DE-AC02-06CH11357.

NUCL 35

Role of multinucleon transfer reactions in making neutron-rich transactinide nuclei

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The synthesis of new heavy elements by complete fusion reactions is becoming progressively more difficult due to very small (~ fb) cross sections. The heaviest nuclei we have made are n-deficient. Multi-nucleon transfer reactions appear to offer a path to synthesizing more n-rich transactinide nuclei. Zagerbaev and Greiner have made pioneering calculations of what might be expected in these reactions. We discuss these calculations along with calculations made with a modified version of the GRAZING code that treats fission decay. We compare these calculations with the results of measurements of fragment yields in the ^{136}Xe + ^{208}Pb reaction ($E_{c.m.}$ =450 MeV). We evaluate the most promising cases for making n-rich transactinde nuclei.

NUCL 36

Relativistic quantum theory for chemical identification of the heaviest elements

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The main aim of chemical studies on the heaviest elements, i.e., those with $Z \geq 104$, is their placement in the Periodic Table of the Elements: By comparing behaviour of these elements with that of lighter homologs in the chemical groups, their unique position in the Periodic Table can be confirmed. Theoretical investigations play an extremely important role in the area of the heaviest elements. First of all, they predict the electronic ground state configurations for the heaviest elements that are lying in the basis of the periodicity and cannot be measured experimentally. They also allow for designing expensive and sophisticated experiments with single atoms and permit interpretation of the experimental results. In the talk various examples of such studies are demonstrated. Accurate calculations of atomic properties are presented for elements till Z=122 and heavier, and the modern structure of the Periodic Table is shown. Predictions of molecular properties and chemical behaviour are discussed for

very interesting cases, particularly for the very volatile elements 112 (Cn) and 114 (Fl). A role of relativistic effects is discussed.

NUCL 37

Heino Nitsche’s contributions to the understanding of Pu reactions at mineral:water interfaces and their implications on present reactive transport modeling

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One of Professor Nitsche’s many research areas was in the field of environmental actinide chemistry. In this presentation, studies of the redox specaition of Pu and other actinides at solid:water interfaces will be discussed in terms of the contributions of Professor Nitsche’s group and data generated by other reserachers. General observations are that regardless of the mineral composition, Pu(IV) was the predominant solid phase oxidation state at the end of each experiment. The stability of Pu(IV), even on oxidizing surfaces such as pyrolusite, is proposed to be due to formation of an energetically favorable solid phase Pu(IV) species. A series of X-ray Absorption Spectroscopy (XAS) experiments independently verified Pu(IV) as the stable oxidation state of Pu sorbed to a suite of mineral colloids including pyrolusite, birnessite, magnanite, hausmaniite, hematite, and goethite. Interestingly, independent XAS studies by Professor Nitsche’s group predicted similar distributions of Pu(IV), Pu(V), and Pu(VI) on the manganese oxide minerals hausmannite and manganite despite a five order of magnitude difference in Pu concentrations in the systems. The observations made from this work have helped to explain the observed mobility of Pu in a series of long term (11 year) field lysimeter experiments at the Savannah River Site. The lysimeter studies indicate that Pu transport can be described as a dynamic system where adsorption and surface mediated reduction of Pu(V/VI) appears to compete with a slow (possibly oxidative) release of Pu. These results demonstrate how field and laboratory studies can be combined to describe Pu behavior in complex environmental systems and highlight the need for a fundamental understanding of actinide environmental chemistry.

NUCL 38

Mass transport in aerodynamic fallout glass from a near-surface nuclear explosion

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In near-surface nuclear explosions, device materials mix with vaporized and melted soil in the fireball, forming aerodynamic glassy fallout. The analysis of device signatures in this fallout glass has been the subject of study for post-detonation nuclear forensics. The interpretation of the compositional variations observed in such glasses remains a challenge, however, and the physical processes that control fallout formation are not well understood. Fallout samples consisting of cm-scale glassy blebs with spherical, tenth-millimeter glassy spherules fused to their surfaces, were obtained from a historical US test. The goal of this study is to constrain the time and temperature intervals that control mass transport in these fallout glasses by studying compositional and U-isotope profiles observed in them. Backscattered electron images of carbon-coated polished sections of the samples were acquired by scanning electron microscopy (SEM). The interfaces between small spherules and the larger host objects are enriched in elements heavier than potassium. The interfaces exhibit what appear to be chemical diffusion profiles of Fe, Ca, and Mg. Concentration profiles across the interfaces were measured using energy dispersive x-ray spectroscopy (EDS), wavelength dispersive x-ray spectroscopy (WDS), and nano-secondary ion mass spectrometry (NanoSIMS). While a better understanding of temperature variation as the fireball cooled and improved data on diffusivities in rhyolitic glasses are needed, our new results provide compelling evidence that the time and temperature of mass transport, and cooling rate in the fireball, can be constrained by studying these diffusion profiles. A thermal model incorporating the time scale and temperature ranges for mass transport in glassy fallout will be discussed.

NUCL 39

Constraints on fallout melt glass formation from a near-surface nuclear test

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We present major element and actinide composition data from a population of 28 aerodynamically-shaped pieces of fallout glass produced from a single near-surface nuclear detonation, and use these data to reconstruct the chemical changes that occurred in these melts prior to solidification. Glass major element compositions indicate that composition of local geology is a primary control on bulk fallout chemical composition. Glass uranium concentrations (14.73-32.85 µg/g) and ^{235}U/^{238}U ratios (2.321-7.725) are enriched relative to bulk sediment, indicating that vaporized, residual fuel was incorporated into the melts prior to solidification, likely within seconds, and are consistent with two-component mixing between naturally-occurring uranium and residual uranium fuel. ^{234}U/^{235}U and ^{236}U/^{235}U ratios are roughly constant (0.01074-0.01103 and 0.00480-0.00506, respectively), suggesting that these ratios are unique to fallout created from this test. Model ages of the residual fuel in fallout, calculated using the ^{234}U-^{230}Th and ^{235}U-^{231}Pa chronometers, are systematically inaccurate, biased towards older ages, and are consistent with two-component mixing between naturally-occurring daughter nuclides in local sediment and decay-derived daughter nuclides from residual nuclear fuel. The contribution of naturally-occurring sediment-derived daughter nuclides precludes the use of radiochronometry to determine the formation age of fallout. Multiple processes such as mixing, agglomeration of melted sediment-derived droplets, and incorporation of condensates must all occur within the timescale between sediment melting and melt solidification.

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NUCL 40

Production of activation species for use with realistic surrogate debris materials

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In support of research and development for post-detonation nuclear forensics, we have been investigating the production of activation species using a fast-spectrum nuclear critical mass assembly at the National Criticality Experiments Research Center (NCERC) located at the Nevada Nuclear Security Site (NNSS). The produced activation species are then incorporated into realistic solid surrogate debris matrices that could be used to validate and exercise radiochemical forensic techniques. We will present production pathways and rates of activation species observed from the irradiation of Ti, Fe, Ni, Ir, Pt, and Au elemental foils with fast-spectrum neutrons and discuss challenges associated with their production, isolation, separation, and quantitation via high-resolution gamma spectrometry when incorporated into a solid debris matrix. A technique using ion-exchange chromatography developed for high-yield extraction of Sc and Co activation species from the parent Ti and Ni target materials, respectively, will be presented as a case study.

NUCL 41

Forensic analysis of urban nuclear melt glass surrogates

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In the aftermath of any nuclear event, it is imperative to determine the composition and origin of the device both accurately and expediently [1,2]. The Radiochemistry Center of Excellence (RCoE), created at the University of Tennessee through funding from the National Nuclear Security Administration (NNSA) is engaged in developing the scientific basis to support these capabilities. The RCoE simultaneously provides academic opportunities and support for students in the fields of radiochemistry, geochemistry, nuclear physics, nuclear engineering, materials science, and radioanalytical chemistry.

A primary objective of the RCoE is to expedite accurate post-detonation analysis of nuclear debris through the development of improved radiochemical separation and analysis methods. Because there is no existing nuclear urban melt glass, surrogate melt glass debris is necessary for both the development of analytical forensic methods and the training of prospective specialists. The process outlined focuses on the analysis of established melt-glass surrogates with the end-goal of providing the nuclear forensics community with a robust method to supply realistic, non-sensitive surrogate materials that simulate a variety of detonation scenarios. Characterization and analysis techniques, including gamma-ray spectroscopy, x-ray fluorescence, and rapid separation via thermo-chromatography, have been performed on these surrogates, and are discussed.

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NUCL 42

Controlled pore glass materials as use for a surrogate nuclear explosion debris (SNED) material

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This work describes controlled experiments to fabricate materials emulating some of the properties of nuclear explosion fallout debris material, which is formed under extreme conditions that can be challenging to recreate on a laboratory scale. Debris composition is of interest for the information it potentially can provide in nuclear forensics analyses applied to the detonation of a nuclear device. Controlled pore glass (CPG) has been loaded with elements of interest as a substrate for preparing surrogate nuclear explosion debris-like particles that mimic some qualities of debris. The CPG material was loaded with 20 elements of interest. The material was heat treated and the volatility of the elements was assessed. The CPG material was then analyzed for elemental concentration using ICP-MS. The experiments were repeated to assess the method reproducibility. Once reproducible methods were established the CPG was loaded with U-235 to create a fission products material as well as a selection of metals (Au, Fe and Ni) to generate an activation products material. This two fold presentation will describe the synthesis methods of the loaded CPG materials as well as present the results of the irradiated CPG materials.

NUCL 43

Surrogate nuclear explosion debris methods:
ICP-fluidized bed reactor and agglomerated laser melt material

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Synthesis of surrogate nuclear explosion debris is vital to work in nuclear forensics; however, the extreme temperature and pressure environment of a nuclear explosion are difficult to replicate in a laboratory setting. The Inductively Coupled Plasma (ICP) and high powered CO_2 lasers offer controlled experimental conditions that can mimic some of the thermal effects that occur during these events. This presentation will examine two different techniques; an ICP coupled to a fluidized bed reactor (FBR) and a new apparatus designed to produce high power laser melting of falling particulates, for generating some of the characteristics found in nuclear debris. The first method combines a fluidized bed reactor with an ICP to create particles coated with atomized material generated by the ICP. The ICP creates a thermal environment similar to the cooling fire ball of a nuclear explosion where vaporized materials condense from the gas phase. The laser apparatus attempts to mimic the fallout of molten debris droplets on the ground where its impact creates a semi-fused glassy agglomeration of particles. Products of surrogate nuclear explosion debris created using these two approaches are compared to each other and to real nuclear test debris such as “Trinitite”.

NUCL 44

Radiochemistry for the production of a realistic post-det surrogate debris

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The post-det nuclear forensic capabilities are baselined through surrogate debris exercise samples. These samples are typically tailored towards testing and optimizing analytical techniques for quantifying elements of interest. One of the primary components of a post-det nuclear forensic sample is the unique fission product distribution and its quantity relative to the fissile material(s). In previous years, surrogate debris samples have included excess source material in comparison to the total number of fissions as a result of performing irradiations at traditional accelerator/reactor facilities. In order to address this issue, separation methods were investigated to isolate the fission products from uranium while minimizing the fractionation of the initial fission product distribution. The most suitable method was then utilized for the production of a realistic post-det surrogate debris. Results from the initial radiochemistry method development and its application for the production of an exercise sample will be discussed.

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NUCL 45

Behavior of U(VI) silicate minerals and Np(V)-doped U(VI) silicates

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The U(VI) silicate minerals such as uranophane (Ura) $Ca[(UO_2)(SiO_3OH)]_2 \cdot 5H_2O$, sklodowskite (Sklo) $Mg[(UO_2)(SiO_3OH)]_2 \cdot 6H_2O$, and Na-boltwoodite (NaB) $Na(H_3O)[(UO_2)SiO_4]$ are common in nature, and also observed as corrosion products in studies of long-term aging of spent nuclear fuel. These solids can control the dissolved concentrations of uranium in groundwater, and also influence the dissolved concentrations of other actinides such as pentavalent neptunium (Np(V)) associated with them. Mineral dissolution and metal ion desorption were tested by equilibrating mineral suspensions containing tracer levels of ^{233}U or ^{237}Np for 7 days at pH 11. Changes in dissolved U concentrations with time indicate initial mineral dissolution, followed by re-precipitation; this observation for dissolved U was consistent whether the system included traces of Np(V) or not. Interestingly, for studies involving U(VI) silicates containing traces of ^{237}Np, the Np was continuously released from the solid, even during re-precipitation of the dissolved U. These studies will be described and discussed in the context of direct disposal of spent nuclear fuel.

NUCL 46

Production and decay studies of ^{265}Sg for chemical studies of seaborgium using the gas-filled recoil ion separator GARIS at RIKEN

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Chemical characterization of superheavy elements (SHEs, atomic number $Z \geq 104$) is an extremely interesting and challenging subject in modern nuclear and radiochemistry. We have been developing a gas-jet transport system at the focal plane of the gas-filled recoil ion separator GARIS at RIKEN Linear ACcelerator (RILAC) to start up SHE chemistry at RIKEN. In this work, we produced an isotope of seaborgium in the $^{248}Cm(^{22}Ne,5n)^{265}Sg$ reaction and investigated its decay properties for future chemical studies [1].

A $^{248}Cm_2O_3$ target of 230 or 280 μg cm^{-2} thickness was irradiated with the 117.8-MeV ^{22}Ne beam from RILAC. The evaporation residues (ERs) of interest were separated in-flight from the beam particles and the majority of the transfer-reaction products by GARIS and were guided to a gas-jet chamber at the focal plane of GARIS. The ERs were thermalized in He gas, attached to KCl aerosol particles, and were transported by the gas-jet method to the rotating wheel apparatus for α/SF-spectrometry.

Based on genetically correlated α-α(-α) and α-SF decay chains, 18 and 24 events were assigned to $^{265}\mathrm{Sg}^a$ and $^{265}\mathrm{Sg}^b$, respectively. The half-life $T_{1/2}$ and α-particle energy E_α of $^{265}\mathrm{Sg}^a$ were measured to be $8.5^{+2.6}_{-1.6}$ s and 8.84 ± 0.05 MeV, respectively, and those of $^{265}\mathrm{Sg}^b$ were $14.4^{+3.7}_{-2.5}$ s and 8.69 ± 0.05 MeV. The cross sections were evaluated to be 180^{+80}_{-60} pb and 200^{+60}_{-50} pb for $^{265}\mathrm{Sg}^a$ and $^{265}\mathrm{Sg}^b$, respectively. Recently, a carbonyl complex of Sg, $\mathrm{Sg(CO)_6}$, was successfully synthesized with the GARIS gas-jet system and its gaseous properties were investigated with COMPACT (Cryo-Online Multidetector for Physics And Chemistry of the Transactinides) by an international collaboration led by research groups from Mainz and Darmstadt [2].

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NUCL 47

Recent advances in uranium cluster chemistry research

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Our ongoing exploration of uranyl peroxide cluster chemistry has resulted in the discovery of 109 distinct nanoscale clusters, almost all of which consist of cages of uranyl bipyramidal polyhedra, and only half of which have been reported in the literature to date. Studies of these clusters in aqueous solution using combinations of SAXS, ESI-MS, Raman, DLS, SLS, and NMR have revealed their unexpected stability and high solubility in water, their resistance to damage by gamma irradiation in the solid and aqueous states, their separation by ultrafiltration, the dynamic interchange between conformations, and complex aggregation behavior. This presentation will explore the properties of such clusters relative to their potential importance in the nuclear fuel cycle and environmental transport of uranium. Finally, a new synthetic approach will be discussed that has led to a significant family of peroxide-free uranyl-based polyoxometalates.

NUCL 48

Use of projectiles with Z ≥ 20 to produce heavy and superheavy elements

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Six new superheavy elements have been discovered using ^{48}Ca-induced reactions, and these superheavy nuclei are likely shell-stabilized and spherical due to their proximity to predicted magic numbers. Future discoveries of new elements will rely on projectiles with $Z_\mathrm{p} > 20$ due to the lack of available targets with $Z_\mathrm{t} > 98$. In order to study the influence of projectiles with $Z_\mathrm{p} \geq 20$, experiments have been performed at Texas A&M

University to study the reactions of ^{44,48}Ca, ^{45}Sc, ^{50}Ti, and ^{54}Cr with lanthanide targets to produce shell-stabilized, spherical nuclei near the $N = 126$ shell. Excitation functions for the *xn* and *pxn* exit channels of a large number of projectile/target combinations have been measured using the MARS spectrometer. The peak cross sections of the (^{48}Ca, 4*n*) reactions are substantially larger than for other 4*n* reactions, and the peak cross sections of the (^{44}Ca, 4*n*) reactions are somewhat larger than for (^{45}Sc, 4*n*) reactions with the same target. The latter two reactions only differ by a single proton in the projectile, and the influence of an odd proton is also observed when comparing reactions with ^{158}Gd and ^{159}Tb targets. In some cases, the (^{45}Sc, *p*3*n*) cross sections are larger than the corresponding (^{45}Sc, 4*n*) cross sections, and this highlights the problems of using this relatively neutron-deficient nucleus as a projectile. The data have been described theoretically by a simple model that incorporates an angular momentum-dependent fission barrier and collective effects. This work demonstrates that the production of nuclei near the $N = 126$ shell using fusion-evaporation reactions is heavily influenced by the projectile, and that cross sections for evaporation residues formed using projectiles with $Z_p > 20$ may be substantially reduced relative to ^{48}Ca-induced reactions. This talk will summarize the most recent experimental results, discuss the theoretical model, and give some observations on the likelihood of future new element discoveries.

NUCL 49

Second break in the actinide series occurs at califorinum

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The 5*f* orbitals contract across the actinide series, and therefore their ability to participate in bonding should diminish among the later actinides. However, despite the fact that californium is a late actinide, there is evidence that Cf(III) utilizes its 5*f* orbital in bonding. Herein, we demonstrate that complexation of Cf(III) by a simple pyridine derivative results in a number of alterations in electronic structure that include a reduced magnetic moment and strongly vibronically-coupled photoluminescence. We expand on this further by characterizing the lighter americium and curium analogs that do not display these pronounced changes in properties. These phenomena are probed using quantum mechanical calculations that support the involvement of 5*f*, 6*d*, 7*s*, and 7*p* orbitals in bonding for trivalent actinides from Pu(III) to Cf(III). We offer a hypothesis that elucidates why these effects are pronounced with Cf(III), but not observed with earlier actinides, and we postulate that these effects will only become more pronounced beyond californium.

NUCL 50

Heavy element studies at the University of Nevada Las Vegas

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In recent years, there has been a renewed interest in studying the aqueous chemistry of the lighter transactinide elements and in potentially expanding these studies to more recently discovered elements, such as element 114, flerovium and element 115. Due to the short half-lives and the low production rates for the transactinide elements, fast and efficient separations are necessary in order to study their chemical properties and the influence of relativistic effects on those properties. New developments in radiochemical separation techniques based on extraction chromatography and solid phase extraction seem to show promise method for achieving the required short separation times, high yields and high separation factors. These techniques are ideal for use in automated or semi-automated systems, especially when combined with a recoil separator as a physical preseparation method. The recoil separator is used to separate the radionuclide of interest from the beam and other unwanted reaction products. The lack of interfering reaction products offers several advantages for the design of chemistry experiments with transactinides. This presentation will give an overview of ongoing Heavy Element Research carried out in the Radiochemistry Program at the University of Nevada Las Vegas.

NUCL 51

Plutonium speciation during interaction with argillaceous rocks

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The study of fundamental processes of actinides in the environment was a main research area of Professor Heino Nitsche. To honor his scientific contributions in the field of actinide molecular environmental sciences, an overview of the speciation of plutonium during sorption and diffusion in argillaceous rocks will be given. These interaction processes have been studied using EXAFS, µ-XANES, µ-XRF, and µ-XRD. CE-ICP-MS has been used to investigate the speciation of plutonium remaining in the aqueous phase. The importance of redox active mineral phases for the transport of plutonium in argillaceous rocks will be highlighted.

NUCL 52

X-ray spectroscopy characterisation of radionuclide-NOM interaction

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Water soluble NOM are of environmental importance in the evaluation of safety scenarios concerning geological disposal of nuclear waste and contaminated legacies, as they are generally polyelectrolytes decorated with functional groups capable of forming complexes with metal cations, including radionuclides[i]. Thus they can potentially serve as vehicles for colloid mediated transport of radionuclides over large distances[ii]. Early structural studies of the interaction between actinide cations and NOM (specifically humic acid, HA) were performed at the Research Centre Rossendorf during the time when Heino Nitsche was director. These investigations involved characterisation of the coordination structure of $[An^{n+}HA_x]^{(n-x)+}$ complexes using An L3 edge EXAFS and comparison to reference complexes. Results revealed the primary interaction to be cation binding via HA carboxylate functional groups[e.g. iii]. Later studies of such complexes from the ligand point of view using C 1s NEXAFS and scanning transmission x-ray microscopy (STXM), in conjunction with quantum chemical calculations to support interpretation of observed spectral trends, support these findings[e.g. iv]. Aging of actinide loaded HA colloids leads to their densification, which has implications for their mobility.

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NUCL 53

Plutonium uptake by mammalian cells

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Plutonium is well known as a highly toxic radioelement. However, the specific chemical and biochemical mechanisms responsible for actual cellular uptake of plutonium remain to be fully defined. Plutonium can be carried into cells by the iron transport protein transferrin, however active cellular uptake of plutonium-transferrin only occurs when plutonium is bound in one of transferrin’s two iron binding sites. These two iron binding sites contain the same donor ligands from the same amino acids in a similar geometric arrangement. Why does the plutonium-transferrin complex behave differently depending on which binding site contains plutonium? To understand this facet of plutonium biochemistry, we have studied the influence of protein-associated anions on the

plutonium-transferrin complexes. Using NMR, optical spectroscopy, small angle scattering, and EXAFS measurements, we determined that the differences in plutonium’s behavior in the two metal binding sites of transferrin are related to the simultaneous binding of multiple co-ligands. The persistence of extra ligands in one of the plutonium-containing binding sites is in contrast to the behavior of transferrin’s natural target, iron. These findings are related to the selectivity of plutonium uptake we observe in cell lines derived from rat liver and adrenal gland tissues.

NUCL 54

Spectroscopic signatures for forensic sciences

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Signatures arising from production, conversion, and aging processes are chemical in nature, and optical measurements reveal the potential to detect persistent molecular signatures characteristic of material origin, age or process history. The ability to quantitatively identify new anthropogenic signatures from natural background signals is an important theme for forensic sciences. The characterization of vibrational structure of uranyl materials and minerals formed under environmental conditions will be used to evaluate spectra collected from anthropogenic uranium – bearing materials and uranium minerals. Here, we describe efforts in material synthesis, and characterization of infrared absorption and Raman spectra.
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NUCL 55

Calibration of femtosecond laser ablation inductively coupled plasma mass spectrometer using a thermal inkjet picofluidic system for sensitive isotopic nuclear material characterization

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Laser ablation inductively coupled mass spectrometry offers rapid quantitative elemental and isotopic characterization of a myriad of materials. In order to quantify the elemental and isotopic species present in the sample particularly for limited mass samples such as particulates, the entire process from laser ablation through detection in

the mass spectrometer must be calibrated. This can only be achieved by creating standards which have known mass and spatial dimensions. Such standards can be created using droplet-on-demand technology such as TIPS (thermal inkjet picofluidic system) which can control both the mass and spatial dimensions of the deposited liquid droplet. This work demonstrates the use of TIPS for calibration of a fs-LA-ICPMS instrument over 6 orders of magnitude ranging from the attogram to nanogram levels for uranium isotopes 235 and 238. In this demonstration, aqueous depleted uranium solutions were deposited onto a silicon substrate using a 300 picoliter volume and creating a 10 x 10 array spaced 500 micrometers apart. The dried spots were about 80 micrometers in diameter. The femtosecond laser spot size was adjusted to match the dried spot deposit. Both individual droplet ablations and entire array ablation of 25 dried residue deposits were sampled. The results show a linear relationship for both 235 and 238 U isotopes with an accurate isotopic ratio of 0.00202 average SD 4.01e-5 for the 235/238 uranium isotopes over the calibration range of 0.03 to 3,000 pg of deposited depleted uranium. This approach can be used with multielement depositions as well as calibrating LIBS sampling for quantification. LA-UR-14-27858

NUCL 56

FIER: A method for forensic attribution of fissile mixtures using beta-delayed gamma-ray signatures

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Beta-delayed gamma rays are an important diagnostic for nuclear forensic analyses. The FIER (Fission Induced Electromagnetic Response) code is a tool to model time-dependent delayed gamma-ray spectra from neutron-induced fission. Using systematically perturbed input parameters (i.e., neutron irradiation scheme, interrogation spectrum, isotopic composition of the sample, etc.), the FIER code is used to generate a database of delayed gamma-ray spectra. Model outputs are stored for comparison with measured data, and those input parameters that mostly closely reproduce the experimental data are identified. Through this, FIER can be applied to inverse problems for nuclear forensics applications using the Berkeley Nuclear Data Cloud (BNDC) framework at the Applied Nuclear Physics Program at Lawrence Berkeley National Lab (LBNL). This work further showcases the sensitivity of delayed gamma-ray experiments to nuclear data uncertainties and illuminates data deficiencies.

NUCL 57

Considerations when using scanning electron microscopy for nuclear forensics

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SEM is a technique of great interest to the nuclear forensics community – particularly for assessing the morphology and texture of samples. Uranium oxides are the most commonly interdicted materials and the relation of morphology to the chemistry of these samples is explored along with the stabilities of SEM-observed morphologies over time in various temperature and humidity conditions. Other observations relevant to the use of SEM as a nuclear forensics tool will also be discussed. LA-UR-14-28072.

NUCL 58

Electrochemistry of a modified-hematite film electrode for the detection of rhenium as a technetium analog

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As part of the 6% fission yield of the 99 isobar and with a half-life of 213,000 years, technetium-99 can be a useful tool for nuclear forensics. Recent research regarding Tc detection for forensics has focused on lowering the Tc detection limit using spectroelectrochemistry. However, noteworthy redox chemistry has been observed between iron-containing minerals (e.g. hematite) and Tc-99, a fission product of importance from the standpoint of contaminated sites remediation. Also, research into hematite electrodes has mostly focused on their use for solar cells, with hematite being an n-type semiconductor. However, hematite electrodes have also been used to investigate hematite interactions with components such as hydroquinone. The present work seeks to understand the interaction of hematite with Tc-99, using Re as a Tc analog. A modified hematite-film electrode was prepared and demonstrated appropriate stability; successful results regarding its use for the detection hydroquinone and rhenium will be presented. This research was funded by the Defense Threat Reduction Agency through grant # HDTRA1-12-0014.

NUCL 59

Stability constants and total dissolution of Tc(IV) and DTPA complexes

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Detection and quantification of fission products can provide valuable information for nuclear forensics, but a thorough understanding of their chemistries in the environment is key for appropriate analyses and conclusions. As part of the 6% fission yield of the 99 isobar and with a half-life of 213,000 years, technetium-99 can be a useful tool for nuclear forensics. While Tc(VII) is highly water soluble, in excess of 11 mol/L, Tc(IV) has only sparing solubility, on the order of 10^{-8} mol/L. These vast differences in solubility makes reductive precipitation of Tc(VII) to Tc(IV) an appealing method for limiting Tc mobility in environmental systems. However Tc(IV) readily oxidizes in the presence of oxygen and ligand complexation has been shown to greatly affect Tc(IV) dissolution and, to some extent, its oxidation. This work utilizes a competitive aqueous/organic extraction method to determine the stability constants of Tc(IV) with diethylene triamine pentaacetic acid (DTPA), which is then used to model Tc(IV) total dissolution as a function of DTPA concentration. The modeled dissolution of Tc(IV) is then compared to experimentally determined Tc(IV) dissolution in presence of DTPA. These determinations are part of a larger project seeking to improve the accuracy of modelling technetium mobility in environmental systems. This research was funded by the Defense Threat Reduction Agency through grant # HDTRA1-12-0014.

NUCL 60

Cathodoluminescent signatures of neutron irradiation

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Proof-of-concept measurements of the effects of neutron irradiation on common cathodoluminescent minerals have been made. Using a small cold-cathode cathodoluminescence system designed to be relatively portable, measurements of cathodoluminescence from replicate samples of two main types of common minerals

(feldspars and carbonates) were made. The samples were subsequently exposed to varying amounts of neutron irradiation from a research reactor and the cathodoluminescence of replicate samples were measured post-irradiation. From these data, the first observation of the neutron dose-response in calcite has been made. We conclude that this technique shows great promise as a nuclear forensics tool using common geological materials to measure a permanent signature induced from neutron irradiation – at least for calcites and most probably for feldspars. Further work has demonstrated the crystalline lattice size dependence of the cathodoluminescent signature for feldspars which suggests how this technique could be expanded for routine forensic analysis.

NUCL 61

Applications for nuclear forensics at the National Ignition Facility

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The National Ignition Facility (NIF) is an inertial confinement fusion facility that produces an intense flux of neutrons through the fusion of deuterium and tritium. By adding materials into the NIF capsule or to the surrounding hohlraum, neutron reactions can be measured to provide nuclear data for the nuclear forensics program. The NIF capsule produces a large number of 14-MeV neutrons, which can be used to measure activation reactions, and downscattered, lower-energy neutrons, which can be used to measure neutron capture reactions. Because of the short burn-time of the NIF shot, excited state nuclear reactions can also be measured, which cannot be done at traditional neutron sources. In addition, a variety of materials can be added to a NIF shot in order to produce isotopes of interest for the creation of realistic exercise debris samples. A program of nuclear forensics measurements at NIF has started with shots that use metal foils attached to the hohlraum as a target for neutron capture reactions. Future experiments and planned diagnostic improvements will be discussed. This work performed
under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. This work was funded by the Laboratory
Directed Research and Development Program at LLNL under project tracking code 13-ERD-
036.

NUCL 62

Boron-rich benzene and pyrene derivatives for the detection of thermal neutrons

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We have developed a synthetic methodology to generate boron rich aromatic small molecules based on benzene and pyrene moieties. The prepared aromatic compounds have a boron content > 7 wt% which is important for neutron capture applications as shown by blends of these molecules in poly(vinyltoluene) matrices having similar scintillation light output and neutron capture as state-of-the art commercial scintillators, but with an advantage of much lower cost. The boron rich benzene and pyrene derivatives were prepared from Suzuki conditions using both microwave and traditional heating affording 40-93% yields. This new procedure is simple and straightforward with potential to be scaled up.

NUCL 63

Plutonium speciation Influence on the ^{22}Na yield from the ^{19}F[α,n] reaction

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The compounds PuF_3, PuF_4, and mixture of $Pu(OH)_4/ZrF_4$ contain stable ^{19}F in the presence of alpha particles. When energetic alpha particles interact with ^{19}F, ^{22}Na is produced with a relatively high reaction cross section (on the order of 100 mbarn). The isotope ^{22}Na is an unstable beta-emitter with a half-life of 2.604 years and can potentially provide a new signature for nuclear forensics analysis. The widespread use of actinide-fluoride compounds in different nuclear processes illustrates the importance of this reaction for nuclear forensics analysis. Fluorine is used in various steps within the nuclear fuel cycle as well as possible weapons production processes. Current nuclear forensics methods are generally concerned with analysis of isotopic compositions of the actinide in question in order to determine source history. While isotopic ratios can provide some information about the history of an interdicted material, the analysis of secondary nuclear reactions, when possible, presents a new pathway to signatures that should also be taken into account. Synthesis and preparation of plutonium fluoride samples will be discussed including the analysis of the production of ^{22}Na from the ^{19}F(α,n)^{22}Na reaction monitored via the ingrowth of the 1275 keV peak in the gamma spectra using a HPGe gamma detector. Samples were counted in regular intervals over the course of 18 months. The ^{19}F[α,n]^{22}Na reaction as it pertains to plutonium III & IV fluoride was studied, as well as the outer sphere reaction of alpha decay from plutonium (IV) hydroxide on zirconium fluoride. Data presented will examine

the implications for nuclear forensic and provide a cross section determined for plutonium alpha decay onto fluorine.

NUCL 64

Division of Nuclear Chemistry and Technology 50th Anniversary celebration

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The ACS Division of Nuclear Chemistry and Technology was initiated in 1955 as a subdivision of the Division of Industrial and Engineering Chemistry. Probationary divisional status was lifted in 1965. The probationary Division's first symposium was held in Denver in 1964 and it is fitting that we celebrate the 50th Anniversary of the NUCL Division in Denver in 2015. Listed as a small ACS Division, NUCL's impact over the past fifty years has been remarkable. National ACS meetings have had many symposia sponsored or co-sponsored by NUCL, including Nobel Laureates, U.S. Senators, other high-ranking officials and students as speakers. The range of subjects has been exceptional as are the various prestigious awards established by the Division. Of major impact has been the 31 years of the Nuclear Chemistry Summer Schools to help fill the pipeline of qualified nuclear scientists and technicians. We will honor the past, celebrate the present and shape the future.

NUCL 65

Division of Nuclear Chemistry and Technology (1990-2015)

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The 25th Anniversary of the ACS Division of Nuclear Chemistry and Technology (NUCL) was celebrated in 1990 at the Boston, MA National ACS meeting with a Symposium entitled, "Nuclear Chemistry and Technology, Yesterday, Today, and Tomorrow" of which I was a co-organizer. Our current status and the importance of NUCL's contributions since then will be compared with the predictions made during that Symposium. Some of the potential challenges for the future that remain to be discussed include whether we are too all inclusive or too narrow? When, how, or why should we encourage more collaborative efforts with other Divisions and scientific societies? In addition to the extremely successful Summer Schools in Nuclear Chemistry, are there other new projects we should sponsor? Methods for attracting new members should be considered. The huge challenge to ensure the future of the Seaborg Award in Nuclear Chemistry by making it an ACS endowed award also still remains. Should we have an Awards Committee (as do some universities) to nominate and promote our members for

ACS or other awards? These are just a few ideas for consideration by the NUCL Division.

NUCL 66

Heavy element chemistry at Berkeley: A distinguished history with a promising future

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The tradition of heavy element chemistry in Berkeley dates backs to the first days of the field and the tradition of excellence in heavy element chemistry has continued well into the present. This presentation will briefly summarize some of the major Berkeley contributions to the field of heavy element chemistry over the years as well as describing the contributions from Berkeley to the NUCL Division and the ACS. Lastly, there will a focus on some of the more recent heavy element chemistry achievements from Berkeley and the scientific directions of the Berkeley heavy element chemistry program into the future.

NUCL 67

Heavy element chemistry and separations science at Argonne National Laboratory: A current perspective

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Argonne National Laboratory (ANL) grew out of Fermi's experiment under Stagg field and subsequent follow-up studies at Argonne Laboratory Site A, located at Red Gate Woods, in the Chicago suburbs. At its inception in 1946 ANL was tasked with developing nuclear power for electricity. By the late 1970’s the fundamental chemistry efforts associated with this task had expressed themselves in two well-established efforts, one focusing on the separation and isolation of transuranic elements and their fission products and the other on building an understanding of the chemical and physical properties of these new elements. Out of this effort came new selective extractants, including the class of organophosphates associated with the TRUEX process and efficient intra-lanthanide selectivity, both important for the advancement of spent fuel reprocessing. Characterization of the new elements included a significant synthesis effort, and a systematic study of *f*-ion optical properties within the context of a parametric crystal-field scheme. This body of work provides the underpinning of the fundamental studies ongoing at ANL today. The combined programs are conducted in purpose-designed hot laboratories, co-located on a site with the Advanced Photon Source, a third-generation synchrotron, and with the guidance provided by theoretical calculations conducted on state-of-the-art large computing facilities. Conceptually built primarily around understanding the partitioning of free-energy in liquid-liquid separations

processes, the current scientific program is centered on characterizing metal-ion solution speciation at varying length scales and using this information to build predictive modeling capabilities. To be discussed are recent results on aqueous-phase correlations and their correspondence to solid-state structures, the multiple length-scale organization of metal-extractant complexes in organic phases and their similarities with more broadly studied soft-matter systems, and new, atomic-scale information on ion-correlations at aqueous interfaces. The implications of this work will be outlined in terms of underpinning new separations opportunities and more broadly in terms of predicting metal-ion behavior in complex systems, including those found in the geosphere. This work was performed for the U.S. DOE, OBES, Division of Chemical Sciences, Geosciences, and Biosciences, Heavy Elements Chemistry, funded at Argonne National Laboratory under contract DE-AC02-06CH11357

NUCL 68

Decades of progress in actinide solution chemistry in NUCL/DNCT

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When the Division of Nuclear Chemistry and Technology was established in 1955, nuclear science was arguable one of the “IT” areas of scientific and technological progress. At the same time, the awe-inspiring power of nuclear technology loomed as a serious threat to civilization. Knowledge about this “hot” topic was growing steadily and nuclear research was thriving around the world driven by the need to better understand this seemingly inexhaustible resource. Actinide research was integral to the progress that was being achieved in harnessing the awesome power of the atom. Though arguably the focus has changed, study of the solution chemistry of actinides is as important and relevant at the beginning of the 21st Century as it was more than 60 years ago at the dawn of the Nuclear Age. In this presentation, the current state of actinide solution chemistry research will be discussed with a secure linkage to the history of this enterprise. Significant focus will be placed on the contributions of the author’s mentors who fostered progress in this field.

NUCL 69

Fifty years of heavy element science: Understanding their elemental states

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While a significant degree of heavy element, actinide science had been acquired prior to the birth of the ACS’s Nuclear Division, a significant change in scientific ability was acquired when the High Flux Isotope Reactor (HFIR) became operational at Oak Ridge. The reactor made major changes in both the quantities and higher atomic masses for the transuranium elements. While programmatic changes have influenced studies in

recent times, overall the collaborative studies obtained during these 50 years has been very significant for understanding the science of these elements, and perhaps even the Periodic Table of the Elements itself. Employing systematic behavior also has been very beneficial in defining and understanding the trends and changes in heavy element science. Presented here are advances that have been made regarding these elements' fundamental properties, and emphasizing these elements' electronic configurations for defining and understanding their scientific behaviors.

The information discussed here had been acquired in part by published studies supported by the U. S. Department of Energy.

NUCL 70

NUCL and the ACS/DOE summer school in nuclear chemistry: A historical perspective

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In 1977 the ACS Division of Nuclear Chemistry and Technology (NUCL) conducted a national survey on the status of training of nuclear and radiochemists to address concerns expressed by Division membership. The survey indicated that there would be an inadequate supply of chemists with training in the fields of nuclear and radiochemistry to meet the growing demand. The reasons cited for this mismatch were dwindling numbers of nuclear faculty at universities, declining student interests, and a severe shortfall in research funding for nuclear and radiochemistry. To address the issue of declining student interest, the NUCL began sponsoring with funding support from the US Department of Energy, an undergraduate fellowship entitled the "Summer School in Nuclear Chemistry." The first summer school was held in 1984 at the San Jose State University for 12 students. Five years later at the request of the funding agency, the program was expanded to include a second summer school at the Brookhaven National Laboratory. Over the history of the program ~685 undergraduates have participated and last summer marked the 30th anniversary of the first summer school at San Jose and the 25th for Brookhaven. This talk will describe the summer school program, how it began, the people responsible for making it happen, and some of the interesting aspects of the early years.

NUCL 71

Helping build a future nuclear forensics and radiochemistry workforce: Education efforts within the Seaborg Institute at Lawrence Livermore National Laboratory

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Although the number of universities that are producing PhDs in nuclear chemistry decreased dramatically over the past two decades, recent national efforts have made a positive impact in changing that decline. I will discuss efforts at Lawrence Livermore National Laboratory as well as provide an overview on other successful national efforts and assess where we need to go in the future.

The Seaborg Institute at LLNL serves as a national center for the education and training of undergraduate and graduate students, postdocs and faculty in actinide chemistry. The Seaborg Institute hosts a yearly summer school for graduate students to conduct research with a staff scientist in radiochemistry and nuclear forensics. Students come for the summer, engage in research, attend weekly lectures, interact with other staff and students, and present their work at the end of the summer. Students engage in research in actinide chemistry, radiochemistry, isotopic analysis, computation analysis, radiation detection, and nuclear engineering. This program facilitates the training of the next generation of nuclear scientists and engineers needed to solve critical national security problems.

Attracting the next generation of top student talent into nuclear science and reversing the declining trend in PhD's awarded requires sustained student programs, and integration between the national laboratories and universities.

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

NUCL 72

Thirty years of bridging the gap: The ACS Summer Schools in Nuclear and Radiochemistry

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Since the 1940s our nation recognized the strategic need for research and training in nuclear science, nuclear chemistry and radiochemistry. These disciplines are essential to the foundation of many 21st century technologies including energy production, the development of nuclear medicine and radiopharmaceuticals, materials science, and national security. Although the subjects of nuclear chemistry and radiochemistry were once prominent in the undergraduate curricula of most US colleges and universities, these courses have slowly disappeared at many academic institutions due to faculty retirements and reductions in research funding in these areas. This history and the resulting manpower shortages are described in the 2012 NAS report "*Assuring a Future US-Based Nuclear and Radiochemistry Expertise*". The report emphasizes that the needs for nuclear and radiochemistry expertise are barely being met by current supply and that future needs may not be met. One of the principal reasons for the current and projected challenges is that there is little nuclear and radiochemistry taught at the undergraduate and graduate level and, as a result, students are not exposed to this critical field. Since they were first introduced in 1984, the ACS summer schools in nuclear and radiochemistry have successfully introduced 651 of this nation's best and brightest undergraduate students to nuclear and radiochemistry. Nearly 20% of the participants have gone on to pursue careers in the nuclear sciences and many of these individuals are now in a position to influence other young people to enter the field. An overview of the history and impact of the schools will be presented.

NUCL 73

NUCL Division strategic plan

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I will present the Strategic Plan for the division for the period 2015-2020. The plan was developing during the 2014 calendar year, and focuses on three main goals: 1) Education and Workforce Development; 2) Awards, Recognition, and; 3) Membership, and Expertise and Communication.

NUCL 74

Thermodynamics of actinide solution chemistry: Complexation by alpha-hydroxy organic acids in mixed solvent systems

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Actinide complexation by organic acids influences actinide chemical behavior in industrial, environmental, and biological systems. Knowledge of the thermodynamic parameters driving these interactions enables design of effective process chemistry applications, environmental risk assessment and clean-up, and bioremediation approaches. We have been studying complexation by alpha-hydroxy carboxylic acids in aqueous and mixed solvent media. In fully aqueous systems, the complexation reactions are sometimes endothermic, but still favorable because of the entropy gained from complexation that disrupts the primary solvation shell around the actinide cation. In mixed solvent media such as solutions of methanol and water, the balance between enthalpy and entropy is different and sometimes surprising. In our work, we combine indirect experimental methods such as potentiometry and calorimetry with direct determination of speciation using spectroscopy (e.g. UV-VIS-NIR, fluorescence, NMR, etc.) to determine thermodynamic parameters. We also use computational tools to aid in the design and interpretation of our experimental studies. In this presentation, our results will be described and discussed in the context of designing chemical processing nd/or environmental remediation schemes.

NUCL 75

EMSL radiochemistry annex: A new international user-facility for the study of radiological samples

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The Radiochemistry Annex, a new state-of-the-art laboratory to facilitate application of advanced analytical methods to environmental samples containing radionuclides, has been operational for less than a year at EMSL, a U.S. DOE Office of Biological and Environmental Research user facility located at Pacific Northwest National Laboratory in Richland, Washington. It supports world-class research in the biological, energy and environmental sciences through integration of computational and experimental capabilities, as well as collaborating among disciplines to yield a strong synergistic scientific environment.

Critical determinants of radionuclide mobility are oxidation state, chemical speciation, and formation of surface and solution complexes. Accurate representation of how environmental conditions impact these determinants is key to predictive modelling of radionuclide fate and transport in terrestrial and subsurface ecosystems. These determinants also impact the chemical behavior of radionuclides in the nuclear fuel cycle from separations processing to the creation of waste forms and aging under repository conditions. Molecular-level characterization of radionuclide containing materials can also be used to trace point of origin in forensic applications. Unfortunately, the application of advanced molecular characterization techniques to radiological samples has often lagged because of the need for dedicated equipment and facilities. Additionally there are fundamental difficulties of observing molecular level processes for radionuclides that are often present in very minor amounts in environmentally contaminated soils and sediments.

The Radiochemistry Annex provides scientific support and specialized environment where scientists are using advanced imaging and spectroscopic approaches together with NWChem, EMSL’s premier computational modelling code, to study radionuclide speciation in environmental samples, nuclear fuel simulants, and in high level nuclear waste storage tanks. Results of initial research will be presented. The user facility consists of approximately 6000 sq ft of lab space for NMR, EPR, XPS, and fluorescence spectroscopies and EMP, FIB/SEM, SEM, and aberration-corrected TEM imaging to enable investigation of radionuclide systems using multiple experimental and computational vantage points.

NUCL 76

Radiochemistry at Los Alamos National Laboratory: Past, present, and future

***Dominic S. Peterson**, dominicp@lanl.gov. MS E549, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Radiochemistry has been a central part of Los Alamos National Laboratory since our founding in the 1940s. Since the Nuclear Division was founded in 1965, the laboratory has contributed to radiochemistry for weapons applications, bioassay, biological behavior of actinides, medical isotopes, and environmental applications. Our involvement in some of these areas has diminished, while other areas have become a focus of our efforts, such as nuclear forensics, environmental management, repository validation, civilian nuclear energy programs, and nuclear non-proliferation. The future of the laboratory will continue to hold great promise for exciting work in radiochemistry for the next 50 years!

NUCL 77

The Radiochemistry Center of Excellence at the University of Tennessee

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In 2013, the National Nuclear Security Administration supported the establishment of the Radiochemistry Center of Excellence (RCoE) at the University of Tennessee. The RCoE involves faculty and students in nuclear engineering, chemistry, chemical engineering, materials science, and UT’s new interdisciplinary PhD program in energy science and engineering.

The RCoE is organized into a set of two major and two minor research thrusts, each selected to develop new scientific understanding in areas of strategic interest and to develop student expertise and interests that overlap with NNSA needs. Those thrust areas are Advanced Radiochemical Separations, Radiochemical Probes For Physical Phenomena, Nuclear Cross-Sections, and Bulk Actinide Oxide Materials Processing and Behavior.

This presentation will review the research acomplishments of the RCoE in its first two years as well as its impact on improving student interest and engagement in the field of nuclear and radiochemistry.

This work was supported by the NNSA through the Stewardship Science Academic Program.

NUCL 78

Molecular electronic structure theory applied to heavy-element chemistry: Some past accomplishments, present challenges, and future opportunities

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The author will present some perspectives concerning the past, present and future of theoretical contributions to heavy-element chemistry and actinide science. The systems discussed will include large organometallic complexes that provide similarities and contrasts to analogous organotransition-metal complexes, small actinide-containing molecules formed experimentally by laser ablation and matrix isolation, and computational explorations of the chemistry of the super-heavy elements. The lecture will close with some thoughts on the future of molecular electronic structure as applied to heavy-element complexes, including some of the grand challenges that this field might ultimately be able to address.

NUCL 79

Savannah River National Laboratory and [NUCL] a joint history

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From its inception to the present, the division of Nuclear Chemistry and Technology [NUCL] and the Savannah River National Laboratory (SRNL) have been partners in history. This talk will start by discussing the first symposium topic, Dr. Clark Ice session co-chaired in Denver in 1964, “Production technology of Neptunium-237 and Plutonium -238 chemistry”. More recent SRS process chemistry will be presented interspersed with SRNL [NUCL] members of note and some of their contributions to the division. Finally, the reason that [NUCL] and the SRNL are expected to continue their interaction in the future, will be given.

NUCL 80

Online chemistry research at Texas A&M University

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The chemical properties of transactinide elements continue to elicit interest due to the influence of relativistic effects and the resulting impact on the periodicity of the elements. These elements must be produced in “online” experiments at particle accelerator facilities, but relatively few facilities are conducting these experiments today. A program to perform online chemistry experiments on the homologs of the transactinide elements is under development at Texas A&M University. A new Recoil Transfer Chamber (RTC) for thermalizing the products of fusion-evaporation reactions has been fabricated and characterized in a series of experiments. The RTC is able to achieve a high efficiency without the complexity of a radiofrequency system. Additionally, the separation of the Rf homologs Zr and Hf in “offline” experiments has been studied at trace levels using commercially available resins, and systems suitable for the study of Rf have been identified. Additional experiments are being conducted to separate the expected element 113 homologs In and Tl using resins and ionic liquids. This talk will discuss the facilities available, the performance of the RTC, and the latest results on offline chemical separations.

NUCL 81

Protactinium: Chemistry at the intersection of the 5f and 6d elements

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The observed chemistry and properties of the early actinide elements are governed by their changing electron configurations. the filling of the 5f electron orbitals, and the relative energetics of these orbitals with respect to the 6d orbitals. This phenomenon gives rise to the well-known redox chemistry and multitude of oxidation states among the early actinides in contrast to the lanthanide series where the stabilized 4f orbitals impart the universally observed trivalent oxidation states. Importantly, the 5f and 6d orbital energies intersect at protactinium, imparting a unique behavior that may be typical of both actinide f- and transition metal d- chemistries. In order to explore this hypothesis we have undertaken a study of protactinium investigating its chemical and structural properties in a series of ligand systems that typify actinide and transition metal behavior, structure, and symmetry. Experimental efforts have been aimed at the chemistry of Pa(V) in aqueous solution containing ligands classically thought of as strong donor ligands, and associated with both the actinides as well as the transition metals Nb and Ta: fluoride and peroxide. Synthesis of a series of fluoride and peroxide complexes of protactinium, niobium and tantalum, and characterization of these complexes using X-ray diffraction is complemented by vibrational spectroscopy, X-ray absorption spectroscopy, and computational studies. Experimentally, stark contrasts between the behavior of protactinium, niobium, tantalum, and the early actinide series are observed. Computational studies have been conducted to shed light on the underlying electronic properties that cause the experimentally observed effects. Studies of these systems provide a framework for the quantitative description of the chemistry of Pa, the element at the intersection of transition metal d- and actinide f- behaviors. Understanding this chemistry is fundamental not only to our understanding of metal-ligand interactions in the actinide series, but in our description of these interactions across the entire periodic table. This work was performed at Argonne National Laboratory, operated by UChicagoArgonne LLC, and supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Early Career Research Program, under contract DE-AC02-06CH11357.

NUCL 82

Radiotracers for biological, environmental, and medical applications

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The inorganic and radiochemistry of technetium, rhenium, rhodium, gold, the lanthanides, gallium, arsenic and others continue to be investigated for potential

biological, environmental and medical applications. Probing plant biochemistry with radiotracers (e.g., Fe-59, Cd-115, S-35) may lead to understanding metal ion transporters and/or potential phytoremediation. Understanding the basic chemistry of technetium with sulfide may lead to improved methods for separations and storage in nuclear fuel cycle chemistry as Tc-99 is a fission product and very mobile in the environment. Development of high specific activity radionuclides (e.g., Rh-105, Re-186, As-72/77) may yield a larger suite of potential radiotherapeutic and/or radiodiagnostic agents. Both the bifunctional chelate approach (Rh-105, Au-199, radiolanthanides) and the integrated approach (Tc-99m, Re-188) have shown utility for targeting receptors on tumor cells (e.g., melanoma, prostate cancer). Radiotracers have applications in many scientific arenas and continue to lead to new and interesting discoveries.

NUCL 83

Recent advances in molecular f-element chemistry centered on TRU elements

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With continuing utilization of nuclear energy and related technologies around the world, in conjunction with efforts related to the clean-up of legacy waste sites and contaminated environments, research into the handling, reprocessing and long-term storage of nuclear waste remains an important issue. In this regard, much interest has been focused on the development of novel extraction agents capable of efficient separations of the minor actinides (An) from the more long-lived lanthanide (Ln) fission products found in spent nuclear fuels. Such efforts have relied on the premise that ligands containing soft-donor atoms (e.g., N, S) preferentially ligate to An(III) ions relative to the more Lewis acidic Ln(III) species, an observation rationalized by an increased covalency within the An-L moieties. Despite extensive research into this hypothesis, there is still no conclusive explanation for the observed behavior. To this end, our research is concerned with exploring the extent of covalency within An-L bonds; specifically, we are interested in *transuranic* (TRU) coordination chemistry with the goal of understanding fundamental bonding and electronic structure within TRU metal-ligand interactions.

Our research takes a multifaceted analytical approach to understand TRU coordination chemistry, using traditional structural analysis in conjunction with theoretical calculations and more recently, X-Ray Absorption Spectroscopy (XAS) to probe the electronic structure and orbital composition of the metal-ligand bonds. We study a variety of ligand scaffolds ligated to both 4f and 5f elements with focus on the TRU elements, Np and Pu. This allows us to study a series of isostructural complexes in order to have a more comprehensive and thorough analysis regarding f-orbital participation. The complexes presented here contain ligands with hard- (e.g. O) and soft-donor atoms (e.g. N, S) with investigation and discussion regarding the bonding and electronic structure within the metal-ligand interactions.

NUCL 84

High field and high frequency EPR study of isotypic herterobimetallics

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Heterometallic compounds containing lanthanides and transition metals, $X_2Cu(TeO_3)_2(SO_4)_2$ (X = Eu, Gd, Sm, Tb,Tm, Y, and Yb), have been studied by magnetic susceptibility and variable frequency electron paramagnetic resonance (EPR). Single crystals of these novel compounds were synthesized by hydrothermal methods. The crystal structure of these isotypic compounds contains LnO_8 polyhedra and CuO_6 octahedra which are chelated by TeO_3^{2-} and SO_4^{2-} anions, forming a three-dimensional (3D) framework, as seen in Figure 1. Magnetic susceptibility measurements on polycrystalline samples reveal antiferromagnetic phase transition occurring at temperatures below 10 K in the Eu- and Tb-analogs. 34 GHz, powder EPR measured at 290K showed slightly asymmetric and broad single lines at g-values in the range 2.1 and 2.25, except in the Dy- and Tb- analogs which showed no signals. The Y-analog displayed a three-line spectrum typical of an S=1/2 system with rhombic symmetry, most likely due to the Cu^{2+} ions. Variable temperature, high field EPR measurements at 240 GHz and 336 GHz were conducted and yielded a wide variety of results for the various analogues. The high frequency EPR data sheds light on the magnetic structure and interactions exhibited by these compounds which go relatively undetected in low field EPR and magnetic susceptibility studies.

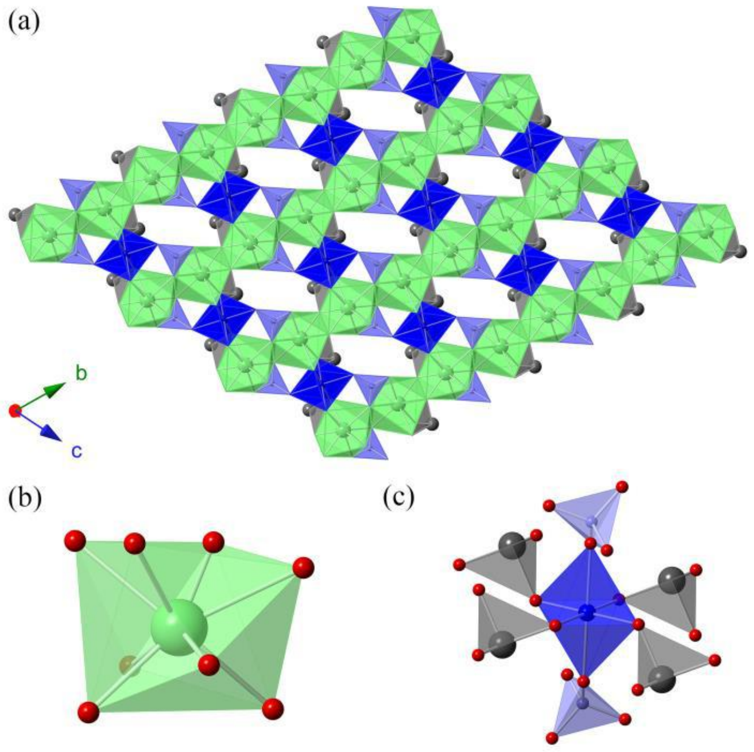

Figure 1. Crystal structure of $Re_2Cu(TeO_3)_2(SO_4)_2$ (Re = lanthanide analogue). Lanthanide polyhedra, ReO_8, are shown in green, CuO_6, polyhedra are in dark blue, TeO_3 polyhedra in grey, SO_4 tetrahedra in purple, and oxygen atoms are red.

NUCL 85

Microstructural characterization of structural alloys for nuclear energy applications

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Materials for nuclear reactor applications must withstand extreme environments of irradiation, high temperature, stress and corrosive media. Advancement of high-performance materials is the key to the development and deployment of advanced nuclear reactor technologies. The performance of nuclear reactor materials is dictated by the precise microstructure of a material produced during the material processing. The microstructure of a material is inevitably modified by various environmental conditions, such as irradiation, high heat and multi-axial loading. The complex microstructure inherent in an engineering material requires a suite of characterization tools, e.g. electron beams, synchrotron X-rays, atom probe tomography. This paper highlights recent development of using advanced in situ characterization tools, including in situ ion irradiation with transmission electron microscopy, in situ straining/annealing with high-energy X-rays for characterization of microstructural evolution under irradiation, temperature and stress.

NUCL 86

Optimization and characterization of a molecular plating technique for homogenous thin film samples

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The measurement and resolution of alpha-emitting nuclides is sensitive to the thickness and uniformity of the sample. Therefore, homogenous thin film samples are important for sensitive alpha spectroscopy measurements. Molecular plating has many advantages to other plating techniques, such as: short deposition time and simplicity of use. A novel in-house designed molecular plating cell was used to plate ~200µg/cm^2 HEU which achieved high recoveries and very uniform deposits. This design and procedure was characterized for the effects of varying the voltage, deposition time, various substrates, and solvent composition. The optimal settings and conditions will be presented and discussed. Alpha spectroscopy and audioradiography were used to characterize the quality of the deposits.

NUCL 87

Fission and the DNCT

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The scientific history of the DNCT is related in many ways to our attempts to understand the fission process since so many nuclear chemists have studied fission. Radiochemistry was the tool initially employed to characterize “post-scission” phenomena like mass and charge distributions. These radiochemical investigations became radioanalytical experiments with the advent of Ge(Li) detectors, leading to a more comprehensive picture of these phenomena and the fragment properties. This was supplanted by purely physical approaches to studying fission which produced information on the correlations between observables, such as υ(A). The radiochemists then seemed to concentrate on the practical part of fission (fuel cycle chemistry, environmental radioactivity) while the physically oriented chemists became “nuclear scientists.” Progress in our understanding of fission slowed as attention focused on the fission of the heaviest elements. Recent advances in the theory of fission along with increased support for programmatic investigations of fission have led to a renaissance of interest in the fission process. I review what seem to be the outstanding problems in fission physics: (a) our shocking ignorance of the energy release in fission and how the excitation energy is partitioned amongst the fragments (b) advances in how the mass and charge distributions in fission are determined and the changes in these distributions as one goes from Hg to Fm or from sub-barrier to supra-barrier excitation energies (c)

uncertainties in calculated quantities such as fission barrier heights (d) dissipative dynamics when there is no liquid drop barrier and (e) messy leftovers like scission neutrons

NUCL 88

Nuclear shape triaxiality in neutron-rich niobium isotopes

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The region of nuclei near 110Ru has maximum shape triaxiality. The niobium (Z=41) neutron-rich fission products are in an interesting fringe region with some bands being pure prolate spheroids and other bands being intermediate shapes between prolate and fully triaxial. Our collaboration uses GAMMASPHERE data to determine level schemes, and more recently has been comparing with advanced theoretical computer calculations, such as, Projected Shell Model (PSM), Total Energy Surface (TES) and cranked Total Routhian Surface (TRS)[1]. The Nilsson state of the odd proton is a strong driving influence on the shape, resulting in shape coexistence within several of the Nb nuclei.

1. “First observation of a rotational band and the role of the proton intruder
orbital π1/2+[431] in very neutron-rich odd-odd 106Nb.” PHYSICAL
REVIEW C 89, 044326 (2014)

NUCL 89

Exploiting fast neutrons: From nuclear structure to neutrinoless double-beta decay

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Inelastic neutron scattering with accelerator-produced neutrons offers many advantages for studying the structure of stable and very long-lived nuclei. With monoenergetic neutrons, nuclear levels can be examined near the threshold for their excitation without the attendant complications of feeding from higher-lying states. Although the recoil velocities of the excited nuclei are small, the Doppler-shift attenuation method (DSAM) has been developed to measure nuclear level lifetimes. Using these experimental techniques, we have been able to study the structure of a large number of nuclei and to identify collective structural features, such as multiphonon excitations of the quadrupole, octupole, and heterogeneous types, and mixed-symmetry excitations. Low-lying collective vibrations in nuclei have been studied for many years, but a new

understanding of these simple excitations is unfolding through measurements such as those performed with fast neutrons at the University of Kentucky Accelerator Laboratory (UKAL). Recently, our attention has turned to providing structural information relevant to neutrinoless double-beta decay and the searches for this rare lepton-number-violating nuclear process. This material is based upon work supported by the U.S. National Science Foundation under Grant No. PHY-1305801.

NUCL 90

New opportunity: coincident spectroscopy in neutron-deficient actinides

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Due to high γ-ray background rates heavy element production facilities are usually not sensitive to the electron capture decay of neutron deficient actinides. We have developed new capabilities at the Berkeley Gas Filled Separator (BGS) that allow us to study these isotopes. The highly selective and efficient separation of compound nucleus evaporation residue products using the BGS couple with a rapid delivery to a low-background detector facility, opens up many new possibilities for nuclear decay and structure studies in the neutron deficient actinides. The decay of these actinides produces vacancies in the K-shell resulting in X-rays uniquely identifying the Z of the decay products. We present the first results of this new methodology in studying the nuclear structure of fermium-254 by observing the γ-rays in coincidence with fermium X-rays. Coincident gamma-decay spectroscopy gives us a new tool to study the nuclear structure of previously inaccessible systems.

NUCL 91

Comparing nuclear counting statistics with the network statistics

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The nuclear statistics and the network event statistics are characterized by several similarities and differences which may be of interest to nuclear professionals. This work has its origins in teaching of the Radiation Measurements Laboratory at SUNY. Within the scope of this course, we teach students nuclear electronics and nuclear counting statistics. During the last several years it became interesting for students to use networks as means of learning electronics and concept of non-standard statistics. We

have observed some new and unexpected features which warranted further investigation and are presented here. We have collected several millions of events from a radioactive decay of Cs-137 as well as background, detected on a NaI detector using a commercial digital signal analyzer. In the case of Cs-137 data, we demonstrate the relationship between exponential interval-time distribution and Poisson counting distribution for a stochastic Markov point process exemplified by nuclear statistics. We have observed that electronic noise causes overdispersion in the background counting distributions: then we show that the Negative Binomial (NB) distribution describes the statistics better than the Poisson distribution. Applying pulse height discrimination restores the Poisson statistics. We have collected several millions of events on the network using a SNOOP software tool. We calculate network utilization in percent, and show that the interval-time distribution for all network events exhibits a power function consistent with a fractal stochastic point process characteristic of chaotic dynamics. Network counting does not conform to any standard distribution. A different picture is observed by selecting broadcast events from all network events. The interval-time distribution for broadcast network events exhibits a power function for short time intervals and exponential function for longer time intervals. The latter is consistent with the overdispersed Poisson statistics which can be quantified with the NB distribution.

NUCL 92

Working toward measurement of nuclear structure in superheavy elements

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Advances in particle accelerators, compound nucleus separators, and detector systems now allow the study of nuclear structure in isotopes of elements from No (Z=102) through Sg (Z=106). Compound nucleus reactions between medium-mass projectiles (^{48}Ca, ^{50}Ti, ^{54}Cr) and ^{206,207,208}Pb or ^{209}Bi targets can produce heavy elements isotopes in isomeric states. These isomers survive through the separation in the Berkeley Gas-filled Separator, and are implanted in the focal plane detector. Gamma-rays from the isomer decays have been used to construct level schemes for these heavy element isotopes. In some cases, we have been able to propose the multiple quasi-particle configurations of these isomeric states. Similar experimental tecniques are now being used in attempts to measure nuclear structure in superheavy elements, formed in compound nucleus reactions between ^{48}Ca projectiles and actinide targets. In the ^{243}Am(^{48}Ca,3n)^{288}115 reaction, we have been able to measure gamma-rays coincident with alpha decay, providing the first level scheme information for superheavy element isotopes. In the next decade, we can hope to determine the single-particle configurations of superheavy element states, providing much-needed guidance and restrictions for models of nuclear masses and structure.

NUCL 93

Response of actinide materials to highly ionizing radiation

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The response of actinide materials to ionizing radiation is of critical importance to their application in fission energy systems with respect to both their in-reactor performance as nuclear fuels and their long-term behavior as nuclear waste forms in geological disposal environments. We have investigated the radiation response of simple actinide oxides (UO_2, UO_3, ThO_2) and their analogues (CeO_2), as well as complex oxides ($A_2B_2O_7$, A_2BO_5, and complex uranyl oxides). The experiments use swift heavy ions that travel at relativistic speeds and deposit exceptional amounts of kinetic energy (MeVs to GeVs) within exceedingly short interaction times (femto to pico-seconds). The high energy densities (up to tens of eV/atom) move the damaged volume in the material to regimes far from equilibrium. The irradiated samples have been examined by an array of synchrotron x-ray diffraction, transmission electron microscopy and spectroscopic techniques.The response of the actinide oxides depends on their electronic structure , because an important factor in the damage process is related to radiation-induced redox processes. This is most evident in the comparison of the radiation response of ThO_2 and CeO_2. The ThO_2 is more resistant to irradiation damage than redox-active CeO_2. We have also observed that the damage accumulation depends on the grain-size (the effects are most prominent at the nano-scale *vs*. micro-scale) of CeO_2. A similar comparison is made among different uranium phases with different oxidation states. These observations provide the basis for the design of radiation toleratnt materials by limiting the extent or efficiency of a reduction of the oxidation state of actinides.

NUCL 94

Reductive routes to low-oxidation states actinide materials

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Studies of trivalent uranium (U^{3+}) and neptunium (Np^{3+}) are restricted by their tendency to oxidize in the presence of air and water requiring manipulations to be carried out in inert conditions to produce trivalent products. While the organometallic and high temperature reduction chemistry of U^{3+} and, to a much smaller extent, Np^{3+} has been explored, the oxoanion chemistry of these species has been limited despite their interesting optical and magnetic properties. We report the synthesis of U^{3+} and Np^{3+} sulfates by utilizing zinc amalgam as an *in situ* reductant with absolutely no regards to the exclusion of O_2 or water. By employing this method we have developed a family of alkali metal U^{3+} and Np^{3+} sulfates that are air and water stable. The structures, electronic spectra, and magnetic behavior are reported.

NUCL 95

Determination of Pu in spent nuclear fuel: Results from field testing of high resolution X-ray (hiRX)

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Plutonium determination is an essential aspect of safeguards operations of spent nuclear fuel reprocessing facilities. High resolution X-ray (hiRX) is a new technique based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) which was developed for quantification of plutonium in spent fuel. hiRX is a highly sensitive and selective technique due to the use of doubly curved crystal optics (DCCs), which provide monochromatic excitation and detection, resulting in high signal-to-noise ratio for the analyte. A benchtop prototype hiRX instrument has been tested with actual spent fuel samples from a reprocessing environment. A custom-designed ultralow volume sample cell, which contains 5 µL of liquid sample when filled with a pipette, was used in the field testing. Calibration was performed using aqueous standards containing plutonium and uranium, since uranium is the primary matrix element of spent fuel and may be present in amounts greater than 100:1 (U:Pu, g/L). Analytical results including accuracy, precision, and limit of detection (LOD) will be presented and compared with laboratory validation results. Linear response (>0.99) over nearly 4 orders of magnitude and LOD of 0.7 ng/µL were demonstrated in the laboratory using strontium as a model element for plutonium. hiRX offers an alternative, nondestructive assay which can provide rapid, direct plutonium quantification in a simple to operate platform. These specific results demonstrate the potential of hiRX for more general analytical applications for sensitive and selective elemental analyses. LA-UR-14-26389

NUCL 96

Accumulation of specific nuclides by fish bodies in Fukushima-Ken (Prefecture) EEZ (Exclusive Economic Zone), Japan in November 2012

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The Tokyo Electric Power Company Fukushima Dai-ichi nuclear power plant in Fukushima-Ken, Japan, was destroyed in March 2011 due to a massive earthquake (magnitude 9) centred offshore to the northeast of Honshu Island and the subsequent historic tsunami on 11 March 2011. Due to nuclear meltdown, damage to the buildings housing the reactors by hydrogen explosions, and the contamination of cooling water from the reactor cores, huge quantities of radioisotopes were emitted to the atmosphere and to the adjacent seawater. Fishing is currently restricted off the coast of Fukushima-Ken. On 22–23 November 2012, the Tokyo University of Marine Science and Technology performed an independent sampling measure radioisotope levels in fishery

species off Iwaki-Shi (City), Fukushima-Ken. These data included detailed measurements of individual fish, such as weight, sex, length, and collection locality.
[1] In spite of Grand Fish Weight % of Okamejei kenojei and Sebastes chenj in Fukushima-Ken EEZ were 26.6 Weight% and 13.7 Weight% respectively, Okamejei kenojei's fish bodies and Sebastes chenj's fish bodies in Fukushima-Ken EEZ had 49.3 becquerel% and 33.0 becquerel% of 134Cs in fish in Fukushima-Ken EEZ respectively and had 50.4 becquerel% and 31.7 becquerel % of 137Cs in fish in Fukushima-Ken EEZ respectively.
[2] It indicates that Acanthopagrus schlegeli, Clupea pallasii Vakenciennes, Engraulis japonica, Lepidotrigla microptena Gunther, Liparis tanakai, Mustelus manazo, Oncorhynchus keta, Oplegnathus punctatus, Pagrus major, Pagrus major (Fry), Paralichthys olivaceus (Fry), Platycephalus sp.2, Platycephalus sp.2 (fry), Takifugu poecilonotus, Takifugu snyderi, Takifugu stictonotus, Trachurus japonicas and Zeus faber Linnaeus fishes do not have ability to accumulate 134Cs and 137Cs radioisotopes. In other words these species have ability to evacuate 134Cs and 137Cs radioisotopes from their bodies.
[3] It has possibility to take accumulation or separation for specific nuclides 134Cs and 137Cs by combination of Sebastes cheni and Kareius bicoloratus and combination of Ditrema temminkii and Cynoglossus joyneri. .
[4] Pagrus major and Platycephalus sp.2 did not have ability to accumulate both 134Cs and 137Cs. They did not have any differences between adult fish and fry for accumulation 134Cs and 137Cs.
[5] It has actual differences between adult fish and fry of Paralichthys olivaceus for accumulation 134Cs and 137Cs.

NUCL 97

Cost effective tank waste characterization at the Savannah River site

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Extensive characterization of tank waste is performed at DOE sites in support of ongoing waste processing, waste disposition, and tank closure activities. At the Savannah River Site, characterization is routinely performed to process/disposition batches of salt waste and sludge waste, and to quantify inventories of residual material prior to closing emptied and cleaned waste tanks. In each case, several dozen radionuclides and stable constituents are quantified to meet waste acceptance requirements, regulatory requirements, and/or repository requirements. Because the radioactivity content of the waste is high, and because the waste matrices are typically highly variable and complex, the characterization activities are extremely resource intensive and time consuming. Correspondingly, the costs of the characterization activities are great.

To reduce characterization costs and accelerate schedules, an effort is currently

underway to identify opportunities for making tank waste characterization more efficient. In order to do this, activities are being performed to: a) gain a sound understanding of the relative costs, time requirements, and relevancy of current characterization approaches/practices; b) assess potential alternative characterization methodologies; and c) identify options for improving characterization practices in the context of reducing cost and schedule. Specifically, the following five primary activities are being pursued:

1) Identify characterization activities driving cost and schedule;
2) Investigate streamlining of characterization requirements based on the relative constituent risks (reduce characterization requirements for “low risk” constituents);
3) Determine the relative usefulness of laboratory analyses, waste receipt history, process knowledge, scaling factors, and other potential characterization bases;
4) Utilize differences between salt, sludge, and post-cleaning residue to hone characterization needs as a function of waste type; and
5) Investigate alternative characterization methods holding promise for being less costly and/or less time consuming.

A summary of the activities, results, and path forward will be presented.

NUCL 98

Elucidation of redox properties, structures, and bonding for cerium and uranium complexes through DFT and experiment

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The varied participation of both f and d orbitals in the bonding of early actinides translates into complex bonding patterns and subtle effects on physicochemical characteristics. Applications of coordination chemistry, such as in separations, must therefore rely on a concert of synthesis, spectroscopy and theory to understand, and ultimately provide, chemical improvements. We have been developing families of coordination compounds of uranium and cerium in an effort to connect spectroscopy, electrochemistry, theory and synthesis to unique electronic properties of f-elements in meaningful ways. Redox characteristics in particular now provide a simple thermodynamic assessment for complex stability that can be treated using DFT and accessible experiments. Our latest results in this area, including new understanding of electronic structures for high oxidation state complexes of cerium and uranium, will be disclosed.

NUCL 99

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

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Of the world's c. 250 tonnes of separated Pu, >100 tonnes 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 PuO_2/H_2O interactions, and all of which are complex, inter-connected and poorly understood.
In light of this, we have recently begun a computational study of the interaction of AnO_2 (An = U, Np, Pu) surfaces with water. Typically, such studies are performed using density functional theory (DFT) in conjunction with periodic boundary conditions (PBC). However, it is well known that standard PBC implementations of DFT using generalized gradient approximation (GGA) functionals often fail to reproduce key features of actinide solids, *e.g.* predicting metallic properties in systems known to be insulating. This failure stems from incorrect description of the strongly correlated 5f electrons, which are overly delocalized by the GGA, and the standard solution to this problem is to correct the GGA functionals with an onsite Coulomb repulsion term known as the Hubbard *U*.
A more elegant solution is to employ hybrid DFT, in which a certain amount of the exact exchange energy of Hartree-Fock theory is incorporated into the Hamiltonian. Such functionals typically produce more localized 5f electrons, and recover insulator behavior. They are, however, extremely expensive to employ in PBC calculations, and are very rarely used in the calculation of actinide solids. We have therefore sought a computational model which allows the routine use of hybrid DFT in AnO_2/water systems, and in this presentation I will report the first results of our use of the periodic electrostatic embedded cluster method [1], in which a quantum mechanically treated cluster is embedded in an infinite 1-, 2- or 3-dimensional array of point charges. This approach allows us to treat a cluster of AnO_2 and adsorbing water molecules using hybrid DFT (PBE0) whilst the long-range electrostatic interactions with the bulk are modelled *via* the embedding of charges. Early results are promising; the technique correctly predicts the insulating behavior of UO_2, NpO_2 and PuO_2, and shows very good agreement with very recent GGA+*U* studies of the adsorption of water onto the (111) surface of UO_2 [2].

[1] A. M. Burow et al. *J. Chem. Phys.* **130** 174710 (2009)
[2] P. Maldonado *et al. J. Phys. Chem. C* **118** 8491 (2014)

NUCL 100

Evaluation of the coordination chemistry and reactivity of trimethylsilylanilido and phosphinimide complexes of U and Th

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New coordination environments developed through rational ligand architecture design can provide access to new modes of reactivity and novel bonding fragments. Structural and spectroscopic analysis of new bond fragments on U and Th will provide new information relevent to understanding covalency, and allow us to develop new efficient extractants for the nuclear fuel cycle. This presentation will highlight our recent synthetic efforts using both phosphinimide ($R_3P=N$) and trimethylsilyl(anilido) ancillary ligands on U and Th.

NUCL 101

Structure and stability of uranyl(VI) and uranium(VI) imido complexes with high-nitrogen ligands

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Electronic structure calculations were performed for uranyl(VI) and the imido analogue complexes with the high-nitrogen ligand bitratrazoleamine, or BTA. For the uranyl structures, we see little change in the uranyl(VI) cation itself with increasing BTA coordination, though the O=U=O angle is slightly bent when coordinated with only one BTA ligand. Analysis of the stability of the complexes through calculation of the free energy pathway indicates that coordination with one instead of two BTA ligands is more stable, and that a uranyl(VI) dimer structure is more stable than the monomer. This is in agreement with the experimental crystal structure for uranyl(VI)-BTA complexes, which indicates that these compounds exist as dimers. The uranium imido analogue behaves similarly, with slightly bent N=U=N angles when the complex is coordinated with only one BTA ligand. We also find that the complexes become more stable with decreasing BTA coordination.

NUCL 102

Bonding and magnetism in tris-cyclopentadienyl neodymium and uranium complexes and their isocyanide adduct

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The trigonal planar tris-cyclopentadienyl complexes, Cp''_3M, where Cp” is 1,3-Bis-trimethylsilylcyclopentadienyl, and M is Nd or U, and their isocyanide base adducts present the opportunity to examine the differences in bonding and magnetism between analogous $4f^3$ and $5f^3$ systems. Tris-cyclopentadienyl neodymium complexes have been extensively studied by D.-H. Amberger and coworkers, but the analogous uranium systems have not been. The crystal field parameters for these systems will be determined from their magnetic susceptibility and EPR measurements. The splitting of the f-orbitals can then be determined from the crystal field parameters. The changes in bonding between Nd and U as well as those created by the isocyanide ligands will be discussed and compared with calculated electronic structure and physical properties.

NUCL 103

Experimental and theoretical determinations of covalency in d- and f-block metal oxides

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The nature of chemical bonds between metals and oxygen is of widespread interest because these interactions control the physics and chemistry of many technologically important processes. Among approaches explored previously, ligand K-edge X-ray absorption spectroscopy (XAS) has emerged as an effective method for quantitatively probing electronic structure and orbital mixing. The presence of covalent mixing is observed as a pre-edge feature in the ligand K-edge XAS, which only has transition intensity if the final state metal orbital contains a component of ligand p orbital character. Recent advances have shown that insights regarding the nature of orbital mixing can be obtained at the K-edge for oxygen through a combination of XAS with a scanning transmission X-ray microscope (STXM), non-resonant inelastic X-ray scattering (NIXS), and hybrid density functional theory calculations (DFT).

Herein, a new effort is discussed that employs these techniques to probe d- and f-block bonds to oxygen atoms. Initial work used oxygen K-edge XAS measurements and DFT studies to examine a series of six tetrahedral oxyanions, MO_4^{2-} and MO_4^{1-} (M = Cr, Mo W and Mn, Tc, Re). Recently, effort has focused on developing benchmarks that can relate O K-edge transition intensities into experimental values for O 2p character in metal–oxygen bonds. The lanthanide dioxides and sesquioxides, LnO_2 (Ln = Ce, Pr, Tb), were chosen for subsequent work because covalency in the Ln–O bonds is already well-established from hard X-ray spectroscopies. Results show that these materials enable many quantitative studies of covalency in a range of d- and f-block oxides. Preliminary efforts to develop new methodologies that will facilitate extension of this approach into the liquid phase will also be discussed.

NUCL 104

Strong correlations and covalency in actinide materials

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I will describe collaborative efforts combining synthesis, characterization and theory in order to assess the predictions of screened hybrid density functional theory (DFT) for the Mott insulator regime. A particular focus will be the counterintuitive prediction from hybrid density functional theory (DFT) that while UO2 is a classic Mott insulator and quite ionic, the PuO2 analogue, also insulating, shows significant Pu5f/O2p orbital mixing and band dispersion, indicative of covalent interactions. This has spurred efforts to synthesize high quality thin films of UO2, NpO2, and PuO2 using the technique of polymer assisted deposition (PAD), and to characterize them with optical spectroscopy, angle-resolved photoemission, and X-ray absorption spectroscopy. I will discuss the results of the experiments, and compare them with predictions of several many-body theories including screened hybrid DFT, the widely used DFT+U approximations, and dynamic mean- field theory (DMFT). As time permits I will sketch the direction we are taking to address the strongly correlated metals.

NUCL 105

Toward controlling the formation of cation-cation interactions in neptunyl(V) compounds

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The unusual bonding motif known as the cation-cation interaction (CCI) involves bonding of an oxo moiety on one actinyl center as an equatorial ligand on a neighboring ion. CCIs not only offer unique assembly mechanisms to link the actinyl cations into diverse moieties in different dimensionalities but also provide potential superexchange pathways that can enhance magnetic interactions between neighboring actinyl cations. As a result, CCI materials provide a superb venue to study the effects of bonding on the interplay between single-ion and collective magnetic properties. To systematically study and ultimately design CCIs in solids, we are using Raman spectroscopy to bridge the CCI species in aqueous solutions and CCI linkages in the final solid products. We have followed the formation of three different neptunyl(V) CCI compounds in the controlled evaporation of a NpO_2^+/HCl solution via changing Raman laser power. The structure of

$Na_xNp(NpO_2)_6(OH)_{1+x}Cl_9(H_2O)_{8-x}$ ($0<x\leq1$) (**1**) consists of cation-cation bound six-membered neptunyl(V) rings in a chair conformation, whereas the structures of $(NpO_2)Cl(H_2O)_4$ (**2**) and $(NpO_2)Cl(H_2O)_2$ (**3**) feature a square arrangement of neptunyl(V) CCI bonds in a two-dimensional layer and a three-dimensional network, respectfully. These in situ studies have suggested that CCI entities beyond the monomer and the dimer pre-exist in the solution and the assembly of these entities in the solid products are extremely sensitive to the evaporation condition of the solution. Compound **3** exhibits significantly different magnetic behaviour from those materials containing similar square arrangement of CCI bonds in lower dimensionalities. This result provides direct evidence for the strong influence of the lattice dimensionality on the collective magnetic properties. This work is supported by the U.S. DOE, OBES, Chemical Sciences, Geosciences, and Biosciences Division, Heavy Elements Program, under contract DE-AC02-06CH11357.

NUCL 106

Combined structural characterization, raman spectroscopy, and theory to promote an enhanced understanding of aqueous speciation

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The presence of f-orbitals in heavy elements leads to unique spectroscopic signals that can be utilized for characterization of materials and development of novel sensors, but data processing and analysis can become quite difficult given the complexity of the system. Raman spectroscopy of hexavalent uranium provides an excellent example of a technique that can be utilized to understand speciation and bonding and also has the potential to be developed for applied applications. The Raman-active symmetric stretching vibration of the uranyl cation is typically observed at 870 cm^{-1} and will red shift 30-100 cm^{-1} depending on the ligands coordinated to the equatorial plane, but the impact on the bonding and prediction of the resulting shift is still unclear. We are exploring the use of structural characterization of molecular uranyl citrate and carbonate species, combined with Raman spectroscopy, to explore these relationships in aqueous systems. These initial studies provide baseline knowledge of the molecular complexes that can then be utilized for Density Functional Theory studies to provide an in-depth understanding of the energetics and bonding within the unit.

NUCL 107

Characterisation of actinide selective N-donor extractants using spectroscopic and quantum theoretical methods

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A number of processes for separating actinides from their chemically similar 4f counterparts exist, many of which being based on liquid-liquid extraction using selective ligands and auxiliary (or ‘synergist’) agents(e.g. 1,2,3). One selective ligand investigated is the nitrogen donor ligand 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-pyridine (BTP), which was the first such separation extractant reported to perform in nitric acid solutions used in the dissolution of spent fuel[4]. Combined XAS, TRLFS and quantum chemical investigations aimed at establishing the reason for BTP’s selectivity have been reported over the past decade. Results point to BTP selectivity being correlated to relative higher covalency of the An-N bond and thermodynamic complex stability for the actinide complexes compared to their lanthanide counterparts[5,6]. More recently, high energy resolution X-ray emission[7] and NMR investigations[8], as well as comparative studies of structurally similar but subtly different An/Ln-ligand complexes systems[9] have been applied to these systems.

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NUCL 108

Actinide interactions with aminopolycarboxyates: Heavy element curiosities

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Research using (poly)aminopolycarboxylate (APC) ligands to achieve trivalent actinide / lanthanide separation has expanded significantly due to the development of derivative TALSPEAK solvent extraction processes that either simplify organic phase speciation (i.e. TALSQueak) or streamline processing steps through combining neutral and organic phase extractants (i.e. TRUSPEAK or ALSEP). Courtesy their applications in over fifty years of actinide separation science, the best defined interactions of actinides with soft donors in aqueous solutions involve APC ligands. These interactions are usually defined in terms of stability constants, especially for the trans-americium actinides, with minimal dialogue regarding enthalpic and entropic contributions to the binding. An argument is presented that expansion of APC thermodynamic data with heavier actinides could be instructive regarding fundamental f-element science. The benefit of producing lanthanide-normalized linear free energy diagrams, modeling previous actinide separations and review of actinide/N-donor enthalpic binding contributions is considered.

NUCL 109

Advances in organometallic chemistry at the bottom of the periodic table

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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 metallocene platforms, we have discovered a variety of unusual reactivity patterns unique to the actinides. This talk will describe recent advances in this area and their implications for the future of actinide chemistry.

NUCL 110

Use of molecular dynamics to evaluate tributyl phosphate and diamylamyl phosphonate containing systems

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Solvent extraction is utilized by the nuclear energy industry as a separations technique for reprocessing used nuclear fuel. In the industry standard PUREX (Plutonium URanium EXtraction) process, an amphiphilic extractant molecule like tributyl phosphate (TBP) selectively transfers metal ions of interest, such as uranium or plutonium or thorium, from a dissolved aqueous solution into a dodecane organic phase. It has been shown that the aggregation chemistry of similar extractant molecules varies drastically despite similar molecular structure. This difference in behavior is evident in third phase formation, an undesirable phenomenon that occurs at high extracted metal ion concentrations. TBP is more prone to this phenomenon than the similar extractant diamyl amyl phosphonate (DAAP). This study examines the structure and interaction of post-extraction TBP-metal ion complexes in their organic diluent using molecular dynamics (MD) simulations. Initial studies involve the development of an MD model of TBP more accurate than those commonly used in the literature. To ensure a

realistic and robust model, comparison to relevant experimental properties was performed. TBP density, average molecular dipole and dimerization constant in dodecane were calculated and successfully validated against experimental values. Neat TBP simulation density and dipole were calculated as 980 ± 2 and 3.28 ± 0.02, compared to experimental values of 972 and 3.32-3.35. The calculated dimerization constant was measured as 0.18 ± 0.04 compared to an extrapolated experimental value of 0.20 ± 0.01. Once the methodology for successfully modeling TBP was determined, alternative extractants like DAAP were also modeled. These extractant molecules will be implemented in molecular dynamics simulations of third phase conditions to identify the role that the molecular-level structural differences between TBP and DAAP play in inter-complex interaction.

NUCL 111

Historical overview of radioisotope thermoelectric generators

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In 1959, Birden and Jordan of Mound Laboratories patented the concept of the radioisotope thermoelectric generator (RTG), which captures the heat generated by natural radioactive decay and coverts that heat into electricity through various forms of energy conversion technology. Over the next 55 years, RTGs have undergone numerous evolutions of technology, including: transitioning from ^{144}Ce, the first radioisotope used in the SNAP-1A, to the ^{238}Pu used in all US RTGs today; establishing the best chemical form for the radioisotope for both safety and practical application; use of thermoelectric, thermionic, and dynamic conversion technologies; and development of a safety envelope that assured intact recovery of the radioactive material from nearly any conceived accident scenario. This historical review will discuss the technological evolution of the US RTG program and will include many of the political pressures that molded the program throughout its history; from the Hall of Fame Invention by Birden and Jordan to the RTG that currently powers the Mars rover, Curiosity. Final remarks will discuss the current state of the US RTG program and cover many of the technological challenges that the program is likely to face over the next several decades.

NUCL 112

Characterization of actinide reactivity and speciation at mineral:water interfaces

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Understanding the subsurface migration of actinides is vital for the development of robust and reliable performance assessment models of actinide bearing waste disposal facilities. The interaction between actinides and soil/rock surfaces is a primary mechanism controlling the mobility of actinides in the subsurface environment. In this work, fundamental studies of actinide interactions with pure minerals and natural soils are presented in terms of the primary interfacial reactions including: sorption, redox reactions, and surface mediated precipitation. The primary focus of this review is the characterization of surface mediated redox reactions between the mineral and actinides and development of quantitative thermochemically based models describing the speciation of the actinides in aqueous and solid phases. The models are used to determine the enthalpy and entropy contributions to the overall free energy of actinide sorption to minerals. General comparisons of these studies indicate that the strength of actinide sorption is proportional to hydration energy and effective charge of the given actinide ion. Observed reactions include formation of monomeric surface complexes, surface mediated redox reactions, aging or hysteretic sorption, and surface induced precipitation. The variability in these observed surface reactions requires a more detailed level of characterization of the surface speciation in order to accurately quantify actinide mobility in the environment. Examples of each type of reaction will be presented and discussed.

NUCL 113

Enhanced immobilization of iodine by biochar in soil-water system

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The potential release of radionuclides into the environment has been a major issue of safety associated with nuclear energy. The technology related to the capture or immobilization of these radioelements is underlined recently due to the accident such as Fukushima. Understanding and control the transport of radioactive elements in the environment especially the soil system is important to evaluate the potential risk to human and ecological systems through food chain. This study was conducted to determine the role of straw-derived biochar on the immobilization of iodine as a typical radioelements. The iodine distribution coefficient (K_d) on biochar (759 L/kg) was much higher than on raw soil (about 88.9 L/kg). As a result, the addition of biochar dynamically enhanced the sorption capacity of iodine from 1.25 mg/g (raw soil) to 2.34 mg/g (1% biochar addition). The addition of biochar also decreased the desorption of iodine from soil particle to soil solution. The residual iodine in soil amended by 1% biochar was 1.6 times higher than the raw soil after a 24 hours desorption. The results indicated that the biochar retard significantly the transport of iodine in soil-water system even at a small amount (less than 1%).

NUCL 114

Studies on the thermodynamics of trivalent lanthanide/actinide extraction by tri-*n*-octylphosphine oxide and bis(2-ethylhexyl) phosphoric acid

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Thermochemical features of biphasic transfer reactions of trivalent lanthanides and minor actinides (Am, Cm) have been measured using two-phase isothermal titration calorimetry and temperature dependent solvent extraction. The extraction measurements were made with tri-n-octylphosphine oxide (TOPO), a neutral solvating extractant and bis(2-ethylhexyl) phosphoric acid (HDEHP), a cation exchanger. Traditionally, thermodynamic parameters (ΔH, and ΔS) for biphasic reactions have been determined indirectly using the van't Hoff method. However, calorimetric measurements of the enthalpy of metal ion transport across the liquid-liquid boundary can provide accurate results and simultaneously highlight important features of a given extraction system. The results in this presentation emphasize the calorimetric approach to determining the heats of extraction for the TOPO extractant system, illustrating the delicate thermodynamic balance between metal ion extraction and acid partitioning equilibria. Thermodynamic parameters describing minor actinide extraction by TOPO and HDEHP are presented and an energetic comparison of the two extraction systems is offered.

NUCL 115

Specific recognition and enhanced luminescence sensitization of trivalent actinides

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Understanding the fundamental bonding interactions of selective *f*-element ligands presents a rich set of scientific challenges and is critical to the development of highly efficient separation reagents. Our approach uses the specific photophysical properties of trivalent lanthanides (Ln) and actinides (An) to study their selective binding and recognition by natural and synthetic hard oxygen-donor ligands. The photophysics and solution thermodynamic behavior of Ln(III) and An(III) complexes formed with selected siderophores and synthetic analogs such as multidentate hydroxypyridinonate ligands were probed. We report the first comprehensive characterization of sensitized Am(III) luminescence through the so-called antenna effect. In addition, while most investigated ligands were shown to sensitize the luminescence of one or several Ln(III) ions as well as that of Cm(III), subsequent specific binding of the metal complexes to secondary entities such as proteins that participate in endogenous metal homeostasis mechanisms resulted in significant enhancement of the intramolecular energy transfer processes. Particular metal-uptake pathways may therefore be used to create "double-antennas" for the sensitization of Ln(III) and An(III) luminescence. Such studies have important

implications for the use of spectroscopic methods to exploit the fundamental knowledge of the role of *f*-electrons in actinide bonding for the development of new sequestering agents, separation technologies, and luminescence-based detection assays.

NUCL 116

Minor actinide separations using a combination of a dithiophosphinic acid and a synergist

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A wide range of neutral and acidic organophosphorous compounds and two nitrogen heterocycle compounds were evaluated as possible synergists for use with dithiophosphinic acid extractants developed at the Idaho National Laboratory. The synergistic interaction of bis-(o-trifluromethyphenyl)dithiophosphinic acid and tri-*n*-octylphosphine oxide (TOPO), butyl bis(2,4,4-trimethylpentyl)phosphinate (BuCy272), or dibutyl butylphosphonate (DBBP) has been confirmed by continuous variation experiments using trifluoromethylphenyl sulfone as diluent.. The solvent composition which yielded the highest value of D_{Am} for each synergist was used to determine D_{Am}, D_{Eu}, and a value of ${}^{Am}S_{Eu}$ from an aqueous phase containing 0.5 M HNO_3. As expected, the highest values of D_{Am} were obtained for solvents using TOPO as the synergist. However, the magnitude of the calculated separation factor increased from ${}^{Am}S_{Eu} = 40$ for TOPO, ${}^{Am}S_{Eu} = 87$ for DBBP, and ${}^{Am}S_{Eu} = 1900$ for BuCy272.

NUCL 117

Probing for differences in the electronic properties of actinides and lanthanides using 1,10-phenanthroline-2,9-dicarboxylic acid

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As nuclear waste continues to accumulate throughout the world the understanding of *f* -element chemistry is becoming more essential. Here soft donor ligands were employed to discriminate between the lanthanides and the actinides in terms of structure and bonding in hopes to gain a better understanding of *f*-element chemistry. The hydrothermal reaction of MBr_3 (M= Nd, Ce, ${}^{239}Pu$) with 1,10-phenanthroline-2,9-dicarboxylic acid (PDA) yielded different structure types depending on the M:L ratio used. The resulting structures are discussed and shed interesting light on the electronic, magnetic, and bonding properties between the lanthanides and actinides.

NUCL 118

Structural and electronic variations in *f*-block containing plumbite clusters

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Comparative studies of structural variations in trivalent f - element borates and dipicolinic acid have provided insight to emerging periodic trends. This exploration of structure in the trivalent actinides and lanthanides has been extended to lead oxoanions. Hydrothermal reactions of PbO and M2O3 (M=Sm-Er) have yielded clusters with the formula [M6Pb18O2(OH)38]12- that contain a hexanuclear lanthanide center enclosed by a lead cage. Structural variations occur when M is substituted (M= La, Yb, Lu, Am). These structural changes along with electronic and bonding changes are compared and discussed.

NUCL 119

Supramolecular coordination polymers of lanthanide and actinide metals featuring the 1,8-naphthalimide tecton

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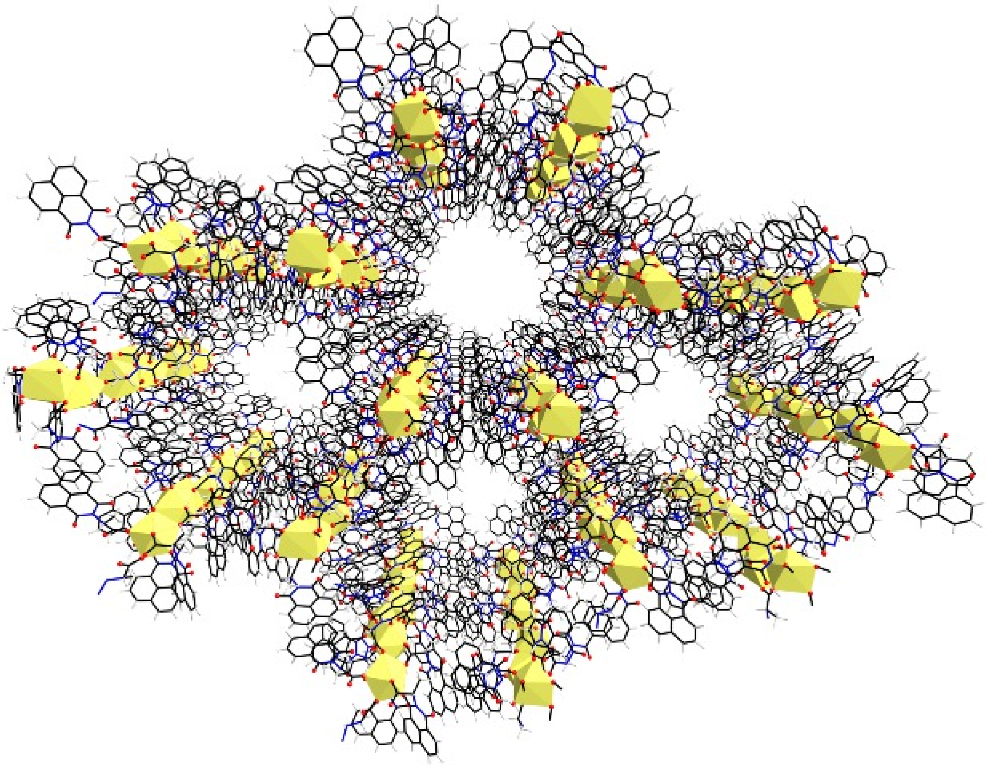
Two multifunctional ligands that contain one and two carboxylate donor groups coupled with the 1,8-naphthalimide pi-stacking supramolecular tecton have been used to prepare new complexes of lanthanide and actinide metals that have extended structures. These complexes are built upon either clusters, one-dimensional rods, or two-dimensional sheets. The covalently connected building units are then held together through strong π-π stacking interactions to generate extended three-dimensional structures in several cases and a two-dimensional structure in one case. The solid-state fluorescence spectra of several mixed metal lanthanide samples were studied and in some cases quenching was observed. The magnetic measurements and additional properties of these unique solids will be discussed.



NUCL 120

Ionothermal flux syntheses of isomorphous metalloborate clusters

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Ionic liquids have received considerable attention for the nearly endless tunability of their properties. The current paradigm for ionic liquids in the field of f-element chemistry to date has focused primarily on liquid-liquid solvent extractions, but the use of ionic liquids as solvents for inorganic synthesis is still relatively underexplored. The vast majority of flux syntheses are carried out hydrothermally or solvothermally, with water or an alcohol typically acting as solvent. However, new structure types may be accessed and tuned by utilizing an ionic liquid as the flux medium. In order to effectively take advantage of ionic liquids for the synthesis of functional materials it is critical that we first establish a basic understanding of how simple ionic liquids affect structure topology by comparing ionothermal flux reactions with more well-understood systems. Ionothermal flux reactions have thus been carried out for the synthesis of new lanthanide and actinide borates, since comparisons can easily be made with borates prepared through hydrothermal flux and boric acid flux syntheses.

The ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) has been employed in the synthesis of a series of isomorphous cluster compounds, all of which have the formula $M_4B_{22}O_{36}(OH)_6(H_2O)_{13}$ (M = La-Nd, Sm-Gd, Pu, Bi). This is surprising since borates have a propensity to polymerize and form extended structures, and all of the previous borate structures that have been produced by our group have had either two-dimensional sheet or three-dimensional framework topologies. It is also remarkable that identical structures are observed for all eight metals, since previous studies with lanthanide and actinide borates by our group have revealed differences not only between the lanthanides and actinides, but also among individual lanthanide or actinide borates within a series.

NUCL 121

Correlation between single-atom adsorption enthalpies and solid-state properties

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In heaviest element chemistry experiments the adsorption behaviour of single atoms on noble metal surfaces (e.g. Au) are measured. Deduced adsorption enthalpies are then compared with theoretical values using relativistic models. However, there are some drawbacks using this strategy: measurements are conducted under ambient carrier gas conditions which prevent surfaces to be clean in a strict sense.

An alternative approach is to correlate experimental adsorption enthalpies measured on boundary layers with sublimation enthalpies. For given classes of compounds (e.g. halides, oxides) or elements on a given surface (quartz, noble metal etc.) highly significant correlations are observed. Such extrapolated sublimation enthalpies can then be compared with values determined by relativistic theoretical solid-state calculations (cohesive energies).

A recent example that validates such an approach is astatine. Theoretical [1] and experimental [2] values for the sublimation enthalpy of At agree well. Application of this strategy to copernicium (Cn) and flerovium (Fl) will be presented.

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NUCL 122

Predicting the redox potentials of actinide complexes (An=U, Np, Pu) using first-principles

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Redox chemistry is inherently important in all aspects of the nuclear fuel cycle (principally for U, Np, and Pu). The redox potentials of Actinyl(V)/(VI) can be tuned by coordination ligands, and the trend across the series is found to be Np>Pu>>U. However, it has been challenging for theory to accurately predict redox potentials for a wide range of compounds due to their complicated electronic structures. Herein, we report a computational method based on density functional theory that can correctly predict the redox trend across the series. We demonstrate the predictive power of this method by investigating the tuning of redox chemistry by equatorial coordination ligands.

NUCL 123

Actinide chemistry in the gas phase: A fruitful interplay between experiment and theory

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During the past two decades a research program has been developed that combines experiment and theory to explore the chemistry and spectroscopy of a variety of gas-phase molecules and complexes, with an emphasis on those comprising actinides from Th through Cm. Model gas-phase systems studied by experiment are sufficiently small, and free of secondary perturbations present in condensed phase, such that theory can be applied with a relatively high level of accuracy. The gas-phase results reveal fundamental aspects of 5f element chemistry and furthermore can in some cases provide a basis to understand more complex condensed phase phenomena. Recent accomplishments include activation of actinyl oxo-bonds, formation of new types of actinide-ligand bonds, hydration and hydrolysis at a molecular level, and infrared spectroscopy of coordination complexes. Highlights will be presented, along with prospects for future advances.

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NUCL 124

Exploring the highest oxidation state in actinide compounds

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The oxidation state is one of the most important concepts in chemistry [1]. As an indication of the electronic state of atoms in a molecule, the "oxidation state" of an atom represents the number of valence electrons it has formally gained or lost when bonded with other atoms in a molecule [2]. The highest known oxidation state is +8, as exemplified in tetra-oxides MO_4 (M = Ru, Os, Xe) of group-VIII metal and less-inert noble gas. Despite claims of octavalent states of Pu and Cm in MO_4 compounds, whether or not such high oxidation state is stable for actinides is still unclear. We have investigated the electronic structures of PuO_4 and analogous MO_4 (M = Fe, Ru, Os, Hs, Sm) complexes by using *ab initio* wavefunction theory and density functional theory [3,4]. It has been shown that the exotic low-spin high-oxidation state of Pu(VIII) is highly unstable against intramolecular electron transfer. The more common plutonyl(V)$^+$ unit may be loosely coupled to a superoxido O_2^- ligand, forming PuO_4 as a high-spin complex of lower oxidation state, $^5C_{2v}$-$(PuO_2)^+(O_2)^-$. The leading valence configuration with open electron shells on plutonium, $(f^3)Pu^{5+}$, and superoxide dioxygen, $(\pi^{*3})O_2^-$, yields a highly correlated valence electronic system. We can thus conclude that the highest oxidation states of the actinides become more and more unlikely from uranium onward in the 5f actinoid series.

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NUCL 125

Spectroscopy and structure of the simplest actinide bonds

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High-resolution photoelectron spectroscopy techniques are being used to eamine the ground and low-energy electronic states of diatomic actinide molecules. Measurements are carried out with ro-vibrational quatum state specificity, and the results are used to benchmark relativistic quantum chemistry models. Recent results for Th and U nitrides and halides will be presented.

NUCL 126

Experimental and quantum chemical studies of alkali-ion promoted formation of uranyl(VI) peroxide rings and a comparison with similar reactions in12-crown-5 and 15-crown-5 systems

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X-ray crystal structures of uranyl(VI) peroxide clusters contain 4-, 5- and 6-membered rings, where the uranyl units are linked by peroxide and hydroxide bridges. The clusters are formed by crystallization from aqueous solution, but the nature of the assembly process is far from clear. In a number of publications we have shown that 4-and 5-membered rings are formed in solution and that these might be precursors to cluster formation. We have also shown that alkali- and tetramethylammonium ions play a role in the ring formation reactions, suggesting a similar role as in the synthesis of crown-ethers. The experimental studies (using potentiometry, spectrophotometry, calorimetry and NMR methods) demonstrate that the reactions are labile, in contrast to the formation of crown-ethers. By using quantum chemical methods we have explored possible structures in solution, reaction thermodynamics (Gibbs energy, enthalpy and entropy of reaction) and the nature of the peroxide bridges. There is a strong similarity between the alkali ion complexes of the peroxide rings and similar crown-ether complexes.

[1] P. L. Zanonato, P. Di Bernardo, V. Vallet, Z. Szabó and I. Grenthe, Dalton Trans., 2014, DOI:10.1039/C4DT02104E.
[2] ibid. in preparation.

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Integration of computational modeling and experiments in actinide chemistry

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Understanding the chemistry and properties of actinides is essential for predicting the fate and controlling the behavior of nuclear materials in the ecosystem, as well as for developing new advanced applications in energy, medicine and forensics. Computational chemistry has become a key pillar in the multidisciplinary research, advancing the fundamental understanding of actinide chemistry through a strong synergy between experiment and simulations. Simulations play an important role in the interpretation of experimental data and are in more and more instances able to reliably predict chemical and physical behavior of actinide species or drive new experimental investigations.

Here we will present some results of projects involving experiment and simulations. We will discuss our latest work integrating gas-phase experiments with simulations to gain insight into the structures and energetics. We will also discuss the results from thermodynamics calculations focused on predicting the coordination and hydrolysis products of actinides across the series.

NUCL 128

Toward accurate ab initio thermochemistry for molecules containing f-block elements

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Utilizing two new series of correlation-consistent-type basis sets currently under active development, one based on relativistic effective core potentials (ECPs) and the other from the all-electron Douglas-Kroll-Hess (DKH) Hamiltonian, a composite thermochemistry methodology based on the Feller-Peterson-Dixon approach has been constructed and applied to selected lanthanide and actinide halides and oxides. The systematic convergence characteristics of the new basis sets are exploited to obtain complete basis set (CBS) limits for both valence and outer-core electron correlation for a variety of reaction and bond enthalpies at the CCSD(T) level of theory. These results are then combined with accurate treatments of spin-orbit coupling, zero-point vibration, and a few other smaller effects to yield thermochemical properties with expected accuracies of 3 kcal/mol or less. In nearly all cases the calculated results lie within the experimental error bars, albeit some of the latter are relatively large. Generally the ECP-based results were within 1-2 kcal/mol of the DKH-based values, except when large changes in oxidation occur, e.g., in the atomization energy of ThF_4 the ECP-based result was 6 kcal/mol larger than the DKH-based value, where the latter was just at the high end of the ±2 kcal/mol error bars of experiment.

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NUCL 129

Reactivity of aqueous thorium(IV) and plutonium(IV) clusters

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There is substantial interest in understanding how aqueous metal cations convert into colloidal particles. The tetravalent actinides exhibit extensive hydrolysis and condensation behavior due to their high charge density and acidity. Electronic structure calculations at the density functional theory level were used to provide insights into the relative stabilities and energetics of oligomers and to develop a mechanism for oligomer formation. The formation and evolution of polyactinyl species in the thorium (IV) and plutonium (IV) selenate/sulfate systems are being explored. The electronic structure calculations have been used to predict the spectroscopic properties of some of the

metal (IV) cation oligomers to aid in interpreting the experimental data. This work is supported by the U.S. DOE Office of Science (BES, Chemical Sciences, Heavy Element Program).

NUCL 130

Tetravalent actinide-small organic molecule containing compounds

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The transport and fate of the actinides in the environment is governed by complexation, precipitation, sorption, colloid formation, and redox reactions. Actinide-organic complexation has been recognized as a particularly important factor in understanding the overall chemical behavior of the actinides. Using a number of synthetic, spectroscopic, and X-ray diffraction techniques, we are therefore exploring the self assembly and structural chemistry of actinide(IV)-small organic molecule complexes in solution and the solid state with an eye towards understanding reactions that occur in aqueous solution and under the influence of various organic ligands. How the functionality of the organic ligand as well as the synthetic conditions (e.g. pH, ionic strength, and temperature) affect the speciation of the tetravalent actinides will be discussed.

NUCL 131

Theoretical study of the electronic spectrum of the UO and UO^+ molecules

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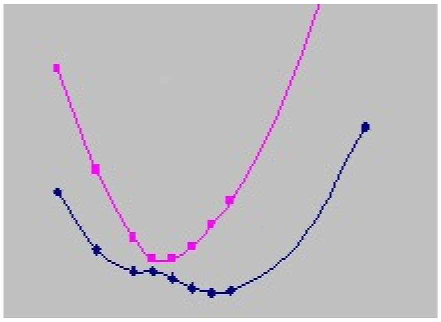
Spin-orbit configuration-interaction calculations are applied to the study of the UO molecule and the UO^+ ion. Relativistic effective core potentials, with the accompanying valence spin-orbit operators, are used along with double-ζ and triple-ζ basis sets. Molecular orbitals are obtained from state-averaged multiconfiguration self-consistent-field calculations and then used in multireference singles-and-doubles configuration-interaction calculations with numbers of millions of terms.

The UO molecule has several U-based non-bonding electrons and many low-lying orbitals so it has a longer bond distance than the most common species with U-O bonds (uranyl ion) and lower excited states. The ground state has $5f^3 7s^1$ open shells, $\Omega=4$, and a spin-orbit induced avoided crossing near the equilibrium internuclear distance. Many excited states are studied with experimental comparisons including rotational constants and intensities.

The ground state of UO^+ has $5f^3$ open shells and Ω=9/2. Many UO^+ excited states are also low-lying and are studied.



UO near-R_e avoided crossing

NUCL 132

Solution and gas phase solvation of f-element ions in binary water/methanol solutions

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Due to their highly ionic character, the trivalent f-element cations impose significant order in polar solvents (e.g. water), and their solvation is an important parameter affecting molecular interactions. This is evident in solution complexation reactions, where entropy gains can often override enthalpic interactions and cation desolvation is a thermodynamic driver. Similarly, solvent interactions can play an important role when the trivalent f-element cations are ionized for gas phase measurements in electrospray ionization mass spectrometry (ESI-MS), where co-solvents such as methanol are often used to improve ionization. In this work, the influence of methanol concentration on ion solvation for Yb^{3+} is investigated by classical molecular dynamics (MD). Force fields have been developed from the quantum mechanically derived two body potential for the dissociation of solvent from the primary solvation shell of the ion, and benchmarked using ab-initio molecular dynamics (AI-MD). Additionally, simulation results will be compared to experimentally observed gas phase ions produced via ESI.

NUCL 133

Computational studies of actinide and metal oxides, fluorides, and chlorides

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Advances in theory, algorithms, software, and computer architectures have made it possible to calculate reliably the properties of a broad range of molecular systems for practical applications. The focus of this talk is on the prediction of such properties, especially thermodynamic properties, for actinide fluorides and oxides. Advanced electronic structure theory approaches mostly at the CCSD(T) level have been used to reliably predict the properties of main group and metal compounds containing fluorine, chlorine, and oxygen. Structures and vibrational frequencies have been calculated and are in good agreement with the available experimental data. Thermodynamic properties including heats of formation, bond dissociation energies, fluoride affinities, ionization potentials and electron affinities have been calculated. Insights into periodic trends (or the lack thereof) will be described. This work is supported by the U.S. DOE Office of Science (BES) under the Heavy Element Program.

NUCL 134

Combining theory with experiment to understand aggregation in solvent extraction systems for heavy element separations

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There is an emerging consensus that aggregation in solvent extraction systems drives properties that underpin the efficacy of metal ion extraction and must be considered as we move toward a predictive understanding of heavy element separations. However, the dynamic self-assembly and supramolecular structure of the solvent is difficult to quantify. Herein we combine molecular dynamic simulations with X-ray scattering and experimental measurements to provide original insights into the aggregated structure and properties of a malonamide-alkane extracting solvent relevant to used nuclear fuel reprocessing. Exploring metal ion extraction from neutral and acidic nitrate aqueous phases reveals the supramolecular impact of acid on the organic phase, suggesting that it facilitates preorganization of reverse micelles that aid in heavy metal ion extraction.

NUCL 135

Role of ionic solute vs. amphiphilic solute on local interfacial properties

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In the PUREX process an organic solution composed of 30% tributyl phosphate (TBP) in a hydrocarbon solvent, is used to extract uranium as $UO_2(NO_3)_2\cdot 2TBP$. Previous works have examined the influence of highly acidic media in ion extraction as well as concentration dependence of the amphiphilic extractants upon the distribution coefficient. On the other hand few studies have examined the affect of $NaNO_3$ solutions and amphiphilic solutes upon the underlying interactions at the aqueous:organic interface. In order to enhance the performance of solvent extraction one must know how

individual solutes effect the local interfacial properties of binary organic:aqueous systems. Toward this end we investigate how amphiphilic solutes with varying solubility in water (solutes tri-butyl phosphate (TBP), hydrogen di-butyl phosphate (HDBP), and di-hydrogen mono-butyl phosphate (H_2MBP)) as well as $NaNO_3$ in 0-10 M solutions impact interfacial properties such as surface tension, water orientation and molecular properties such as microsolvation. Our results have revealed that TBP can change the microsolvation events within 20 Å from the P-atom, while different concentrations of $NaNO_3$ affect the surface tension but they do not impact upon microsolvation events. These studies suggest that amphiphilic TBP not only binds uranium ions but also may alter the permeability of aqueous:organic interfaces.

NUCL 136

Examining covalency in actinide complexes with soft donor ligands and metal-ligand multiple bonding

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The role of f orbitals in the structure, bonding, and reactivity is still a fundamental question yet to be definitively answered in actinide chemistry. To examine this issue, we are exploring the coordination chemistry of ligands with sulfur, selenium, phosphorus, and arsenic atoms. Soft donor ligands have potential applications in the separation of actinides from lanthanides presumably due to enhanced covalent bonding in actinide-ligand bonds. Additionally, actinide-ligand multiple bonding also allows for probing enhanced covalent character and our attempts in actinide-carbene and -phosphinidene complexes will be presented.

NUCL 137

Revealing the hydration of thorium(IV) with combined techniques involving EXAFS, HEXS and molecular dynamics simulations

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The hydration shells of an ion can be probed by various theoretical and experimental techniques, which are complementary in their ability to accurately predict structural details, including coordination numbers and metal-solvent hydration shells. Accurate molecular-dynamics simulations reveal that very subtle changes in the metal-solvent and solvent-solvent interactions have a direct impact on the coordination shell, by displacing the equilibrium between competing isomers. Synchrotron experiments including high-energy x-ray scattering (HEXS) and x-ray absorption fine structure (XAFS) provide metrical information to compare with theory. Combining both new experimental and theoretical information, we will focus on a detailed analysis of Th(IV) hydration from small gas-phase droplets to the bulk, probing as well the influence of bromide counter-ions.

[1] R. E. Wilson, S. Skanthakumar, P. C. Burns and L. Soderholm, *Angew. Chem. Int. Ed.*, 46 (2007) 8043–8045.
[2] F. Réal, M. Trumm, B. Schimmelpfennig, M. Masella, V. Vallet, *J. Comput. Chem.* 34 (2013) 707.

NUCL 138

Effects of strong π-donors on actinides: bent uranyl(VI) and molecular Pu(IV)

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The PUREx process is the nuclear fuel recycling procedure which operates by initiating a change in properties of specific radioactive materials so that they may be efficiently separated and extracted from nuclear waste. One variation of this process is to coordinate 5*f*-elements with chelating agents and remove the complex based on the properties of the ligand or the product as a whole. In the late nineties, formohydroxamate (FHA) was believed to provide novel coordination environments for uranyl(VI) for fuel recycling purposes, though no materials characterization techniques were performed on this complex. In this presentation, the red uranyl(VI)$(FHA)_2$ complex will be discussed thoroughly, providing experimental and computational insight into the unique properties of the structure. Extension of the peculiar nature of the FHA ligand continues with $Pu(FHA)_4$, whose structure can be described as a molecular dimer, and whose charge-transfer band largely encompasses most of the visible spectrum and low-energy ultraviolet. Experimental and computational results will be discussed for $Pu(FHA)_4$. The unique properties of this pair of actinides offers potentially interesting coordination environments for transuranic elements.

NUCL 139

Covalency in f-element materials probed with ligand K-edge X-ray absorption spectroscopy

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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. In this talk, I will discuss a relatively direct probe of f-orbital involvement in bonding, ligand K-edge X-ray absorption spectroscopy. Experimental and theoretical investigations for a number of actinide complexes and solids will be presented and compared with the analogous transition metal complexes. The evidence for f-orbital —

ligand bonding interactions, their origin, and the ramifications for actinide electronic structure will be discussed, and the distinction between overlap driven and energy driven covalency emphasized.

NUCL 140

Solvation thermodynamics of trivalent actinide (An=U, Np and Pu) ions using polarizable force field

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The average structures, hydration free energies and dynamic behavior of aqueous trivalent actinide (An) ions (An=U, Np and Pu) have been examined using polarizable (AMOEBA) and non-polarizable (SPC and TIP3P) force fields in molecular dynamics simulations. Various An-OH_2 interaction potentials are developed using ForceFit program. The potentials have been generated on the basis of fitting to the *ab initio* gradients of the H_2O dissociation potential energy surface (PES) of $[An\text{-}(H_2O)]^{3+}$, $[An\text{-}(H_2O)_8]^{3+}$ and $[An\text{-}(H_2O)_9]^{3+}$ species. Molecular dynamics simulations of An^{3+} solvation in bulk water have been subsequently performed with all the three water models using the best-fitted potentials. While both polarizable and non-polarizable potentials can reproduce average hydration numbers very well compared to experiment, the dynamic features are incredibly dependent upon the specific force field implemented. Further, only the force fields that are fitted within a polarizable framework are able to accurately determine the free energy of solvation of these trivalent ions when using the Bennett acceptance ratio (BAR) method. This work thus highlights that much care needs to be taken when developing force fields for actinides and that average structural parameters are not necessarily good metrics of force field quality.

NUCL 141

Divergence between plutonium and americium in oxoanion materials

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The electronic characteristics of actinide complexes have been a rich research area for many decades because these elements behave unlike any other group on the periodic table. They generally retain the spectroscopic and magnetic properties associated with the number of f-electrons regardless of coordination environment, but can still form partially covalent bonds due to symmetry and energy matching of the 5f and 6d orbitals. This partially covalent interaction can lead to a discontinuity between low valent actinides and their lanthanide congeners either through shorter bond lengths, different structures, or differences in electronic character. This discontinuity is not always observed, and the expression of covalent effects depends greatly on the nature of the ligand. The more ionic ligands such as the aquo triflates, phosphonates, and phosphites

generate very similar 4f and 5f compounds. Conversely, softer, more polarizable ligands such as borate, imidodiphosphinochalcogenides, and cyclic π-donors show differences between the lanthanides and actinides.
We have recently explored the reactions of oxyanions with high hyperpolarizabilities and the actinides to probe this discontinuity as we believe that there is a direct relationship between the hyperpolarizability of a single M – O bond and the polarizability of the entire oxyanion. These oxyanions include molybdate and tungstate which have significantly high hyperpolarizabilities. This combination of a d^0 metal with an actinide should result in interesting bonding as seen with other polarizable ligands.

NUCL 142

Combined theoretical and experimental study of the binding features of the super uranyl-binding protein

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The capture of uranyl, UO_2^{2+}, by a recently engineered protein with high selectivity and femtomolar sensitivity has been examined by a combination of density functional theory, molecular dynamics and free-energy simulations. We found that UO_2^{2+} is coordinated to five carboxylate oxygen atoms from four amino acid residues of the super uranyl binding protein, (SUP). A network of hydrogen bonds between the amino acid residues coordinated to UO_2^{2+} and residues in its second coordination sphere also affects the protein's uranyl binding affinity. Free-energy simulations show how UO_2^{2+} capture is governed by the nature of the amino acid residues in the binding site, the integrity and strength of the second-sphere hydrogen bond network and the number of water molecules in the first coordination sphere. Alteration of any of these three factors through mutations generally results in a reduction of the binding free-energy of UO_2^{2+} to the aqueous protein as well as of the difference between the binding free-energies of UO_2^{2+} and other ions (Ca^{2+}, Cu^{2+}, Mg^{2+}, and Zn^{2+}), a proxy for the protein's selectivity over these ions.