NUCL 1

Influence of environmental effects on post-detonation debris chemistry

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The high temperature chemistry of rapidly condensing matter is under investigation using a plasma flow reactor to understand the influence of environmental effects on post-detonation debris chemistry. The goal is to evaluate how uncertainty in the condensation behavior of debris affects the interpretation of radiochemical data. The reactor has a nested set of gas flow rings that provide flexibility in the control of hydrodynamic conditions and mixing of chemical components. Tests were run using aqueous solutions of metal nitrates (cerium, iron, etc.). Chemical reactants passing through an inductively coupled plasma torch undergo non-linear cooling in a flow reactor from ~5,000K to 1,000K on time scales of tens of milliseconds depending on flow conditions. Changes in the particle sizes were seen depending on the cooling rates along the reactor tube. We also varied the oxygen concentration during our tests and studied its effects on chemical speciation and particle size. Our results enable us to gain insights into the competition between kinetically driven processes of gas phase speciation, nucleation of particles from vapor phase, and condensation in rapidly cooled systems.

NUCL 2

Innovative sample preparation methods for post detonation debris analysis of lanthanides and actinides

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The concentration of lanthanides and actinides in post-detonation debris samples is important as the ratio of these trace elements can be used to determine the type of nuclear device used. Various geological reference materials were dissolved with a rapid, high temperature ammonium bifluoride (ABF) fusion. The reference material and ABF were heated at 540 °C, followed by a reflux of the residue with 8M HNO_3. The total dissolution time using this method is approximately 30 minutes. Uranium and plutonium were separated using TEVA and UTEVA chromatographic resins, and close to 100% recovery was obtained for both elements. High performance ion chromatography (HPIC) was subsequently used to separate lanthanides from the dissolved geologic matrix, as well as from polyatomic and isobaric interferences using a mixed-bed cation and anion

exchange column, with oxalic acid and diglycolic acid as the mobile phase. After the separation, the REEs were analyzed using an “offline” method, where fractions were collected and measured through inductively coupled plasma mass spectrometry (ICP-MS). A rapid “online” analysis in which the HPIC was connected directly to an ICP-MS and the analytes were measured immediately as they came off the column was also evaluated. After verification of the sample preparation methods using reference material, NIST surrogate post-detonation urban debris (SPUD) will be analyzed.

NUCL 3

Effects of process history on the surface morphology of uranium ore concentrates extracted from ore

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The effects of process history on uranium ore concentrate (UOC) surface morphology may carry significant implications for the source attribution of unknown nuclear materials. Whereas previous UOC morphology studies have worked with high-purity materials, this work compares UOCs extracted from ores and purified by two different solvent extraction and back extraction (SX/BX) methods used commercially by the uranium mining and milling industry. Each route began by leaching uranium from the ores with sulfuric acid. The clarified post-leach solutions were then purified by either the Amex process using Alamine® 336 or the Dapex process using di-(2-ethylhexyl) phosphoric acid (DEHPA) and tributyl phosphate (TBP). UOCs from either SX route were precipitated from their respective strip solutions as ammonium diuranate (ADU) by the addition of ammonium hydroxide and subsequently calcined to UO_3. Impurity concentrations were correlated to process history by powder X-ray diffraction (P-XRD) and inductively coupled plasma mass spectrometry (ICP-MS). Particle morphology was quantified from scanning electron microscopy (SEM) images using the *MAMA* segmentation software, and the unique morphology signatures were compared. Additionally, a deep neural network was trained on the SEM micrographs to distinguish between process histories. This work provides a real-world representation of how particle morphology will likely change based on processing at commercial facilities.

NUCL 4

Nuclear forensics research at Texas A&M University

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This talk will give an overview of nuclear forensics research at Texas A&M University, including major research goals, facilities, and future plans. The original goals of the program were to develop techniques for determining the history of chemically purified high-grade Pu produced by reactor irradiation of UO_2 in a variety of different reactors. MCNP6 simulations of each reactor type were conducted to develop a library of datasets with varying burnups which could then be decay-corrected. A maximum likelihood method was developed that used experimentally measured isotope ratios to estimate the reactor type, burnup, and time since irradiation. This technique was successfully applied to two separate samples of UO_2 irradiated in pseudo-fast and thermal neutron environments, and an additional future irradiation is also planned. Future work will examine forensic information contained in molecular contaminants and will develop techniques to identify spoofed materials.

NUCL 5

Measurement of short-lived Fission products of Pu-239

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The energy dependence of fission product yields in a weapons post-detonation scenario provides crucial information on both the energetics and fuel type of the weapon. The yield of a fission product produced directly from fission, or the independent yield, is required for accurate analysis of an unknown sample. The scarcity of independent yields in the nuclear database restricts current analysis to using cumulative fission product yields, which reduces accuracy. Additional measurements are therefore required to expand the independent yield measurements in the database. Obtaining independent yields can be difficult, as the measurement of short-lived fission products places a time constraint on detection methods available. The use of a monoenergetic neutron beam and a cyclic activation method works to quantify these short-lived fission products and extract independent yields within the timeframe of short-lived nuclides. In a joint-collaboration between LANL, LLNL and TUNL, quasi-monoenergetic neutrons were used to irradiate a Pu-239 sample foil at 4.6 MeV. A rabbit system then transferred the sample between the irradiation site and two shielded HPGe detectors during cyclic activation, with different irradiation/counting cycles used. This presentation will highlight the identified short-lived fission products from the Pu-239 sample irradiated at 4.6 MeV and different irradiation/counting cycles.

NUCL 6

Uranium concentration using reactive polymer thin films and thin-film composite membranes for spectroscopic analysis

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This contribution describes the development of reactive polymer films for the concentration of uranium from circumneutral pH solutions for spectroscopic analyses. These films were prepared by grafting uranium-selective polymers from polyethersulfone (PES) films via UV-initiated polymerization, and by introducing uranium-selective functional groups to polyacrylonitrile (PAN) films by chemical reaction. Ellipsometry was used to study poly(phosphoric acid 2-hydroxyethyl methacrylate ester) film growth kinetics on PES films. X-ray photoelectron spectroscopy of modified PAN films revealed conversion of nitrile groups to amidoxime groups to be as high as 40% and showed that the extent and depth of reaction could be varied precisely. Static uptake experiments with solutions of depleted uranium spiked with ^{233}U were conducted to determine uranium binding capacities and kinetics of the modified polymer films at different pH values from 4 to 8. Sorption isotherm data were fitted to the Langmuir model, and the highest sorption capacities of $1.09\times10^{-2} \pm 1.03\times10^{-3}$ mmol m^{-2} and $1.02\times10^{-2} \pm 3.00\times10^{-3}$ mmol m^{-2} were obtained at pH 6 for modified PAN (M-PAN) and PES (M-PES) films. Capacities at pH 4 and 8 were lower and could be explained by differences in sorption mechanisms. Uranium batch uptake kinetics followed a pseudo-second order rate model. Alpha spectroscopy pulse height spectra were analyzed to study the role of selective layer film thickness on peak energy resolution. Full width at half maximum values from 29 to 41 keV were recorded for M-PAN film and from 26 to 45 keV for M-PES film. Whereas uranium uptake increased with selective layer film thickness and varied with polymer chemistry/extent of modification, the peak energy resolution was independent of layer thickness and polymer chemistry within the experimental measurement uncertainties. Results from this work were used to modify PES and PAN ultrafiltration membranes with the same experimental conditions to develop uranium selective membranes. Flow through uptake experiments were performed to study the effect of residence time on detection efficiency. This membrane-based detection method can enable the rapid, fieldable analysis of radionuclides in water for nuclear forensics investigations and environmental studies.

NUCL 7

3D printed microfluidic supported liquid membrane modules for actinide separations

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Supported liquid membrane (SLM) separations use the high selectivity of an organic phase extractant immobilized in a hydrophobic porous polymer membrane to combine liquid-liquid extraction and stripping in a single unit operation. Since the concept was first proposed over fifty years ago, fundamental and applied studies of SLMs for industrial-scale applications, including nuclear fuel cycle separations, have been extensively reported in the literature. However, the application of SLMs to analytical scale actinide separations has not been explored. In this work, we report the design, fabrication, testing, and mass transport modeling of 3D printed microfluidic SLM modules. Experimental tributyl phosphate (TBP) SLM uranium extraction trends are consistent with a mass transport mechanism combining advection and diffusion, with no mass transport resistance at the liquid-liquid interfaces. The modules are demonstrated to be effective for the purification of uranium, with preliminary separations following the well-known trends in TBP selectivity.

NUCL 8

Measuring forensic signatures in legacy super-grade Pu at Los Alamos National Laboratory

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Four samples of legacy super-grade Pu have been identified at Los Alamos National Laboratory in a steel canister labeled “Clinton Pu.” The four samples total 85 mg of Pu assayed at (99.946 ± 0.001)% ^{239}Pu. Each sample of Pu was individually dissolved and separated using a series of ion-exchange and solvent-extraction chromatography columns to isolate trace U, Am, and some fission product (FP) elements. Chronometry was performed on each of the four samples to determine the period of last separation; chronometry proved difficult due to the advanced age and small masses of ^{240}Pu, ^{238}Pu, ^{241}Pu, and ^{242}Pu. To compensate, the ^{239}Pu – ^{235}U and ^{240}Pu – ^{236}U chronometers were measured multiple ways and checked against the measurable masses of ^{241}Am and ^{234}U for consistency.

No historical records were found of the material’s receipt, transfer, or use within the laboratory. Pu isotope ratios are compared against reactor model simulations to confirm the stated reactor origin of the material. Trace metals in each of the four samples were

identified using ICP-MS and compared to known trace metal contaminates in US Pu processing. Final conclusions, proposed reactor origin, and reported ages of the four samples are to be presented along with a comparison to the information printed on the original steel canister.

NUCL 10

To β or not to β: A first look at the Raman spectrum of pure β-UO_3

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After a reexamination of known synthetic routes, β-UO_3 has been synthesized via rapid calcination of $UO_2(NO_3)$●$6H_2O$ in air. Powder X-ray diffraction and elemental analysis using energy dispersive X-ray spectroscopy indicate a pure product. For the first time, Raman spectra are presented for pure β-UO_3 including the low energy (35–100 cm^{-1}) region. Infrared spectra collected for β-UO_3 agree well with previously reported results. Phonon modes, derived using density functional perturbation theory, are reported for density functional theory–optimized β-UO_3 and guided vibrational mode assignments.

NUCL 11

^{226}Ra uptake by the $(Sr,Ba)SO_4$ solid solution

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The migration of radionuclides in the geosphere is to a large extend controlled by sorption processes onto minerals and colloids. On a molecular level, sorption phenomena involve surface complexation, ion exchange as well as co-precipitation reactions. Co-precipitation leads to the formation of structurally incorporated radionuclides in a host structure. Such solid solutions are ubiquitous in natural systems – most minerals in nature are atomistic mixtures of elements rather than pure compounds. Recent studies have shown that the formation of a $(Ba,Ra)SO_4$ solid solution significantly reduces the solubility of ^{226}Ra in aqueous systems. This result is very relevant for the direct disposal of spent nuclear fuel in a deep geological formation, where ^{226}Ra would dominate the dose after 100,000 years. However, in natural systems sulfates often occur as $(Ba,Sr)SO_4$ rather than pure barite. Therefore we have extended the binary $(Ba,Ra)SO_4$ solid-solution and assessed the Ra-uptake and Ra-solubility in aqueous solution within the system of $(Sr,Ba,Ra)SO_4 + H_2O$.
Our recent atomistic and thermodynamic modelling study predicts a significant uptake of Ra into the ternary $(Sr,Ba,Ra)SO_4$ solid-solution. Here we present experimental results

from long-term batch-recrystallisation experiments on Ra-uptake into well characterized (Ba,Sr)SO_4 solid-solutions, starting from compositions on the Ba-rich as well as in the Sr-rich region. Complementary electron microscopy (SEM,TEM) was used to assess the homogeneity of Ra-uptake and the intermediate stages of recrystallization. Our results show final Ra-concentrations in solution similar or close to predicted levels in most experiments. However, a more complex recrystallization process than in the binary (Ba,Ra)SO4 solid solution takes place, involving the formation of Ra-rich intermediate phases. The formation of the intermediate phase is interpreted based on structural and kinetic considerations.

NUCL 12

Fabrication and structure of plutonium pyrochlore nuclear waste forms: A combined experimental and computational study

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Rare earth zirconates ($A_2B_2O_7$) with the pyrochlore crystal structure have been suggested as potential nuclear waste forms for actinide immobilization, e.g. separated plutonium from nuclear weapon dismantling. This study presents a wet-chemical co-precipitation route to fabricate $Nd_2Zr_2O_7$ pyrochlores with 5 and 10 mol% Pu. All work was performed in a glovebox-line dedicated to actinides. The co-precipitated metal hydroxides were dried, calcined and the pressed pellets sintered at 1450 C under reducing atmosphere (Ar-5%H_2). SEM analysis indicated homogeneous Pu uptake within the pellets and XRD measurements confirmed crystallization in the pyrochlore crystal structure. X-ray absorption spectroscopy revealed the majority of Pu to be in the tetravalent oxidation state. Pu L_{III}-edge EXAFS measurements showed Pu to occupy the A-site within the pyrochlore structure. The A-site is characterized by eight nearest neighbors with six longer A-O_{48f} and two shorter A-O_{8b} bonds. In order to obtain a reasonable fit of the EXAFS data the degeneracies of the two Pu-O1 paths were inverted to give six short Pu-O and two long Pu-O paths, indicating significant distortion of the A-site environment in a pyrochlore. On average the nearest neighbor Pu-O bond lengths were determined to be 2.35 Å ± 0.03 for $Nd_{1.9}Pu_{0.1}Zr_2O_7$ and 2.33 Å ± 0.03 for $Nd_{1.8}Pu_{0.2}Zr_2O_7$. These findings were supported by the bond valence sum approach. DFT *ab initio* calculated bond distances for Pu-O, with Pu being immobilized on the pyrochlore's A site are in good agreement with these experiementally derived values. Charge compensation for Pu(IV) on the usually trivalent a site via oxygen atoms at former vacant sites resulted in the lowest solution energies of Pu in pyrochlore. Eventhough the incorporation of Pu(IV) at the A-site results in significant distortion of the A-site local geometry, XRD confirmed the long range pyrochlore structure and the structural uptake of Pu(IV) into the pyrochlore structure.

NUCL 13

Oxygen K-edge spectromicroscopy of uranium oxides in spent nuclear fuel

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The exact nature of uranium oxides in spent nuclear fuel is a primary concern in the storage of nuclear fuels resulting from both the volumetric expansion of uranium oxides and change in solubility with an increase in oxygen content. In particular, the growth of hyper–stoichiometric uranium dioxide has been linked to fracturing of spent fuel, resulting in further oxidation and the release of short-lived radionuclides trapped within the UO_2 matrix. Oxygen K-edge x-ray absorption spectroscopy (XAS), utilizing a scanning transmission x-ray microscope (STXM) at the Advanced Light Source, is an excellent method to distinguish between different uranium oxide stoichiometries, but specimens must be extremely thin as a result of the short penetration length of soft x-rays. Low burnup pressurized water reactor spent nuclear fuel pins were processed at Idaho National Laboratory utilizing focused ion beam (FIB) sectioning, resulting in specimens ideal for soft x-ray spectroscopy. Measurements of oxygen K-edge near-edge XAS, using the Beamline 11.0.2 STXM have been conducted on several FIB sections of spent nuclear fuel. The FIB sections present challenges in normalization and data analysis. The sensitivity of the oxygen K-edge XAS spectrum between the different uranium oxides has allowed for species-specific mapping of the spent nuclear fuel at the sub-micron scale, showing UO_2 as the bulk of the fuel, with U_3O_7 localized near defects. Additionally, spectral results at the uranium $N_{4,5}$ edges and the cerium $M_{4,5}$ edges are analyzed and will be discussed.

NUCL 14

Use of microfluidics and carbothermic reduction to synthesize ZrC_xN_{1-x} microspheres

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The generation of ceramic microspheres of controlled sizes has been of interest for decades. Typical microsphere synthesis utilizes internal gelation of droplets formed with a fine-gauge needle. The droplets are passed through a veil of hot silicone oil to commence the gelation reaction. However, producing sintered microspheres of uniform size below 100µm becomes challenging due to difficulty of controlling droplets of those

size. Microfluidics offer a viable route for generating uniform spheres on the order of 25µm when sintered. Additionally, the material feedstock and post-fabrication treatments are of the utmost importance at controlling the composition and morphology of the resulting material. Controlled particle additions generate microspheres impregnated with C necessary for carbothermic reduction. The resulting material underwent nitridation to produce ZrC_xN_{1-x} microspheres. Adjusting the amount of C added to the feedstock and the composition of the exposure gases changes the final composition of the material.

NUCL 15

Investigation of Nd- and Ce-doped ammonium diuranate microspheres during the conversion to $U_{1-y}Ln_yO_{2\pm x}$

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Partitioning and transmutation (P&T) is a key strategy to reduce spent nuclear fuel's radiotoxicity and heat generation. Long-lived minor actinides (MA) are partitioned from spent nuclear fuel and subsequently converted to fuel precursors for fast reactor systems, where the actinides are fissioned to short-lived radionuclides. The sol-gel route via internal gelation is a process currently explored for the production of such MA containing transmutation fuel. A solution containing mixtures of actinides is converted into a homogeneous precipitate with a spherical geometry. The resulting particles are thermally treated and can be used as particle fuel or compressed into fuel pellets. The advantages of the process are to avoid handling of fine powder and to facilitate automation for the production of nuclear fuel precursors.

The structural changes in ammonium diuranate (ADU) gels doped with Nd or Ce, prepared by internal gelation, were investigated during the conversion to $U_{1-y}Ln_yO_{2\pm x}$. Nd and Ce molar metal fractions up to 30 mol% were introduced, acting as surrogates for the actinides Am and Pu. The conversion consists of a two-step thermal treatment of the dried *Ln*-doped ADU gels. A calcination under oxidising conditions at 900 °C, followed by a sintering in a reducing atmosphere at 1600 °C (10 h). The behaviour of the dried gels during both thermal treatment steps was studied by high temperature scanning electron microscopy and thermogravimetric analysis coupled with differential scanning calorimetry. The combined application of these *in-situ* methods provides novel insights on the thermal treatment of microspheres and reveals the impact of dopants and the oxidation state of their precursor on this process, which is also relevant for the production of Pu and/or minor actinide containing UO_2 transmutation fuel.

NUCL 16

Evaluating uranium chemical states via X-ray absorption spectroscopy

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Actinide elements often display a complex redox chemistry. Their speciation depends mainly on the behavior of electrons in the 5f orbitals, which can be quite diverse. In uranium, electronic states associated with $5f^2$, $5f^1$, and $5f^0$ are available, resulting in respectively U(IV), U(V), and U(VI) environments. The tetravalent oxide of uranium, UO_2, has a principal use as nuclear fuel in fission reactors. Its fluorite-type crystal structure provides a stable matrix to cope with the extreme conditions imposed by nuclear fission. However, owing to the electronic configuration of uranium, UO_2 is quite susceptible towards oxidation. The binary uranium-oxygen system is remarkably complicated and contains phases having mixed tetra-, penta- or hexavalent characters. To ensure the safe storage of nuclear fuel, it is important to understand the speciation of such phases.

In order to evaluate the valence state distribution in uranium compounds, X-ray absorption near- edge spectroscopy (XANES) at the U L3-edge is commonly applied. It requires a relatively simple experimental setup, and the spectral resolution can be increased by utilizing high-energy resolution fluorescence detection (HERFD-XANES). Recent work, however, highlighted several pitfalls at this absorption edge, and demonstrated that a quantification cannot be confidently performed. This has important implications towards the application of XANES on nuclear materials. In the present contribution, we will compare and discuss XANES results at different U absorption edges, which allow either a qualitative or quantitative assessment of the valence state distribution in mixed-valence uranium compounds.

NUCL 17

Aluminum-doped U_3Si_2 composite fuels with enhanced oxidation resistance

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Al-doped U_3Si_2 composite fuels with controlled microstructure were fabricated by spark plasma sintering (SPS) that display greatly-improved oxidation resistance as compared with monolithic and Al-doped silicides prepared through standard powder metallurgy or arc melting. The effects of Al additives and microstructure control from both micron and nano-sized grain structures of U_3Si_2 on their thermal-mechanical properties and oxidation resistance under air atmosphere were investigated. A minimal addition of 1.8 at% Al is effective to increase the onset oxidation temperature of as-fabricated U_3Si_2 pellets to 550 ^oC, which can be further improved to 575-580 ^oC at greater Al addition

(7.2 at%). Post-sintering thermal annealing was also applied to form passive alumina oxide and further increase the onset temperature of the 1.8 at% Al doped nano-sized U_3Si_2 pellet to 610 ^oC. The Al-doped U_3Si_2composite fuels also display simultaneously higher hardness and fracture toughness than un-doped U_3Si_2. These results highlight an effective strategy by integrating minimal Al additives, microstructure control and post-thermal annealing to design advanced silicide fuels with excellent oxidation resistance, desired thermal-mechanical properties and maintained high fissile element density. The discovery of the doped U_3Si_2 fuel pellet with minimal additive of Al is of significance for further exploring the potential of high density U_3Si_2 as the leading candidate of accident tolerant fuels.

NUCL 18

Investigating the grain growth and grain subdivision in U_3Si_2 using modeling and simulation and experiments

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Uranium silicide is being considered as a possible accident tolerant fuel, with particular focus on the U_3Si_2 phase. However, a better understanding of its material behavior is needed to more accurately predict its fuel performance. In this work, we use a combination of multiscale modeling and simulation and ion irradiation experiments to investigate the grain growth and grain subdivision behavior of U_3Si_2. We first demonstrate how we have used atomistic and mesoscale modeling, along with in-situ annealing experiments, to develop a model for the normal grain growth of the material. We then couple a phase field model of irradiation damage and fission gas bubble evolution with a ballistic Monte Carlo simulation to investigate the driving force for grain subdivision in U_3Si_2. We compare the simulation results with in situ ion irradiation experiments that induce grain subdivision.

NUCL 19

Covalent bonding in actinide compounds

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The covalent mixing of metal and ligand orbitals makes an important contribution to the properties of actinide compounds, yet there is a dearth of estimates that quantify the extent and the energetic importance of the covalent character of these compounds. Novel theoretical methods have been developed to provide reliable information about

the covalent bonding and their application to selected actinide compounds is presented. Compelling evidence is presented for important aspects of the covalent mixing: (1) The contributions of the actinide 6d orbitals and the actinide 5f orbitals to form covalent bonds with the ligand frontier orbitals are both important and the 6d covalency should not be neglected. (2) The covalent mixing depends on the nominal oxidation state of the actinide cation. It is larger for higher oxidation states. (3) The relative importance of the 6d covalency increases as the 5f occupation increases. And, (4) the extent of the covalent mixing depends strongly on the separation of the actinide cation and the ligand. While this distance dependence is not surprising, the extent of the changes in the covalency with bond distance and the consequences for an observable are discussed. The focus will be for differences between oxides of U and Pu. The theoretical analysis of the covalency is based on the use of wavefunctions for cluster models of the compounds and of the fragments. The extent of the covalency is estimated from projections of fragment orbitals on the orbitals of the compound. The energetic importance is estimated by constraining the variation of the orbitals of the compound where the covalent mixing is allowed or forbidden.

NUCL 20

Heavy-element chemistry from the perspective of relativistic multi-reference configuration interaction

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The accurate description of electronic properties of heavy-elements and their molecular complexes requires an electronic structure method be able to treat both relativistic and electron correlation effects. On the one hand, relativistic effects, including both scalar relativities and spin-couplings, give rise to unique chemical reactivities, magnetic properties, and optical responses of heavy-element compounds. On the other, highly degenerate outer-shells of late-row elements require a multi-configurational method that incorporates important electron correlations in the underlying electronic structure theory. In this talk, electronic structure properties of heavy element complexes are discussed in the context of a variational multi-reference electronic structure approach recently developed in our group. Particularly, emphases will be placed on how different orbital shells are involved in different types of electron correlation and how they affect the ground state energy and fine structure splittings.

NUCL 21

Developing a computational protocol for understanding binding selectivity in lanthanide and actinide systems

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Simulating lanthanide and actinide chemistry through accurate computational methodologies is important to better understand binding selectivity of lanthanides and actinides in nuclear and radiochemical applications. This is crucial for nuclear forensics, designing separation agents, and understanding spectra. Theoretical predictions determined with accurate methods including effects from relativity, spin-orbit coupling, and core correlation are discussed. Various computational methodologies ranging from ab initio and DFT including single- and multi-reference and relativistic effects in lanthanide- and actinide-containing compounds will be presented with focus on level of theory dependence and computational cost, and the dependence of predicted results on basis sets of choice.

NUCL 22

Dependence on orbital occupations for density-functional theory (DFT) calculations of uranium compounds

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Density-functional theory (DFT) is the workhorse method to model nuclear material properties. The results of these calculations can be used as inputs for multi-scale, multi-physics codes, such as BISON, to model fuel performance in nuclear reactors. It is therefore imperative that calculated results are at least qualitatively correct. However, it has been shown that the ground state energy of uranium compounds greatly depends on the f-orbital occupations. The semi-local nature of DFT functionals does not necessarily place electrons in the lowest energy orbital configuration. Non-physical fractional occupations can also occur. It is possible that orbital occupations could affect the calculation of physical properties, such as lattice constant and bond lengths. This talk presents a systematic study of how orbital configurations affect calculated physical and energetic properties for UC, UCl3, UN and UO2. The effect of how Hubbard U and dispersion corrections affect orbital occupancy is also discussed.

NUCL 23

Selective binding across the lanthanide and actinide series

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Selective binding to lanthanides and actinides is critical in separations needed for nuclear- and radiochemistry for applications in critical materials, nuclear waste, and radioisotope production. Separating contiguous elements in the f-block can be particularly challenging due to the similar behavior these elements present. Evaluations of computational methods across the lanthanide and actinide series with focus on selective binding will be presented. Performance and efficiency of computational methods applied to selective binding of lanthanides and actinides will be discussed including multi- and single-references characteristics, and relativistic effects.

NUCL 24

Towards robust image texture features of uranium ore concentrate morphology for source attribution tasks

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In recent years, the morphology characteristics of nuclear materials has been studied as a means to identify the chemical process history of unknown samples. Previous characterizations of uranium ore concentrate (UOC) surface morphology have focused on qualitative descriptions, quantitative measurements of particle size and shape distributions by segmentation, and direct image classification by convolutional neural networks (CNN). With the exception of angle measurement technique (AMT), image texture analysis methods have been mostly ignored. This work compares AMT, gray level co-occurrence matrices (GLCM), and feature extraction by pre-trained CNN for scanning electron microscopy (SEM) images in the University of Utah's UOC Morphology Database. This database primarily consists of UO_3, U_3O_8, and UO_2 materials synthesized from the following starting materials: ammonium diuranate, ammonium uranyl carbonate, magnesium diuranate, sodium diuranate, and uranyl peroxide. The extracted texture features are used to train and evaluate several classifiers. Test set images that are dissimilar to the training set images will be used to evaluate the extent to which each texture feature/ classifier combination generalizes to more realistic image data and UOC compositions.

NUCL 25

Quantifying actinide sorption to hematite at elevated temperatures: Variable temperature batch sorption and calorimetry studies

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This work seeks to characterize actinide sorption to mineral surfaces under the elevated temperature and ionic strength conditions to allow for more accurate prediction of actinide behavior in geologic waste repositories where such conditions may persist. Batch sorption of Eu, U, Np, and Pu to hematite and rutile was examined at variable temperatures and ionic strengths using variable temperature batch sorption and isothermal titration calorimetry. The primary focus was the 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. When possible, surface complexation models were constrained using speciation at solid:water interfaces determined using x-ray absorption spectroscopy and quantum mechanical modeling. A more detailed level of characterization of the surface speciation is required given variability in observed surface reactions of actinides including formation of monomeric surface complexes, surface mediated redox reactions, aging or hysteretic sorption, or surface induced precipitation. Differentiation of enthalpy and entropy contributions can help to evaluate the dominant interfacial reactions as well as provide a more rigorous and technically defendable model of actinide sorption. All systems exhibit positive sorption entropies which are hypothesized to be mechanistically driven by displacement of solvating water molecules from the actinide ion and the mineral surface during sorption.

NUCL 26

Effect of microstructural features on dissolution of NpO_2(s)

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Actinide oxides (AnO_2(s)) are common materials throughout the nuclear fuel cycle, yet published thermodynamic data for the oxides has noticeable discrepancies, creating uncertainty in management of legacy nuclear waste. The variability in existing solubility data is often attributed to differences in particle and grain size, morphology, and crystallinity, which can affect not only solubility, but dissolution rate as well. Advances in high resolution electron microscopy techniques can be useful to visualize microstructural features, such as grain size and morphology, of actinide oxides. Transuranic (Np, Pu) oxides have not been thoroughly investigated with such techniques, which may be key to elucidate why differences in solubility measurements persist. A nanocrystalline NpO_2(s) produced on the HB-line at Savannah River Site was dissolved under oxidizing conditions in the laboratory over a 10-month period, with emphasis on characterization of the solid phase throughout the experiment using scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS). Dissolution of the nanocrystalline solid occurred preferentially at the grain boundaries, producing both aqueous and colloidal neptunium in solution.

$NpO_2(s)$ was also synthesized in the laboratory to induce different particle sizes in the nanocrystalline matrix by varying calcination temperature of the material. Batch solubility studies of the varied particle size materials demonstrated a sizable difference in dissolution of $NpO_2(s)$ based on calcination temperature and resultant particle size, which we hypothesize is the result of free energy differences of the materials, stemming from the variant particle sizes. Overall, these studies suggest the need for consistent and thorough evaluation of microstructural features of actinide solids used to generate thermodynamic data.

NUCL 27

Chemical behavior of the $Np(V)O_2Cl_4$ complex: Characterization by structural, spectroscopic, electrochemical and theoretical approaches

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Synthesizing and characterizing simple molecular compounds containing the $Np(V)O_2^+$ or $Np(VI)O_2^{2+}$ cation is vital for understanding speciation and chemical behavior of high valent actinide elements in solution. We are particularly interested in how intermolecular interactions, like hydrogen bonding, influences the spectroscopic signals and chemical properties of the neptunyl cation under aqueous conditions. In this study, we focused on the neptunyl tetrachloride species, $[NpO_2Cl_4]^{2-/3-}$, which offers a simple molecular complex to explore with cations that engage in charge-assisted hydrogen bonding (piperazinium, pyridinium, morpholinium). Room-temperature evaporation experiments resulted in the crystallization of the $[Np(V)O_2Cl_4]^{3-}$ unit with piperazinium and morphonlinium counter ions that exhibited hydrogen bonding interactions with the neptunyl oxo group. These crystalline materials were characterized by single crystal X-ray Diffraction and Raman spectroscopy. Solid-state Raman spectroscopy showed an unusually high number of vibrations bands in the spectral window of interest (650-900 cm^{-1}) and atypical positions for the neptunyl v_1 band, which we relate to the second sphere coordination (H-bonding). Computational studies highlight the appearance of combination modes and aid in the assignment of a strongly red-shifted neptunyl stretch. Influence of the counter cations on the neptunyl unit in solution was further evaluated with Raman titration studies and electrochemical analysis. Spectroscopic results confirm the oxidation state of neptunium in the solution to be stabilized in the pentavalent state, but indicate a shift in redox potentials for Np(V)/Np(VI) in solutions containing either morpholine, piperazine, or pyridine.

NUCL 28

Flux crystal growth and structure determination of the new quaternary plutonium silicate $Cs_2PuSi_6O_{15}$

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The novel Pu(IV) silicate, $Cs_2PuSi_6O_{15}$, was synthesized using a flux crystal growth method and its stability was predicted and confirmed from a combination of crystal chemical reasoning and DFT calculations. While new phases are often obtained serendipitously from traditional exploratory crystal growth methods, this work demonstrates the feasibility of targeting analogous compositions of a given structure type based on their relative stabilities, an approach which may be valuable for the study of novel compounds containing transuranium elements. Formation enthalpies of the $A_2MSi_6O_{15}$ (A= Na-Cs; M = Ce, Th, U-Pu) compositional family were calculated and indicated the Cs analogs should preferentially form in the $Cmc2_1$ structure type, consistent with experimental findings. The formation enthalpies of a second set of compositions, $A_2MSi_3O_9$, were also calculated and a comparison between the two compositional families correctly predicted $A_2MSi_6O_{15}$ to be on average more stable than $A_2MSi_3O_9$.

NUCL 29

New quaternary uranium and plutonium fluorides crystallized via mild hydrothermal methods

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Low temperature syntheses can be used to obtain complex U(IV) containing fluorides; however, these reactions are very sensitive to the choice of starting reagents. Using different precursors and reaction conditions that stabilize the reduced U(IV) state, we have prepared numerous simple fluorides, such as $U_3F_{12}\bullet H_2O$, and complex fluorides, such as $RbU_3F_{13},$ $Na_4MU_6F_{30}$ and $Na_4M^{+2}U_6F_{30}$, as well as recently a new fluoride family $Cs_2MU_3F_{16}$, exhibiting long range magnetic order. To extend this series, we successfully prepared $Na_3MCe_6F_{30}$ (M = Al^{3+}, Ga^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}). Given the similar ionic radii of Ce^{4+} and Pu^{4+}, we used the cerium fluoride phases as a guide to predict which of the plutonium fluorides could be formed, and our initial work on this system has successfully resulted in the novel composition $Na_3FePu_6F_{30}$ which was obtained from mild hydrothermal synthesis methods. In addition $Na_3GaPu_6F_{30}$ and $Na_3AlPu_6F_{30}$ were successfully prepared. Attempts to incorporate larger divalent ions into the structure such as Mn^{2+} have resulted in the nominal disordered composition $Na_{2.4}Mn_{1.6}Pu_6F_{30}$; an unanticipated result considering that electroneutrality necessitates disordered Mn^{2+}/Mn^{3+} in the structure. This presentation will focus on the crystal growth approach, structures and magnetic properties of the obtained phases.

NUCL 30

Computational database approach to discovering hierarchical nuclear waste forms

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While high level nuclear waste is currently being effectively converted to glass for disposal, issues remain such as improving the loading of waste forms or handling the particularly difficult elements to sequester. Computational methods, such as density-functional theory (DFT), can be used to increase efficiency in discovery of novel waste forms that can help develop improve those systems. Database approaches to materials science, such as the *Materials Project* and the *Open Quantum Materials Database*, have aided in the discovery of new materials with targeted properties. This presentation discusses a new database approach to hierarchal waste form discovery. Relative stabilities of over 500 structures containing trans-uranic elements were calculated and ranked. Trends regarding composition and structure are discussed.

NUCL 31

Topological complexity of uranium thiophosphates

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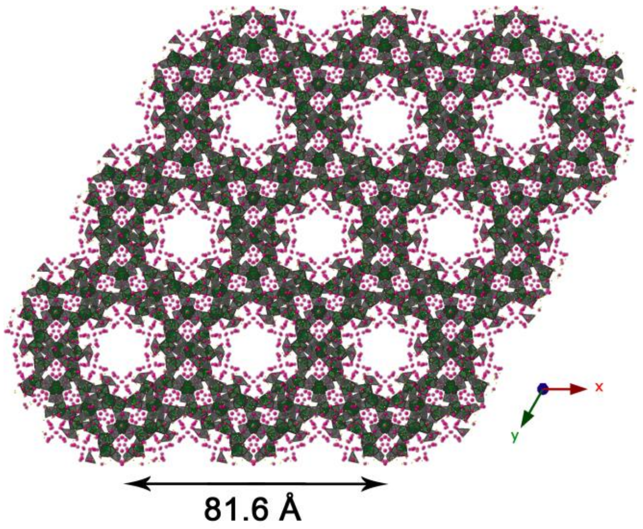
One commonly observed trend in chemistry and crystallography is that simple building units of ionic nature, e.g. Na^+ and $Cl^–$, usually give rather simple structures with a small unit cell (e.g. NaCl with a = 5.64 Å), whereas a more complex moiety, such as an organic molecule, a polyoxomolybdate wheel, or even a protein, will always give a large unit cell (a, b, and c are more than 20 Å) with a significant information content (atomic coordinates and thermal ellipsoids) in it. Furthermore, creating either a simple structure from a complex molecule or vice versa is an unlikely, although not a completely impossible, event. In this presentation we will discuss how comparatively simple groups, specifically U^{4+}, $PS_4^{3–}$, Cs^+, Rb^+, $Cl^–$ and $I^–$, served as building units for the structure of a uranium thiophosphate with a large hexagonal unit cell, $a = b = 40.79$, and $c = 20.83$ Å. The structure, which consists of a uranium thiophosphate framework exhibiting large channels filled with a “quenched” salt melt, will be discussed with respect to its topological complexity.



NUCL 32

Hydropyridinone-based stabilization of Np(IV) for its separation in the adapted purex process

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^{237}Np is generated by (n, y) reactions of ^{235}U and by (n, 2n) reactions of ^{238}U, followed by β^- decay of ^{237}U. It is produced in nuclear fuel with a rate of ~0.75 and ~0.25 kg/tHM, respectively in thermal and fast reactors, and is present in far larger quantities than the combination of all other isotopes. Being the longest-lived member of the 4n + 1 radioactive decay series, ^{237}Np is thus an important and problematic long-term constituent of high level liquid waste (HLLW). Np used to be treated as a waste through HLLW vitrification but it has become worthier of recovery, to solve radiotoxicity issues and to apply it in the production of ^{238}Pu, a heat source for thermoelectric devices.

Np^{3+} is a strong reducing agent and $Np^{4+}/NpO_2^{+}/NpO_2^{2+}$ are the existing forms in acid-dissolved used nuclear fuel. Np^{4+} and NpO_2^{2+} are greatly extractable, in contrast to NpO_2^{+} since the low charge of the neptunyl ion NpO_2^{+} forms much weaker complexes. Operating conditions of the PUREX process create an environment where most Np exists as NpO_2^{+} and NpO_2^{2+}. In the first cycle of the PUREX process, where Np is co-extracted with Pu and U, the more extractable NpO_2^{2+} is the major species thanks to oxidation by indigenous HNO_3 and HNO_2. Remaining Np stays with trivalent fission-produced lanthanides (Ln). In the second cycle, where Pu is separated from U, reductants must be added to reduce Pu^{4+} to Pu^{3+} and NpO_2^{2+} to NpO_2^{+}, if Np is chosen to follow Pu instead of U, most favorable route in the Adapted PUREX process. The main issues in this step are sensitivity to HNO_3/HNO_2 concentration and incomplete

separation caused by the production of Np^{4+} that stays with U. Previous studies have shown that an aqueous complexant called 3,4,3-LI(1,2-HOPO) has high affinity to Np^{4+} and can assist the separation of Np both from U and from Ln. Extraction and stripping profiles of Np were determined as a function of pH. Valence profiles of Np were concluded by UV-vis and cyclic voltammetry (CV). The thermodynamics and kinetics of the Np reduction and complexation by HOPO were attempted.

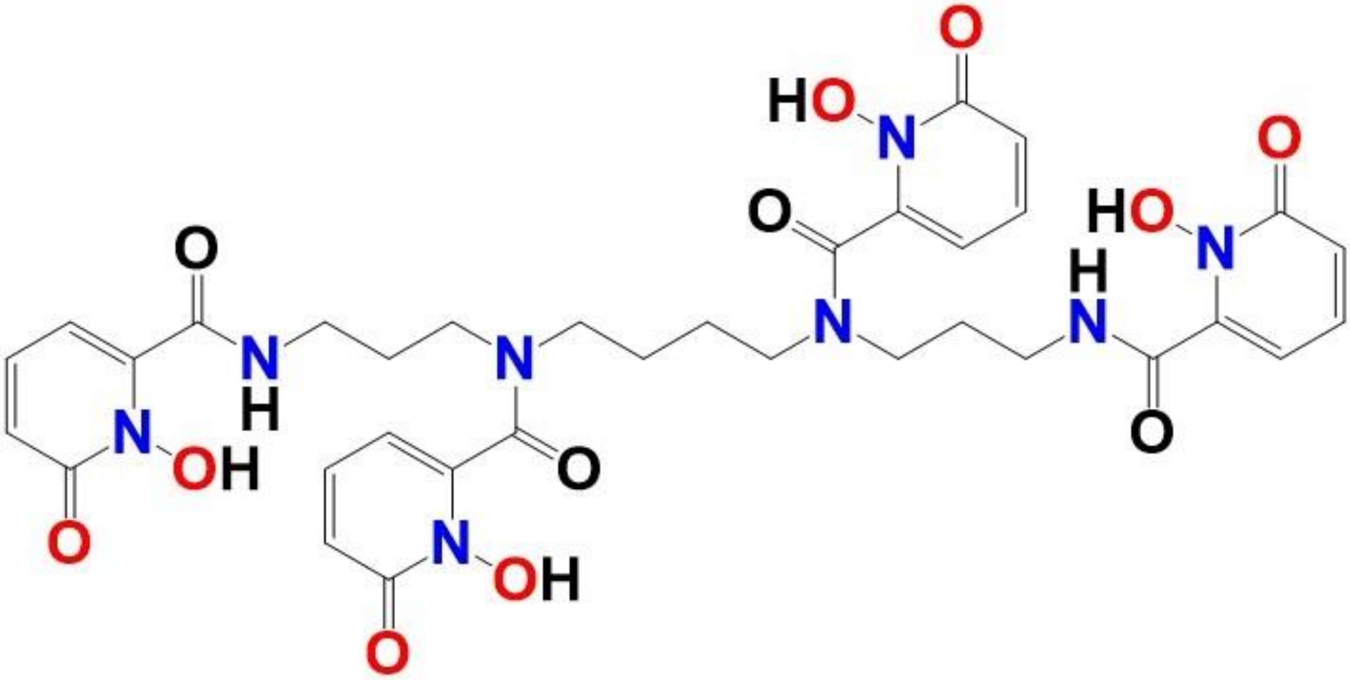

Fig 1. Structure of 3,4,3-LI(1,2-HOPO)

NUCL 33

Surface behavior of Di-alkyl phosphoric acids and derivatives in biphasic solvent: A molecular dynamics investigation

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With the continued generation of nuclear power, management of high-level waste is becoming increasingly relevant. Transuranium actinides (e.g. neptunium, americium, and curium) are of particular interest as these elements have been identified as the major contributors to long-term radiotoxicity of nuclear waste and are the main targets for transmutation. Even so, satisfactory transmutation can only be achieved after the separation of the actinides from lanthanide fission products – a herculean task that has daunted scientists since the discovery of transuranium actinides. Since actinide separations shifted to utilizing solvent extraction techniques in the 1950s, alkyl organophosphorus acids have been extensively applied as “cation exchangers”. Yet, much remains to be understood regarding the influence of partial charge distribution on the behavior of these extractants. Herein, di(2-ethylhexyl)phosphoric acid (HDEHP), 2-ethylhexylphosphonic acid mono 2-ethylhexyl ester (HEHEHP), and bis(2-ethylhexyl)phosphinic acid (HBEHP) were investigated under Actinide-Lanthanide SEParation (ALSEP) conditions in biphasic *n*-dodecane + water solution. By molecular dynamics simulation, surface behaviors and coordination environments near the Gibbs dividing surface were scrutinized to understand the impact of head group (phosphorus acid unit) polarity on dynamic interfacial behavior. Specifically, this work aims to provide a complete molecular picture by probing the respective chemical interactions, spatial distribution of extractants, interfacial orientation, and extractant conformation.

NUCL 34

Radiation-induced interfacial hydroxyl transformation on boehmite and gibbsite

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Understanding mechanistic pathways to radiolytic hydrogen generation by metal oxyhydroxide nanomaterials is challenging because of the difficulties of distinguishing key locations of OH bond scission, from structural interiors to hydroxylated surfaces to physi-sorbed water molecules. In this work, we exploited the interface-selectivity of vibrational sum frequency generation (VSFG) to isolate surface versus bulk hydroxyl groups for gibbsite and boehmite nanoplatelets before and after ^{60}Co irradiation at dose levels of approximately 7.0 and 29.6 Mrad. While high-resolution microscopy revealed no effects on particle bulk and surface structures, VSFG results clearly indicated up to 83% and 94% radiation-induced surface OH bond scission for gibbsite and boehmite, respectively, a substantially higher proportion than observed for interior OH groups by IR and Raman spectroscopy. Rehydration of the irradiated surfaces showed incomplete recovery of the surface hydroxyl groups with differences in the re-hydration behaviour between gibbsite and boehmite. Using ab initio molecular simulations, we performed a detailed analysis of the water-boehmite (010) and water-gibbsite (001) interfaces interactions and evaluated the effect of hydrogen surface vacancy on the strength of the hydrogen bonds. A defect energetic analysis indicates that H_2 and H_2O are the energetically most favorable products species to form from radiation induced surface H and OH defects. By performing nudged elastic band (NEB) calculations, we give an atomistic level description of the proton transfer mechanisms, as could be involved in rehydration and dehydration processes, at the water-boehmite (010) and water-gibbsite (001) interfaces.

NUCL 35

High resolution actinide speciation using a tensioned metastable fluid detector (TMFD)

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Gross alpha counting systems all suffer from some degree of cross-talk when beta-emitting radioisotopes are also present in the sample matrices. In addition, numerous alpha-emitting isotopes emit alpha particles with energies not resolvable with commercially available alpha spectrometry systems which have a resolution of at best ~20 keV. Radiochemical separations followed by alpha spectrometry can be used to resolve isotopes with overlapping alpha energies such as Pu-238&Am-241, Np-237&U-234 and Cm-242&Cf-252. Mass spectrometry is required to resolve elements with isotopes with overlapping energies such as U-235&U-236, U-233&U-234, Pu-239&Pu-240, and Cm-243&Cm-244. No laboratory or field deployable systems exist capable of resolving any of these pairs with unresolvable energies. Tensioned Metastable Fluid Detector (TMFD) technology has been developed by Purdue University for the purposes of special nuclear material detection via neutron detection. The team continued to study the capabilities of the device by detection of alpha emissions through measurement of alpha-emission induced isotope recoil. Initial experiments conducted by the team indicated energy resolution of 1.4 keV may be achievable which allows for the resolution of Pu-238 from Am-241. The Purdue team has determined that TMFD detectors also may not suffer from beta crosstalk issues which plague commercially available gross alpha counting systems by having essentially zero response to externally applied beta-gamma radiation. SRNL has collaborated with Purdue to further study the TMFD technology's potential to support radioanalytical applications with the wide suite of radiological materials at SRNL. The results of these SRNL evaluations to date will be discussed.

NUCL 36

Development of optical spectroscopy and multivariate analysis for the monitoring of ^{238}Pu radiochemical processing streams

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Neptunium-containing targets are being irradiated at Oak Ridge National Laboratory's (ORNL) High Flux Isotope Reactor to produce plutonium-238 for NASA. The irradiated targets are processed through a series of radiochemical separations at the ORNL Radiochemical Engineering Development Center (REDC). To meet the projected needs of NASA (1.5 kg of plutonium oxide per year) by the mid-2020s, ORNL is developing

advanced capabilities to increase production. Remote analysis and monitoring of radiochemical processing streams with optical spectroscopy and multivariate analysis is being developed for real-time analytical measurements within shielded hot cells at ORNL. Regression models were developed using a systematic approach to optimize a matrix of calibration standards with the experimental design and were compared to more traditional approaches for building calibration models. The key findings from several stages of the processing flow sheet and interesting areas for future research and development will be discussed.

NUCL 37

Magnet model of nucleon structure based on nucleon charge density, RMS charge radii, magnetic moments, and nucleon binding energy demonstrates magnetic potential energy barrier

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Mechanisms of nuclear fusion likely derive from the composition, structure, and forces of the atomic nucleus. A classroom model of a potential barrier would ideally reflect the structure and the behavior of constituent forces leading to fusion. An understanding of the substructure of light nuclei is necessary towards constructing an accurate understanding of fusion. The structure of light nucei, including charge distribution, must manifest in the physical properties of charge density, RMS charge radii, magnetic moments, and nucleon binding energy. An analysis of these physical properties may indicte a nucleon structure in which up and down quarks alternate sequentially within nucleons and light nuclei. A magnet array model is demonstrated in which the +2/3 up quark charge is represented by 2 N-facing magnets, and the -1/3 down quark charge by a single S-facing magnet. A pair of such arrays set opposite one another create a magnetic potential energy barrier analogous to the Coulomb barrier. Magnetic contour maps are shown demonstrated near-range attraction and far-range repulson. The magnetic force/distance curve of two approaching magnet arrays reproduces the fusion potential curve. Audience members holding the arrays feel repulsion at a distance 3-4 cm, then powerfully attract within a distance of 1cm. A special case is presented in which the ratio of the maximum attractive force to the maximum repulsive force between two arrays very closely approximates the strong force constant 137.

NUCL 38

ICP-MS analysis of plutonium and other actinides in brain tissue of occupationally exposed individual

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The United States Transuranium and Uranium Registries (USTUR) has studied the biokinetics and tissue dosimetry of actinides in former nuclear workers. USTUR conducts autopsies and measures actinide concentrations in various organs. Acid-digested human brain sample was obtained from the USTUR. This individual was exposed to plutonium through inhalation and wounds during a glove box explosion at nuclear defense facility. The total body systemic activity of ^{239}Pu, 51 years after intake, was 2,200 Bq. It is of interest to quantify ^{239}Pu levels in brain tissue as current plutonium systemic biokinetic model does not include brain as an individual model compartment.

Measurement of plutonium in brain is analytically challenging because of its low levels and complexity of brain tissue matrix. In this work, a direct ICP-MS method and a method with separation of actinides prior to ICP-MS were developed for measurement of ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, and ^{241}Am. The potential interference of polyatomic isobars were evaluated for the direct method. The indirect method used TEVA, UTEVA, DGA resin cartridges to separate plutonium, uranium, and americium from the brain matrix. ^{239}Pu, ^{240}Pu, and ^{241}Am were analyzed by isotope dilution mass spectrometry. The uranium was analyzed using an external calibration curve. The $^{235}U/^{238}U$ as well as $^{240}Pu/^{239}Pu$ isotope ratios were also measured. The method limit of detection, tracer recovery, and analysis of duplicate samples were investigated. The results showed 0.69 ± 0.05 ng/kg ^{239}Pu and 0.043 ± 0.005 ng/kg ^{240}Pu in the brain tissue with the $^{240}Pu/^{239}Pu$ = 0.063 ± 0.012 reflecting weapons-grade material. ^{238}U was 0.11 ± 0.01 µg/kg with the $^{235}U/^{238}U$ at 0.0068 ± 0.0004, which is consistent with the natural isotopic composition for uranium.

NUCL 39

p-NCS-Bn-NODAGA as a bifunctional chelator for radiolabeling with the ^{186}Re/^{99m}Tc-tricarbonyl core: Radiochemistry with model complexes

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With the continuing goal of developing theranostic agents for application in radiopharmaceutical chemistry, in this work, we studied p-NCS-Bn-NODAGA (**1**) as a bifunctional chelator for the *fac*-$[M(CO)_3]^+$ core (M= ^{nat}Re, ^{186}Re, ^{99m}Tc). Chelator **1** was conjugated with pyrrolidine in water (pH 9) at room temperature to yield p-NCS-Bn-NODAGA-Pyr (**2**) as a model of a conjugated biomolecule, for exploring its radiochemistry. After a thorough radiolabeling optimization process, the $[^{186}Re][Re(CO)_3(\mathbf{2})]^+$ model complex (^{186}Re-**3**) was synthesized by reacting $[^{186}Re][Re(OH_2)_3(CO)_3]^+$ with **2** to give >94% radiochemical yield (RCY; estimated by radio-HPLC, t_R= 13.3 min). The $[^{99m}Tc][Tc(CO)_3(\mathbf{2})]^+$ complex (^{99m}Tc-**3**) was synthesized by reacting $[^{99m}Tc][Tc(OH_2)_3(CO)_3]^+$ with **2** under similar conditions to give >95% RCY (estimated by radio-HPLC, t_R= 13.4 min). For characterization purposes, the non-radioactive Re tricarbonyl complex (^{nat}Re-**3**) was likewise synthesized by reacting $[Re(OH_2)_3(CO)_3]^+$ with **2** in a 1:1 ratio (HPLC t_R= 13.2 min). The stability of ^{186}Re-**3** was challenged against L-histidine and L-cysteine (1 mM in PBS; pH 7.4, 37 °C) and remained intact through 7 days. Similarly, stability studies in rat serum at 37 °C showed 98 (±2)% intact ^{186}Re-**3** complex through 5 days. Non-specific rat serum protein binding of ^{186}Re-**3** was found to be 40 (±2)% at 24 h. The ^{99m}Tc-**3** complex was also found to be stable in L-histidine, L-cysteine and rat serum at 37 °C through 24 h, with 40 (±2)% non-specific protein binding in rat serum at 24 h. In summary, the new ^{186}Re/^{99m}Tc-labeled bioconjugate model complexes were prepared in high RCY and exhibited matching behavior with excellent *in vitro* stability, indicating their promise for use in theranostic

radiopharmaceutical development. Therefore, studies with chelator **1** conjugated to a gastrin-releasing peptide receptor (GRPR) antagonist peptide, RM2, are ongoing.

Synthesis of $[M(CO)_3(p\text{-NCS-Bn-NODAGA-Pyr})]^+$ complexes, where M= ^{nat}Re, ^{186}Re, ^{99m}Tc.

NUCL 40

Inductively coupled plasma optical emission spectroscopy method improvements for the analysis of high-level nuclear waste matrices at the Savannah River National Laboratory

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The Savannah River National Laboratory (SRNL) utilizes Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) techniques in a radiological environment to support the inorganic elemental analysis of numerous programs at the Savannah River Site (SRS). The most common application of the ICP-OES technique at SRNL is for characterizations of high-level nuclear waste required for the Defense Waste Processing Facility (DWPF). To address SRS demands for elemental characterization, the ICP-OES instrumentation has been upgraded to meet the need for increased method sensitivity, capability and robustness. In addition, the ICP-OES upgrade provides synchronous vertical dual viewing capabilities and better complements other techniques at SRNL such as the Inductively Coupled Plasma Mass Spectrometry. The discussion details recent developments and improvements of the ICP-OES techniques for analyzing high level nuclear waste samples.

NUCL 41

Low LET gamma and high LET alpha degradation studies of the ALSEP process pre and post metal extraction

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An organic solution comprising the Actinide Lanthanide Separation Process (ALSEP) extracting solvent consisting of 0.5 M 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and 0.05 M N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) in *n*-dodecane were subjected to low LET gamma and high LET alpha irradiation before and after equilibration with 3 M HNO_3. Degradation dose constants revealed greater ligand degradation due to gamma irradiation than alpha irradiation for both ligands and equilibration with nitric acid did not have a significant impact on degradation kinetics for either irradiation source. Identified degradation products were similar for both gamma and alpha irradiation and occurred mostly through the rupture of the $N\text{-}C_{carbonyl}$ and $C\text{-}O_{ether}$ bonds for T2EHDGA and the $C\text{-}O_{ether}$ bond in HEH[EHP], and acid contact appears to alter the degradation pathway by favoring the formation of higher molecular weight recombination products. Mixed T2EHDGA-HEH[EHP]-NO_3 complexes were formed with Nd(III) after extraction from 3 M HNO_3, and low LET gamma irradiation of the Nd(III) loaded organic solution produced similar degradation products as the organic solution absent of Nd(III). Additionally, likely due to the greater radiolytic susceptibility of T2EHDGA than HEH[EHP], a HEH[EHP]-Nd(III) complex appears to form with increasing absorbed dose.

NUCL 42

Beyond ocean extraction of uranium (VI): Polyamidoxime nanofiber materials for specialized point-of-use water treatment applications

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Uranium (VI) extraction from Earth's oceans using advanced sorbent materials functionalized with the amidoxime ligand receives considerable research attention to augment terrestrial uranium resources for nuclear power. Amidoxime selectively binds the uranyl cation and amidoximated polymer membranes are regenerated for reuse with ease. In field deployments of amidoxime-functionalized technologies, competition from other dissolved metals in seawater frequently interferes with exclusive isolation of uranium. These results are undesirable for ocean extraction, however, removal of other metals and minerals observed in field trials are of great benefit in drinking water treatment applications for both membrane units in large treatment plants and home point-of-use and point-of-entry devices. Herein, we have developed an electrospun polyamidoxime nanofiber membrane material that removes 97-100% of magnified concentrations of uranium (1 ppm) from complex aqueous solutions, where highly

soluble uranyl carbonate species dominate. Removal to non-detectable uranium concentrations from environmentally relevant levels (>200 ppb) elucidates real-world application for compliance with the U.S. Environmental Protection Agency Maximum Contaminant Level of 30 ppb in drinking water treatment. Polyamidoxime membrane materials indicate especially great promise for use in point-of-use and point-of-entry devices in resource-constrained communities in the southwest United States, where the legacy of uranium mining continues to impair source water quality.

NUCL 43

Role of Mn(III,IV) oxide on the environmental stability of Tc-99 insoluble phases: Oxidative dissolution of TcO_2 at anoxic conditions

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Tc-99 is a radionuclide of environmental concern due to its long half-life, radiotoxicity and high mobility under oxidizing conditions. Tc-99 is produced through U-235 fission during nuclear power generation. Poor past waste management practices led to the release of release of Tc-99 in the environment. The mobility of Tc-99 in the environment is highly dependent on its oxidation state. Under oxidizing conditions, Tc exists as TcO_4^-, which is highly soluble and does not sorb onto mineral surfaces giving it high mobility. Under reducing conditions, immobile Tc(IV) forms predominate. Because of this dichotomy, remediation efforts for Tc-99 have focused on immobilization through reduction, which makes the potential re-oxidation of Tc(IV) phases a question of importance.

Our experiments examine the potential for re-oxidation of $Tc(IV)O_2$ by birnessite, a Mn(III,IV) oxide. Birnessite is common in nature and it is known to be an effective oxidizing agent, due to the fact that the high redox potential of Mn(IV)/Mn(II) makes the oxidation of any reduced metal or metalloid species almost always thermodynamically favorable.

We performed a series of batch dissolution experiments under anoxic conditions, in order to exclude Tc(IV) oxidation due to oxygen, at a range of environmentally relevant physico-chemical parameters, such as pH, ionic strength and the presence of ligands. Samples contained 0.25 mg of solid TcO_2 suspended in a 0.01 M buffer solution (PIPES at pH 6.5 and HEPES at pH 8) along with 5, 50 and 150 mg of birnessite. The presence of aqueous Tc-99 was monitored as a function of time and it was measures using Liquid Scintillation Counting. Birnessite induced rapid and substantial dissolution of TcO_2 over the course of 30 days. Birnessite was equally effective at oxidizing TcO_2 at pH 6 and 8 (~60% of TcO_2 dissolution). Furthermore, we performed Ca^{2+} and Mn^{2+} sorption experiments on birnessite at pH 6 and ~100% of Ca^{2+} and ~55% of Mn^{2+} (initial cationic concentration: 100 ppm) sorbed on birnessite. The sorption of these two cations on birnessite had a significant effect on the mineral's ability to oxidize TcO_2 and the release of Tc-99 in the aqueous phase decreased. To sum up, we showed that the presence of manganese minerals constitutes a liability for the environmental stability of TcO_2 even at

anoxic environments and the presence of manganese minerals should not be discounted when it comes to remediation efforts of Tc-99 in the environment.

NUCL 44

Targeted alpha therapy: Characterization and evaluation of lysine-based Ac-225 radioimmunoconjugates against *Yersinia pestis*

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Targeted alpha therapy (TAT) is a rapidly advancing subdivision of radioimmunotherapy (RIT) which has shown increasing promise in recent years as a treatment for cellular pathology. As the majority of research into targeted alpha therapy has evaluated the therapeutic efficacy of antibody-drug conjugates (ADC) against a select pool of tumor cell lines, much is left to be discovered with regard to optimal construction and application of radioimmunoconjugates (RIC's) as treatment for a greater diversity of pathogens. To address these avenues of inquiry, this work investigates refined synthesis and characterization methods for RIC's, as well as the novel application of Actinium-225 (Ac-225) RIC's against the etiologic agent of the bubonic plague, *Yersinia pestis*. To achieve the aforementioned objectives, a lysine-based conjugation of antibodies is selected as the ideal method of construction to be investigated, with further discussion on characterization of the resulting ADC's drug-antibody ratio (DAR), degree of conjugate heterogeneity, and retention of native antibody structure. Following metalation with alpha-emitting radionuclide Ac-225, resulting ADC efficacy was assessed by following growth inhibition of *Y. pestis* in an in vitro cell killing (IVK) assay and in vivo depletion of spleen colony-forming units (CFU) in Swiss Webster mice.

NUCL 46

Simultaneous removal of radioactive Cs^+ and Sr^{2++} ions from wastewater by facile solid-state alkali-activation of montmorillonite

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Despite the fact that the nuclear power industry has been greatly developed at present, the nuclear power plant is considered a danger due to a large amount of radioactive material leaked from the nuclear accidents such as in Fukushima. In particular, radionuclides such as cesium-137 and strontium-90 were the most damaging in the Fukushima accident, since they have long half-lives (30 years) and emit strong gamma rays. In order to minimize the volume of these radionuclides generated in large quantities, it is necessary to develop a practical adsorbent able to selectively remove for both.

For the synthesis of the effective adsorbent for both cesium and strontium ions, we

demonstrate an effective modification of montmorillonite (MT) using solid-state NaOH thermal treatment at 300 °C. Through this facile activation by desilication, porosity was enhanced and abundant surface functional groups for ion-exchange were generated. It was possible to optimize the adsorption performance of the activated montmorillonite (NaMT) by adjusting the mass ratio of NaOH (unity to MT). The adsorption mechanism analysis from XRD and XPS studies showed that cesium ions were mainly exchanged with intercalated cations in MT, and strontium ions were adsorbed on the surface functionalities (Si-O-Na^+). As a result, the enlarged BET surface area (117 m^2) and functional groups enabled adsorption of strontium (capacity of 185 mg/g, pristine MT: 16 mg/g), and cesium adsorption capacity was also increased (137 to 291 mg/g). In addition, NaMT exhibited the simultaneous removal of cesium and strontium ions, and selective removal of them under groundwater conditions where competing cations exist, such as sodium, potassium, and calcium. Furthermore, it showed stability under a wide range of pHs (3-11) and following irradiation of gamma-ray (at 6 Gy/h for 30 min). This improvement removal performance of adsorbent synthesized from cost-effective montmorillonite has increased the applicability to realistic conditions.

NUCL 47

Activation of actinyl-oxo bonds to form actinide-nitridos, and the reverse process

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Fundamental gas-phase reactions of actinide complexes better define the scope of their chemistry. Gas-phase studies provide uniquely detailed information on underlying chemical properties that influence bond activation, which also pertains to condensed-phase reactions. Activation of the strong An=O bond in actinyl complexes $An^{VI}O_2^{2+}$ and $An^{V}O_2^{+}$ (An = Pa, U, Np, Pu, Am) is challenging. Using isocyanate as the activating ligand, an An=O can be converted to an An≡N bond upon heating (i.e. ΔE > 0), as shown by reaction (1) for an An^{VI} anion complex. Furthermore, the reverse of reaction (1), to activate CO_2, occurs spontaneously at low energy for An = U.
$AnO_2Cl_2(NCO)^- + \triangle E \rightarrow NAnOCl_2^- + CO_2$ (1)
By comparing reactions such as (1) for different An^{VI} and An^{V}, as well as for different coordination environments, systematic variations in bonding and bond activation can be assessed. Preliminary results suggest that U^{VI} is more difficult to activate than Np^{V}. Such insights can provide guidance for synthetic strategies.

NUCL 48

Cyclotron production and radiochemistry of Sc and Ti radiometals for imaging and radiotherapy

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The use of new imaging and theranostic agents in nuclear medicine allow for patient-specific strategies that combine diagnosis and therapy. In particular, our group has developed cyclotron targetry, dissolution and purification strategies for radioactive first row transition metals including ^{43,44,47}Sc and ^{45}Ti.

The radiometal isotopes of scandium have been of interest for the creation of theranostic strategies using diagnostic and therapeutic radiopharmaceuticals with identical structures. Our group has focused on the use of titanium metal and titanium oxide targets to optimize a robust strategy for the production of the diagnostic isotope, ^{43}Sc and the therapeutic isotope ^{47}Sc via the p,alpha reactions on titanium targets. Recent work has resulted in optimized, robust dissolution and separation processes with high yields and specific activity.

In a similar fashion, ^{45}Ti is a positron emitting isotope ($t_{1/2}$ = 3 hrs) which can be produced via the proton irradiation of natural scandium foils. While the production method is relatively straightforward, purification and radiochemistry of this interesting isotope has been challenging due to the multiple oxidation states of titanium. Our work in this area illustrates that some of these challenges can be overcome and that ^{45}Ti can be readily produced on medical cyclotrons. Preliminary studies also provide the groundwork for the development of stable bifunctional complexes with this isotope as a starting point for the development of ^{45}Ti PET imaging agents.

NUCL 49

Lutetium-177 production at ORNL

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Lutetium-177 is rapidly becoming an important radioisotope for a variety of medical uses, including bone-targeted palliation therapy and treatment of gastroenteropancreatic neuroendocrine tumors. Production of ^{177}Lu must be done in such a manner as to minimize the amount of ^{177m}Lu, which has a long half-life that makes it unsuitable for radiation therapy. It can be made directly or indirectly by the neutron irradiation of enriched ^{176}Lu or ^{176}Yb targets. The production of high specific activity carrier-free ^{177}Lu, or ^{177}Lu without the metastable product, can be achieved by irradiating highly enriched ^{176}Yb via the (n,β^-) reaction . The High Flux Isotope Reactor at Oak Ridge National Laboratory has a high neutron flux that can produce very high specific activity ^{177}Lu. Removal of the ^{177}Lu radioisotope from the bulk ^{176}Yb must then be performed to achieve a high enough specific activity for radiotherapy use and for the valuable enriched ^{176}Yb to be recycled. The specific activities that can be achieved and the subsequent processing parameters required to produce high specific ^{177}Lu were explored via a series of small-scale target irradiations in the High Flux Isotope Reactor.

NUCL 50

Purification of francium via cation exchange chromatography

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Francium has gone relatively unstudied in the past 50 years due to the short half life of its isotopes, but developing a better understanding of the element is crucial for knowing its homeostatic behavior within the human body when generated in vivo from targeted radioimmunotherapy agents. Despite 37 known isotopes of Francium, only three have been actively researched: Fr-212 (t1/2 = 20 min) in magnetic moment evaluations, Fr-221 (t1/2 = 4.9 min) as a daughter of the targeted alpha therapy isotope Ac-225, and Fr-223 (t1/2 = 21.8 min) studied here as a longer-lived Fr-221 surrogate that can be milked from parent Ac-227. In addition to its short half-life, characterization of Fr-223 requires complete separation from other Ac-227 daughters due to overlapping gammas from other isotopes in the decay chain (see figure).

A DOWEX resin column is used to separate Th-227 from Ac-227 and all of its other daughters. In order to view Fr-223 using a liquid scintillation counter before it has decayed to background levels, a fast-running secondary column resin is required for washing the Fr-223 off of the Ac-227 column. Initial experiments using DGA-Normal resin demonstrated effective separation but were too slow for later chemical experimentation with Fr-223. Additional resins, such as DGA-Branched and AG 50W-X4, were tested to determine the fastest runtime while maintaining high separation capacity.

NUCL 51

Medical radionuclide production research at the University of Washington: Facilities and cyclotron produced medical radionuclides

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The Scanditronix MC-50 cyclotron was installed at the University of Washington Medical Cyclotron Facility (UWMCF) in 1983 for delivering Fast Neutron Therapy. The cyclotron is capable of producing variable energy H^+, H_2^+, $^2H^+$, $^3He^+$, $^3He^{2+}$ and $^4He^{2+}$ beams. Our radionuclide production activities have focused on α-emitter (i.e., ^{211}At) and theranostic Auger electron- or β-emitters. We routinely produce ^{211}At batches of up to 5.55 GBq using the 29 MeV $^4He^{2+}$ beam for preclinical and clinical evaluation of potential radioimmunotherapies. We also provide ^{211}At to external U.S. investigators through the DOE National Isotope Development Center. The $^4He^{2+}$ beam has also been used for the production of the Auger-emitter ^{117m}Sn via $^{116}Cd(a,3n)$ and positron-emitter ^{72}As (imaging partner for ^{77}As) via $^{70}Ge(a,2n)^{72}Se\rightarrow^{72}As$ in collaboration with other research entities. Thick ^{116}Cd target irradiations demonstrated the α-particle induced reaction (AIR) provides ^{117m}Sn of highest specific activity and radioisotopic purity compared with ^{117m}Sn obtained from other reactions in the literature. As the product radionuclide is generally two charge units higher than the target nuclide, AIRs can present a smaller challenge for the chemical separation of the product and the target material, resulting in products of higher chemical and radionuclidic purity. However, AIRs require more intensive target cooling and specialized targetry. Partnering with the University of Missouri (MU), Brookhaven and Argonne National Laboratories (BNL & ANL), we are evaluating various routes of production of high specific activity (HSA) theranostic Re radioisotopes. The $^2H^+$ and $^4He^{2+}$ beams have been used to evaluate the $^{186}W(d,2n)^{186}Re$ and $^{186}W(a,p)^{189}Re$ reactions, respectively. MU, BNL and ANL are investigating γ ray- and proton-induced reactions for the production of HSA Re radioisotopes from Os and W targets. With Los Alamos and Oak Ridge National Laboratories, we are investigating the $^{232}Th(p,3n)$ reaction for production of ^{230}Pa, the parent of ^{230}U, for development of a $^{230}U/^{226}Th$ generator system to make ^{226}Th available for targeted alpha therapy. Due to the lack of remote target retrieval and hot cell infrastructure, our capability of processing radionuclides other than ^{211}At has been

limited to the research scale. This presentation will provide an overview of the UWMCF and our collaborative research efforts towards production of medical radionuclides in short supply.

NUCL 52

Reinvigorating Francium chemistry research to enable better understanding of targeted alpha therapy decay chains

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While francium isotopes have been widely studied in nuclear physics because of their unique electronic and magnetic properties, the chemistry of francium has gone largely unstudied over the last 75 years. Nonetheless, Fr-221 is the first daughter of the much-lauded targeted alpha therapy isotope Ac-225. Though it only lasts for a few minutes before decaying, understanding the chemical behavior of francium in biological systems will enable better targeting agents for Ac-based cancer therapy. Using the isotope with the longest half-life (Fr-223, 21.8 min), it is possible to begin chemical characterization without the intervening variable of in situ production from Ac-225. We have developed a robust column separation procedure at Lawrence Berkeley National Lab to elute radio- and chemically-pure Fr-223 from its Ac-227 parent as frequently as every couple hours. With those elutions, tracer-level solution thermodynamics measurements are possible for chelators being investigated for Ac-225 targeted alpha therapy (HOPO, DOTA, DTPA), and various calixarenes, common chelators for Cs^+ ions.

NUCL 53

Transport model predictions of Actinium-225 production cross sections via energetic proton, deuteron and α irradiation of Thorium-232 targets

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Monte Carlo transport codes PHITS and MCNP6 were used to calculate the cross sections of $^{225,\,227}$Ac, $^{227,\,229}$Th, ^{223,225}Ra, and ^{229,230,231}Pa via the bombardment of a ^{232}Th target with energetic protons, deuterons, and α-particles. The incident projectile energies ranged between 10 and 800 MeV/nucleon. When possible, the predicted production cross sections were compared with the available experimental data and

other predictions. The degree of the codes' abilities to match the measured data provides a level of confidence in the codes' abilities to predict data from similar, but unmeasured projectile/target systems. In addition, a comparison between calculated cross sections and data may provide insight into possible improvements in the physics models employed by those transport codes.

NUCL 54

Thorium-229 production through deuteron breakup fast neutron irradiation of Actinium-225 at the 88-inch Cyclotron facility

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Thorium-229, and specifically its daughter products ^{225}Ac and ^{213}Bi, are important alpha-emitting radioisotopes with applications in cancer treatment that are currently in short supply. To address this shortage, we evaluated a novel method to produce ^{229}Th using fast neutrons. After characterizing a legacy stock solution of $Th(NO_3)_4$ containing ~81% ^{230}Th by mass, 7.6 µg of ^{230}Th was evaporated on a quartz target slide at Oak Ridge National Laboratory. Phosphor imaging of the slide displayed relatively uniform thorium deposition across the surface of the slide. The target slide was then encapsulated with a quartz cover slide and epoxy and shipped to Lawrence Berkeley National Laboratory for irradiation at the 88-inch Cyclotron Facility. The target was irradiated for 4.5 days in the fast neutron beam ($10 < E_n < 20$ MeV) generated by the thick target deuteron breakup beam incident upon a beryllium target (~5 µA) to determine the ^{230}Th(n,2n)^{229}Th reaction cross section. Based on recent measurements of the ^{232}Th(n,2n)^{231}Th and ^{238}U(n,2n)^{237}U reactions, we expect that the excitation function for ^{230}Th(n,2n)^{229}Th reaction peaks at ~1.5 b at $E_n \approx 11$ MeV. The target will soon be returned to Oak Ridge National Laboratory for chemical separation of thorium from impurities via ion exchange chromatography methods and analysis, including gamma ray spectroscopy, alpha spectroscopy, and mass spectrometry. The nuclear data generated in this work and presented herein will be invaluable for future ^{229}Th production.

NUCL 76

Synthesis and characterization of actinide-based metal–organic framework materials

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Metal–organic frameworks (MOFs) are an emerging class of solid-state materials built up from metal-based nodes and organic linkers. They exhibit permanent porosity and unprecedented surface areas which can be readily tuned through coordination chemistry at the inorganic node and organic chemistry at the linkers. This talk will be centered on the synthesis and characterization of actinide-based MOFs.

NUCL 77

Advancements in actinide metal-organic framework chemistry via synthesis of Pu-UiO-66

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We report the synthesis and characterization of the first plutonium metal-organic framework (MOF). Pu-UiO-66 expands the established UiO-66 series, which includes transition-metal, lanthanide, and early actinide elements in the hexanuclear nodes. The thermal stability and porosity of Pu-UiO-66 were experimentally determined and multi-faceted computational methods were used to corroborate experimental values, examine inherent defects in the framework, and decipher spectroscopic signatures. The crystallization of a plutonium chain side product provides direct evidence of the competition that occurs between modulator and linker in MOF syntheses. The existence of a plutonium-based MOF is of interest to the many facets of the nuclear fuel cycle. Such a structure could provide opportunities for the simultaneous sequestration of plutonium and fission product or other actinides into a stable form. Incorporating an alpha emitter as the metal node could satisfy more fundamental curiosities regarding the radiation stability of MOFs. Actualization of a plutonium MOF provides a platform for nanoscale control of a high-profile nuclear material and has been executed for the first time in this work. Ultimately, the synthesis of Pu-UiO-66 demonstrates adept control of Pu(IV) coordination under hydrolysis-prone conditions, provides an opportunity to extend trends across isostructural UiO-66 frameworks, and serves as the foundation for future plutonium MOF chemistry.

NUCL 78

Structural features of zirconium-based metal–organic frameworks affecting radiolytic stability

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Metal–organic frameworks (MOFs) have shown promise for the capture and sensing of off-gases at civilian nuclear energy reprocessing sites, nuclear waste repositories, and nuclear accident locations. However, little is understood about the structural features of MOFs which contribute to their stability levels under the ionizing radiation conditions present at such sites. This study is the first of its kind to explore the structural features of MOFs which contribute to their radiolytic stability. Both NU-1000 and UiO-66 are MOFs that contain Zr metal-centers with the same metal absorption cross section. However, the two MOFs exhibit different linker connectivity, linker aromaticity, node density, node connectivity, and inter-ligand separations. In this study, NU-1000 and UiO-66 were exposed to high (423.3 Gy/min, 23 min and 37 s) and low (0.78 Gy/min, 4320 min) dose rates of ^{60}Co gamma irradiation. NU-1000 displayed insignificant

radiation damage under both dose rates, due to its high linker connectivity, low node density, and low node connectivity. However, low radiation dose rates caused considerable damage to UiO-66, a framework with lower aromaticity and smaller inter-ligand separation. Results suggest that chronic, low radiation environments are more detrimental to Zr MOF stability than acute, high radiation conditions. Additionally, gamma and helium ion irradiation studies were performed on UiO-66 derivatives to test the effect of additional functional groups on MOF stability. This is the first observed analysis of MOFs under helium ion irradiation and the highest gamma radiation dose observed in MOF irradiation studies to date (200 kGy).

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Synthesis, topology, and properties of a phosphate-functionalized uranyl peroxide cage cluster

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An extensive family of uranium peroxide nanoclusters has been developed, researched, and characterized over the past decade. These studies shed light on the behavior and properties of the actinides at the nanoscale level. Single crystal X-ray diffraction data allowed for the refinement of the uranium, phosphorus, and oxygen atoms of the U60P32cluster with chemical formula (Z=1): $[Li,(NH_4)]_{64}[(UO_2)_{60}(O_2)_{60}(HPO_4)_{32}(H_2O)_{24}]*nH_2O$ characterized by pseudo cubic T_h symmetry. The cluster is formed by twelve structurally identical pentagonal rings of *Ur*$Ø_6$ bipyramids (where *Ur* represents the uranyl ion, (UO_2)2+ coordinated to six oxygens, Ø, in the form of peroxide (O2-), hydroxide (OH-), or water). The pentamers are decorated by two phosphate tetrahedra with the general formula being $[Ur_5(O_2)_5Ø_6(PØ_4)_2]$n-. Eight additional $PØ_4$ tetrahedra are placed between the pentamers, completing the cluster. There are two types of phosphate environments; one environment involves a phosphate tetrahedra sharing vertices with three different uranyl polyhedra, and in the other environment the phosphate tetrahedra shares an edge with one uranyl polyhedron and shares a vertex with a different uranyl polyhedron. Bond valence calculations confirmed equatorial non-bridging oxygens of the uranyl polyhedra are water, and also suggests there is a predominant occupation of hydroxyl groups on non-bridging axial phosphate vertices. In addition to the uranium pentamers (five membered rings, 5R), the cluster consists of 10-membered rings (10R, formed by four $PØ_4$ tetrahedra and six $UrØ_6$ bipyramids) and 6-membered rings (6R, formed by two $PØ_4$ tetrahedra and four $UrØ_6$ bipyramids) with the total ratio 10R:6R:5R=6:12:24. Raman, IR, and XRF spectra as well as LA-ICPMS data were collected to further characterize the compound.

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Heat responsive uranyl peroxide cage clusters

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Self-assembly of uranyl ions (UO_2^{2+}) and peroxide in aqueous solution containing alkaline or alkaline-earth cations produces uranyl peroxide clusters (UPCs) in which the uranyl peroxide polyhedra are arranged intotopological squares, pentagons and hexagons. Amongst the reported UPCs, some adopts fullerene topologies and tend to be inert in response to heat. In this work, we modified a fullerene-topology U_{20} structure through the insertion of organic ligands, which results in a U_{19}structure, $[(UO_2)_{19}(O_2)_{26}(OH)_2(C_6H_4P_2O_6)_4]^{32-}$, that features a geometrically unstable topology. In response to the increasing temperature, $U_{19}$is fragmented into uranyl polyhedra that subsequently reassemble into a U_{24} cage cluster, $[(UO_2)_{24}(O_2)_{24}(OH)_{24}]^{24-}$, above 60°C. Above 100°C, the cage cluster species in the reaction solution disassemble and precipitate as metashoepite, $((UO_2)_4O(OH)_6)(H_2O)_5$, which has a sheet structure.

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Breaking down of the energy landscape of uranyl peroxide nanoclusters

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Actinyl peroxide nanoclusters are a unique large family of polyoxometalates (POMs) and provide an exciting opportunity to explore the limitless potentials of POMs. Furthermore, they offer are an important tool to enhance our understanding of the actinide elements. By using new techniques and state of the art calorimeters, the energetic formation of the clusters can be broken down into two steps: formation of aqueous clusters and their crystallization. This rigorous study lays down the energy landscape of several carefully selected uranyl peroxide nanoclusters and provides calorimetric methods for other POM scientists to study their systems.

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Uranyl peroxide capsule without templating

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Uranyl peroxide capsules represent the newest family of polyoxometalates, and the only family in the f-block. Nearly 15 years of experiment and computation have shown the importance of alkalis in self-assembly, templating, and solubility of these capsules. We have discovered that with only tetramethylammonium (TMA) as a countercation, a cluster with approximately 180 uranyl polyhedra forms (denoted U_{180}). We can only estimate the nuclearity because crystal growth is challenged by the tendency of this cluster to morph into other forms if anything is added to the cluster solution to promote crystallization. The small-angle X-ray scattering data is sufficiently strong and detailed enough to predict a structural model by computation of possible structures, and simulation of the scattering data from these models. This cluster affords opportunity to 1) determine a structure from solution phase-data and computation, and 2) determine inherent structural assemblies within this family of nanocapsules, without the influence of the alkali countercations. We will describe the process of creating a feasible structural model from experimental and computational data. In addition, we will report on the restructuring of the U_{180} capsule with the addition of alkalis, as well its supramolecular assembly.

NUCL 83

Exploring pathways of uranyl oxalate cluster assembly

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The uranyl peroxide nanoclusters are a diverse family of polyoxometalates with important implications for the solubility, storage, and aging of uranium oxides. However, aqueous speciation of the cluster-forming solutions is often complex, making it challenging to characterize the pathways leading to assembly and the role that smaller “building block” species might play in this process. The uranyl oxalate clusters may provide a unique insight into these questions due to their closely interrelated and fragmented topologies and the stability of these fragments outside of the larger cluster geometry. Electrospray ionization mass spectroscopy (ESI-MS) and nuclear magnetic resonance (NMR) spectroscopy have been previously underutilized in investigating the solution dynamics of the clusters and their fragments and may provide greater insight into the pathways and kinetics of these systems.

NUCL 84

Electronic structure and speciation of actinide molecular metal oxides

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The understanding and control of the speciation and self-assembly of aqueous molecular metal oxides is fundamental since our ability to manipulate the evolution of transient species in solution lies at the core of nanotechnology. In this aspect, actinide molecular metal oxides and peroxides are highly relevant in an advanced nuclear energy cycle including fuel reprocessing and long term waste storage. On one hand, uranyl-peroxide nanoclusters have emerged as a unique family of self-assembled actinide nanocapsules. Behind the apparent structural simplicity of these species hides a highly complex chemical space with a myriad of accessible nucleation pathways controlled by the pH, counterions, and the concentrations of the different species in solution. On the other hand, the speciation of transuranic molecular metal oxides is very complex and relatively little is known regarding their composition, structure, and properties in solution. Here we will present our recent developments in the study of the electronic structure, speciation, and nucleation of uranyl-peroxide nanoclusters and transuranic molecular metal oxides.

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Radiation effects on the formation and stability of uranyl peroxide clusters

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Actinide peroxide nanoclusters self-assemble in aqueous solution across a wide pH range. Irradiation of water generates reactive species, including peroxide, that may produce conditions favourable for nanocluster formation. The impact of radiation on uranyl peroxide cluster formation is unexplored, although earlier studies have demonstrated the formation of the peroxide mineral studtite during irradiation. The three most readily synthesized uranyl peroxide clusters are U24, U28, and U60. This study aims to investigate how radiation impacts the formation of these uranyl peroxide clusters as well as their stability in a gamma radiation field after formation.

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Solution and solid-state supramolecular assembly of large actinide-oxo clusters and superatoms

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The mining and milling chemistry of U and Th is complex, with many unknown compound intermediates. Simple compounds such as uranium(IV) sulfate, come from the dissolution of uranium-bearing ore with sulfuric acid. Yet, U-bearing ore contains other metals, such as lanthanides and transition metals, that make the simple dissolution of uranium to uranium sulfate far more complex. Herein, we provide a solution and solid-state study of a new class of actinide-oxo clusters using novel counterions: trivalent lanthanide and divalent transition metals. Single x-ray diffraction (SCXRD) provides information on the speciation and assembly of uranium sulfate as a function of the hetero-metal ion. By systematically changing the synthetic conditions and the counterion, and with the use of SCXRD, it has, so, thus allowed the discovery of three new actinide-oxo cluster families; An_6, An_{70}, and An_{84} (An, actinide). Each family-type structure is a framework comprised of anionic uranium-oxo sulfate clusters, where the counterion has a direct effect on size and crystal framework assembly. Solution characterization using small-angle x-ray scattering (SAXS), is used to determine the solubility and stability of the new uranium-oxo clusters. In organic solvents, solution-based supramolecular assembly of the clusters can be observed, with size-dependency on the counterions used. The characterization on a series of clusters expands the aqueous and organic chemistry of tetravalent actinide sulfates; by studying its interaction with other metals and crystallizing the resulting effects and characterizing and resulting compounds properties can lead to new discoveries.

NUCL 88

Thermodynamic and crystallographic analysis of uranyl sulfate minerals with unique structures

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More than 50 uranyl sulfates are recognized by the International Mineralogical Association as minerals, which are typically found in sheltered mine adits due to most species' high solubility in water and their formation under acid mine conditions. Approximately half of the uranyl sulfate minerals have been found within the mines of the White Canyon district in southeastern Utah and these species vary in crystal structure and complexity, hydrogen content and M:U:S ratio (M = Na, Mg, Al, NH_4, Y, or no cation). The thermodynamic properties of these new species are mostly unknown, limiting understanding of the architectural relationships between the mineral structures.

This project investigates these minerals through a combination of thermodynamic and

crystallographic analysis. Synthetic analogs of uranyl sulfate minerals are prepared by evaporating solutions of UO_3 dissolved in sulfuric acid. The laboratory analogs were characterized through single crystal X-ray diffraction, powder X-ray diffraction, inductively coupled plasma optical emission spectroscopy, and thermogravimetric analysis. 5 mg pellets of the ground samples were dropped into an Alexsys high-temperature molten solvent calorimeter to measure the enthalpy of dissolution, from which the enthalpy of formation (DH_f°) was calculated. Crystal complexity was quantified using ToposPro.

Preliminary results have found linear relationships between structural complexity and stability, DH_f°, suggesting that the predominant formation mechanisms of this mineral suite may be energetic rather than entropic in nature. Further work will focus on measuring the entropy (DS_f°) of these mineral phases in order to determine the full extent of the relationships between their thermodynamic properties and crystal structures.

NUCL 89

In-situ generation of peroxide in non-aqueous systems and the formation of uranyl peroxide species

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Uranyl peroxide species and solid state materials are important phases within the nuclear fuel cycle and have been extensively investigated within aqueous solutions. Formation of peroxide in non-aqueous conditions is less understood, but also has important implications in the separation of waste products using liquid-liquid extractions. In this presentation, we will discuss current efforts to understand in-situ peroxide generation in organic solvents and the formation of uranyl peroxide coordination complexes and larger macromolecules. In particular, we will focus on the autoxidation of benzaldehyde in benzyl alcohol solutions in the presence of uranyl and phosphonate ligands. Raman spectroscopy of the solution phase provides our mechanistic understanding of the reaction pathway and confirms consistent levels of peroxide generated in-situ over an extended period of time.

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Preparation of uranium oxide thin films by combustion synthesis for nuclear target applications

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Basic nuclear science as well as stockpile stewardship require non-traditional approaches for developing target and projectile combinations. This work reports on the implementation of advances in material science towards the development of robust thin-film actinide targets. Typically, to produce such targets, thin films (20 - 200 nm thickness) of radionuclides are deposited on backings (carbon foil or aluminum disk) by thermal evaporation or electrodeposition. These methods, however, exhibit low material collection efficiency (10 – 90 %) of the radionuclides of interest and/or results in low adherence of deposited layers to the backings, as well as instability under high beam intensities. This work investigates a combustion synthesis process in uranyl nitrate - glycine thin solution layers deposited on backings to prepare robust uranium dioxide (UO_2) films. Raman spectroscopy and single-crystal X-ray diffraction were used to study the chemical mechanism of interaction in reactive solutions. The results of these investigations suggest that a coordinate compound forms in a reactive solution ($[(UO_2)_3(Gly)_2O(OH)_3](H_2O)_3NO_3$), which exothermically decomposes during the combustion to uranium oxides. Powder X-ray diffraction analysis of bulk combustion products shows that a pure UO_2 phase can be produced with a glycine/uranyl nitrate molar ratio of 1.5. Thermogravimetric analysis coupled with differential scanning calorimetry investigations confirm the product formation pathway through the decomposition of the coordinate compound. The spin coating or electrospraying of reactive solutions with optimized composition followed by short (20 min) heat treatment at 300^{o}C allows depositing thin UO_2 layers on carbon or aluminum backings. Control over the UO_2 layer thickness can be achieved by changing the spraying duration or multiple spin coating procedures. The uniformity of deposited UO_2 layers was characterized by high-resolution electron microscopy along with Rutherford Backscattering Spectrometry and α-particle spectroscopy and can insure more precise nuclear measurements. These results suggest the novel method’s ability in producing robust targets with precise control of the thickness (20-200 nm) and the thickness uniformity (1-3%) of the UO_2 layer.