NUCL

Phase behavior and critical phenomena in liquid-liquid extraction of lanthanides

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Lanthanide separations using liquid-liquid extraction is an important aspect of critical materials recovery and nuclear fuel reprocessing. Poorly understood aspects of this process include aggregation and liquid-liquid phase transitions (third phase formation) in the nonpolar (organic) phase. Using small angle X-ray scattering, we find that organic phase structure is dominated by critical fluctuations over the entire range of process-relevant conditions resulting from the critical point associated with the third phase formation phase transition. We describe how the concentration of extracted lanthanide, in the form of a nitrate salt, shifts the third phase formation phase envelope to higher temperatures, acting as a temperature-like parameter. Then, we investigate how changing lanthanide identity affects the maximum loading of the metal before phase splitting and the extractant concentration of the critical point. This suggests an important interplay across length scales, where small changes to ionic radius across the lanthanide series influences mesoscopic critical composition fluctuations and, ultimately, the macroscopic phase behavior.

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Astatine interaction with ion exchange and extraction chromatography resins in nitric acid media

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Astatine-211 is considered one of the most promising radionuclides for Targeted Alpha Therapy. In order to develop reliable procedures to label biomolecules and utilize efficient delivery vehicle principles, one should understand the main chemical characteristics of astatine. The short half-life of ^{211}At (~7.2 h) and absence of any stable isotopes of this element are limiting factors towards studying the behavior of astatine. Our team has developed a procedure for rapid and efficient isolation of astatine from irradiated bismuth material in nitric acid media based on 3-octanone and 1-octanol extraction chromatography resins. Our next step is to consider commercially available resins and their applicability in astatine purification in the same media. Results obtained along with the corresponding sorption mechanisms will be discussed.

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Investigations of technetium-metal and technetium-metal-TBP binding in PUREX-like solvent extraction conditions

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One of the original systems for spent nuclear fuel reprocessing, plutonium uranium reduction extraction (PUREX) is a large-scale solvent extraction process in which the organic phase is composed of tributyl phosphate (TBP) in kerosene and the aqueous phase is comprised of nitric acid. Both uranium (U) and plutonium (Pu) are extracted into the organic phase by nitrate and TBP complexation. Pu is then chemically reduced to its trivalent state and back-extracted into the aqueous phase, thereby separating the two.

This process, however, is complicated by several other elements present in the spent nuclear fuel. Of particular interest for this work is technetium (Tc), particularly Tc-99, a high yield fission product of U-235 with a half-life of 211,000 years. Tc has a wide range of oxidation states from 1- to 7+, which results in complicated redox chemistry that is induced by the radiolysis that occurs from the high radiation fields of spent nuclear fuel. It is also sensitive to the reductants and oxidants used to control the oxidation states of U and Pu to tune their extraction and back-extraction behavior. These factors, as well as the presence of other high yield fission products such as cerium (Ce) and zirconium (Zr), result in Tc being extracted into the organic phase with uranium as either the pertechnetic acid-TBP complex or mixed Tc-metal-TBP complexes. The exact speciation of these complexes has not yet been determined.

This work focuses on understanding the Tc speciation that occurs under PUREX-like solvent extraction conditions. Current investigations focus on cataloging the ways in which Tc, Ce, Zr interact and complex with the TBP-containing organic phase, both separately and together in solution, and what conditions are required for these complexes to form. TBP is known to degrade under radiolysis into dibutyl phosphate, monobutyl phosphate, and phosphoric acid, so current studies also probe the influence of these degradation products on Tc-metal-TBP complexation and on the extractability of high yield fission products into the organic layer.

NUCL

Recent advancements in using metal oxide matrices to investigate non-pertechnetate Tc species

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Technetium-99 (Tc-99) is a long-lived (2.13x10^5 years) radionuclide and exists in large quantities in waste tanks at national labs. Its nine accessible oxidation states make it highly reactive and complicate its redox chemistry. The development of long-term storage solutions for Tc require a fundamental understanding of its stability and redox chemistry in the relevant matrices. The $[Tc^I(CO)_3(H_2O)_3^+]$ species may also be present; the chemistry of Tc(I) in environment and waste tank matrices has been sparsely studied. We extend study of $[Tc^I(CO)_3^+]$ species using highly controlled metal oxides as models for minerals and solid-state materials. Keggin polyoxometalates (POMs) ($[PW_{12}O_{40}]^{3-}$) are air stable metal oxide clusters, which can be tuned for size, charge, acidity, and redox potential. Experimental and theoretical research has shown that W substitution with one, two or three lower valent transition metals such as Vanadium(+5) or Niobium(+5) increases the surface Lewis basicity of the POM, thus rendering the surface more reactive to low valent metals and offering favorable tripodal coordination. Specifically, Nb and V substituted Keggin POMs, $[PM_xW_{12-x}O_{40}]^{(3+x)-}$, where M = V, Nb and x=1,2, or 3 provide surfaces that vary in basicity, electronic environment and lability to probe the speciation and stability of Tc(I). Herein, we present an alternative approach to low pressure CO synthesis of the $[Tc^I(CO)_3^+]$ core and provide an update on the surface stabilization of $[Tc^I(CO)_3^+]$ on electron-rich metal oxide surfaces.

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Solvent extraction chemistry for transuranic recovery in acidic and salt-rich chloride waste streams using a quaternary ammonium ionic liquid

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Process improvements for the separation of plutonium (Pu) and americium (Am) from nuclear waste streams is of pressing importance to reduce activity, dose, and hazard classification of waste and recovery of valuable products. Solvent extraction using liquid:liquid methods of reprocessing acidic and salt-rich aqueous chloride waste streams was evaluated under process-relevant conditions. The quaternary ammonium ionic liquid Aliquat 336®, which extracts anionic metal-chloride species, was used as the organic extractant. Pu is favored to form anionic species in high hydrochloric acid (HCl) solutions, while Am is not, indicating separation of the two can be achieved.

Distribution ratios, K_D (calculated as $K_D = [Me]_{org}/[Me]_{aq}$, where $[Me]_{org}$ and $[Me]_{aq}$ are the final concentrations of metal in organic and aqueous, respectively), were determined through batch extractions using neodymium (Nd) as an Am surrogate and iron (Fe) and uranium (U) as Pu surrogates and likely co-contaminants. The metals were dissolved in a range of HCl and salt eutectic mixtures and contacted with 3 wt % Aliquat 336® in xylenes. Results thus far (Figure 1) indicate that Aliquat 336® diluted in xylenes is a promising extractant to provide efficient separation and recovery of Pu from Am in acidic and salt-rich chloride waste streams.

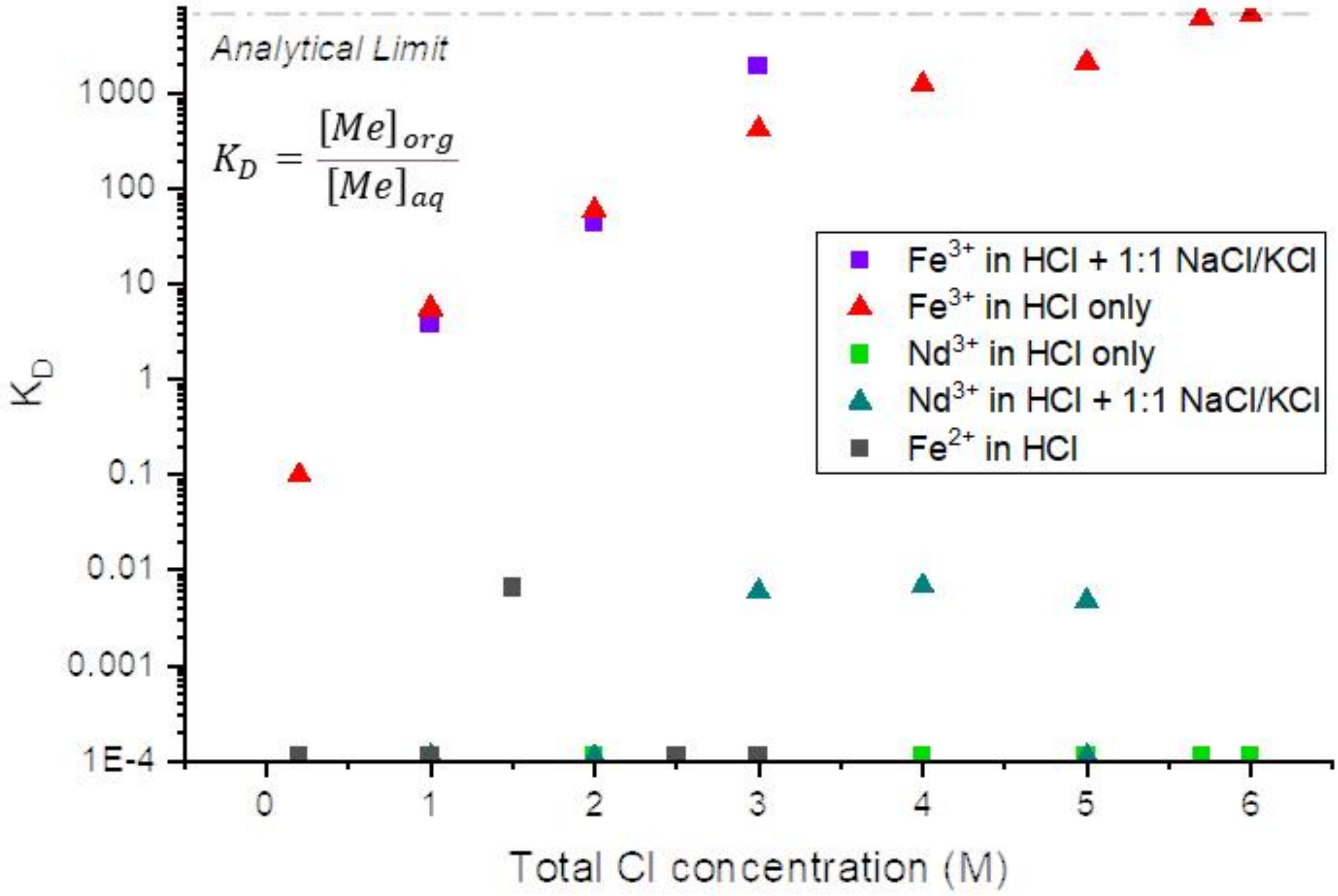

Figure 1 - Distribution ratios (KD) for Fe and Nd in a range of HCl and salt eutectic mixtures contacted with 3 wt % Aliquat336® in xylenes.

NUCL

Effects of closed-shell metal-oxo interactions on uranyl bonding and spectroscopy

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The uranyl cation is the most environmentally relevant form of uranium and is often found in close contact with a variety of heavy metals due to its role in the nuclear fuel cycle. As such, an understanding of how these metals interact with and are able to affect the properties of the uranyl cation is of utmost importance for the purposes of nuclear forensics and nuclear waste stewardship. The research presented herein focuses on the interactions between the uranyl oxo group and two closed shell metal cations, Pb^{2+} and Ag^{+}, in a large family of compounds. The structures of these compounds were determined using single crystal X-ray diffraction and their properties were probed using spectroscopic and computational measurements. From these techniques, we show that close interaction between the oxo group and the metal cation can weaken the U=O bonds as evidenced by a red-shift in the Raman active UO_2^{2+} symmetric stretch peak. This observation was rationalized by computations performed using Natural Bond Orbital analysis which indicated a depopulation of U=O bonding orbitals and a population of U=O anti-bonding orbitals as a result of strong interaction with orbitals on the metal. The stabilization energy associated with these interactions increases as the metal approaches the uranyl-oxo. Close interactions with Pb^{2+} also quench the characteristic uranyl luminescence, likely due to a weakening of the U=O bonds leading to a disruption of the electronic structure of the uranyl unit, though the exact mechanism remains unclear. The effect of the Ag^+ on the U=O bond is comparatively weaker than that of the Pb^{2+}, where only the two compounds with the closest metal-oxo interaction displayed a loss in luminescence. Additionally, interaction with the Ag^+ results in smaller Raman shifts and smaller stabilization energy values at similar metal-oxo interaction distances. Quantum Theory of Atoms in Molecules analysis indicates a loss of electron density in the U=O bonds where the oxo groups interact closely with the Pb^{2+} but did not indicate a similar loss with Ag^+. The difference in the effects of these two metals likely occurs as a result of the lower charge density on the Ag^+ though it is also possible that other properties of the metal cations such as size or the presence (or absence) of a stereochemically active lone pair also play a role.

NUCL

Uranyl-viologen materials as a platform for probing uranyl photoreactivity in the solid-state

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The study of uranium has benefitted greatly from the use of chemical and analytical platforms that serve as bellwethers of the properties of actinide based materials. Herein, we use luminescence quenching kinetics as a platform to measure the photophysical and reactive properties of uranyl materials more broadly and how they are tuned as a function of their characteristics such as composition and structural features. To this end, we synthesized a series of materials featuring the uranyl tetrachloride anion paired with 1,1’-dialkylated-4,4’-bipyridinium cations (i.e. viologens) and characterized their crystal structure, photophysical properties and electronic structure through DFT calculations. Preliminary studies revealed that these materials exhibited photoreactivity in the form of luminescence quenching upon exposure to UV radiation. Subsequent kinetic analysis indicated that the rate of quenching is second-order in nature and the derived rate constants showed a dependence on the identity of the viologen present (methyl, ethyl, or propyl). We have built on these results by expanding our selection of uranyl anionic species to include uranyl acetates, thiocyanates, and bromides to pair with our suite of viologen cations. We assess the photophysical properties of these new materials and investigate whether the character of their photoreactivity is indicative of an underlying property of the given uranyl species, such as ligand bonding character (ionic versus covalent) or favorable charge/energy transfer pathways to the cation. In this way we may provide a simple platform with which to systematically study the reactivity of uranyl-bearing materials, writ large. We expect that this work will inform the design of uranyl functional materials and the establishment of tunable properties when considering uranyl reactivity.

NUCL

Spectroelectrochemistry for characterizing neptunium processing streams to support the plutonium-238 supply program

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Spectrophotometry and electrochemical methods were combined (i.e., spectroelectrochemistry) to simultaneously measure neptunium (0.01–1.0 M), nitric acid (0.1–4 M), and temperature (15–45°C). Measuring neptunium (Np) species in aqueous solutions is challenging because Np persists in multiple oxidation states, has high extinction coefficients, is susceptible to hydrolysis, and coordinates with a wide range of ligands. In nitric acid solutions, Np(IV) exists as a hydrated and/or coordinated ion, while Np(V) and Np(VI) persist as the *trans*-dioxo cations NpO_2^+ and NpO_2^{2+}, respectively. In situ thin-layer spectropotentiometry was used to control Np oxidation states (IV/V/VI) while visible/near-infrared absorption spectra were measured, without compromising the optical properties of the sample. Spectrum features including peak intensity, position, and shape were characterized using multivariate data analysis and revealed interionic associations (e.g., between NpO_2^+ and NpO_2^{2+}) at high Np concentrations. Key findings from partial least squares regression and multivariate curve resolution analyses will be discussed. This work establishes spectrophotometry to accurately quantify Np process solutions for the Plutonium-238 Supply Program.

NUCL

Reactivity of Zn^+ in high-temperature water radiolysis

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Understanding radiation effects on materials and the consequent enhanced corrosion is crucial for the success of both current and next-generation nuclear reactors. The corrosive environment generated due to water radiolysis continues to be a major challenge facing the nuclear industry. It can result in serious plant problems, such as primary stress corrosion cracking of alloys, the deposition of corrosion products on fuel

assemblies and high out-of-core radiation fields.
Zinc injection has been found to reduce Co-60 deposition and prevent primary stress corrosion cracking. Zinc ions are reported to replace Ni, Fe, Co ions in oxides formed on alloys and stainless steels, and this reduces the corrosion release rates. However, the various roles of zinc metal ions in complex reactor chemistry at high temperatures remains unclear.
In the presence of divalent zinc ions in the coolant, radiolytically-generated hydrated electrons generate short-lived monovalent zinc transients, Zn^+. These monovalent ions will subsequently react with the oxidizing species also formed in the system during the water radiolysis. The present study is aimed to provide a detailed understanding of the radiation chemistry of the $Zn^{2+/+}$ system in the temperature range of 25–300°C.
Here we report results from pulse radiolysis experiments using an 8MeV linear accelerator with a specially designed high-temperature titanium cell. We find that the optical absorption spectrum of Zn^+ in water shows an intense temperature-independent maximum at 310 nm with a temperature-dependent extinction coefficient. We demonstrate that the maximum absorption of Zn^+ occurs at neutral pH and any changes in the pH of the medium lead to significant changes in the intensity of the spectrum. This can be explained in acid solution by the number of protons in the system, which compete in the reaction with electrons, and by the formation of Zn^+ hydroxo-forms in an alkaline medium. The kinetics data demonstrate that Zn^+ ions are reactive toward the radiolytically-produced oxidizing species from water. Reaction rates of most of the recombination reactions investigated follow an empirical Arrhenius relationship at temperatures up to 300°C. A bimolecular disproportionation reaction of Zn^+ is not observed under the conditions investigated.
This information is of particular importance in not only understanding the effect of zinc ions in water coolant radiolysis but also in developing kinetics modeling for nuclear reactor design.

NUCL

Role of surface chemistry of several nitrides, carbides, and oxides on water radiolysis under ionizing radiation

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Safety and economic challenges drive the search for new robust materials to enable more efficient and sustainable nuclear energy. Zirconium and silicon carbides and nitrides were recently proposed as fuel cladding materials, and their stability under irradiation needs to be fully understood. One of the concerns is water radiolysis leading to the formation of oxygen, hydrogen peroxide, and hydrogen, which are not favorable in nuclear reactor operation. In this work, we explore the effect of the surface composition on water radiolysis for zirconium carbides, nitrides, and silicon nitrides by evaluating hydrogen production under gamma irradiation. It was found that only the materials that have a significant amount of adsorbed water produce a detectable amount of hydrogen under 1 MGy of gamma irradiation. At the same time, in the presence of the water excess in slurries containing 20-90% of water, the difference between the studied materials was less pronounced. All ceramic powders have slightly increased hydrogen production under gamma irradiation in comparison with pure water. It was previously found that certain oxides, including zirconium oxide, can increase hydrogen yield, while others, like silicon oxide, do not affect hydrogen production. One of the possible suggested mechanisms requires hydroxyl groups present at the surface, and weekly bounded water available in close proximity to the surface. We demonstrate that the surface of zirconium carbide and nitride, as well as silicon nitride, have different amounts of oxygen present in the forms of water and oxides. The role of the oxide film and weakly bonded water on the surface of the ceramic powders in water radiolysis will be discussed.

NUCL

Quantification of molten salt composition for molten salt advanced nuclear reactors

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The aim of this work is to demonstrate a quantification method for chromium in molten fluorides salts. The focus is on the quantification of chromium which is a corrosion product of stainless steel alloys in molten salts.

Elemental composition of FLiNaK is performed in this study by acid digestion followed by inductively coupled plasma optical emission spectroscopy (ICP-OES). FLiNaK samples are doped with varying concentrations, between 100ppm and 1000ppm, of chromium fluoride, CrF_2 and CrF_3 . The effect in the digestion and analysis of chromium when there is a difference in oxidation state of chromium will be noted. The samples are melted in order to have an homogenous mixture, frozen and then digested using the CEM Discover Microwave Digester in a combination of acids. The samples are analyzed by ICP-OES and the chromium concentration measured by the instrument is compared to the known amount added.

NUCL

Observations from un-shielded HPGe background measurements in a nuclear facility

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We have recently had the opportunity to acquire some extended duration un-shielded background measurements using a large volume high-purity germanium (HPGe) detector located in a cold laboratory room but within a Los Alamos National Laboratory nuclear facility. We will report on our observations from analysis of the acquired spectra.

NUCL

Alternating quark nuclear structure effects Coulomb barrier height in H2-H2' fusion

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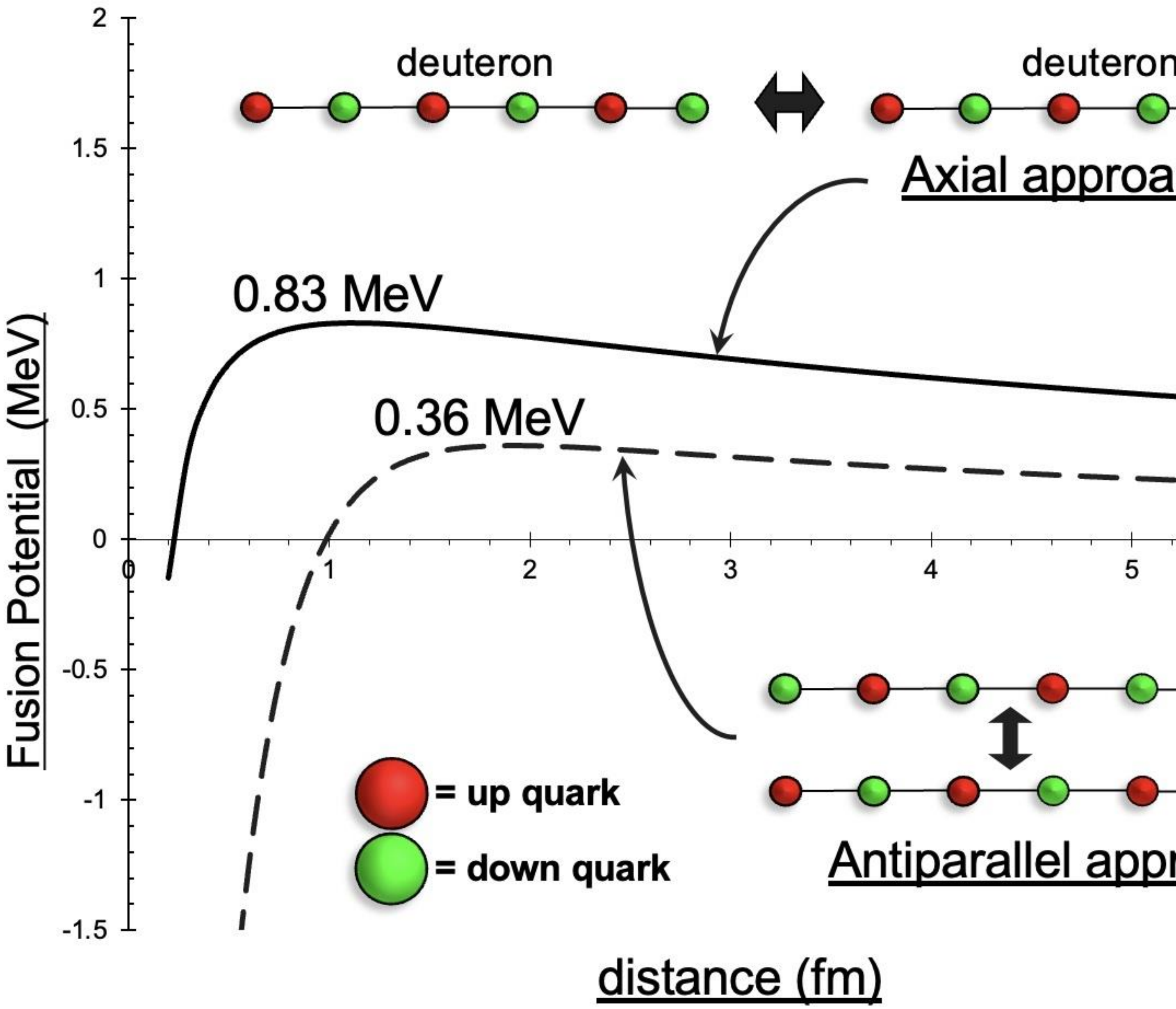
The fusion of hydrogen isotopes promises abundant power at a time when fossil fuels are increasingly problematic. Billions have been spent on hot fusion, and NASA has recently validated low-energy nuclear fusion. Fusion ignition requires confinement of a critical concentration of reactants over time, and sufficient translational kinetic energy to overcome the Coulomb barrier. Reactant structure generally informs reaction kinetics, yet considerations of nuclear structure are notably absent from current theoretical approaches. The textbook Coulomb barrier calculation of 0.48 MeV for d-d’ fusion ignores nuclear steric and rotational effects, treating the deuteron as a point charge at the center of a sphere. The nonzero magnetic moment and unexpected radius-to-mass of the deuteron, however, provide clear evidence that the deuteron is neither a point charge nor a sphere. The alternating quark model (AQM) posits the deuteron as a linear sequence of 6 alternating quarks producing an aspherical Coulomb barrier. AQM is a structural model of the atomic nucleus demonstrating near-perfect correlation ($r(33)=.99$, $p<.001$) with accepted RMS charge radii of stable nuclei through Ar-36. Within the model, quarks occupy average positions and the deuteron has a (-) down quark and (+) up quark on either end. Precession of quark charge explains the deuteron's nonzero magnetic moment, while the rotational radius of its 6-quark sequential structure explains its unusually high radius-to-mass. More importantly, d-d’ fusion is shown to depend on steric effects with a nearly 3-fold difference in Coulomb barrier height depending on whether fusing deuterons approach end to end (0.83 MeV) or antiparallel (0.36 MeV). Magnetic and electric fields within the reaction environment affect the deuteron’s orientation, and suboptimal orientation requires greater input energy to achieve ignition. Deuteron structure thus plays a critical role in fusion kinetics and reactor design.



Nuclear orientation determines Coulomb barrier heights in H2-H2' fusion.

NUCL

Tritium diffusion in Fe-Al aluminide coating bulk phases

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Density functional theory simulations have been carried out to investigate the diffusion of interstitial tritium (T, ^3H) in three Al-rich (>60% at. Al) iron aluminide phases found in the Fe-Al coating of Tritium Producing Burnable Absorber Rod (TPBAR). The phases identified by STEM imaging were hexagonal $FeNiAl_5$, monoclinic Fe_4Al_{13}, and orthorhombic Fe_2Al_5. An atomistic analysis of the structures of $FeNiAl_5$ and Fe_4Al_{13} indicates that these phases can be viewed as the stacking of two layers. The structural particularity of Fe_2Al_5, is that channels are present along the *c*-axis. These channels have a variable Al vacancy content, giving rise to an approximate composition of Fe_2Al_5. Therefore, three stoichiometries for Fe_2Al_x phase, namely Fe_2Al_4, Fe_2Al_5, and Fe_2Al_6, have been studied to evaluate the impact of Al vacancy concentration on tritium diffusion behavior. Simulations using the nudged elastic band method indicated that tritium has preferential diffusion pathways in $FeNiAl_5$ and Fe_4Al_{13}. In $FeNiAl_5$, tritium preferentially diffuses along the *a*-axis in between layers, while in Fe_4Al_{13}, tritium preferentially diffuses across layers, along the *b*-axis. In the case of Fe_2Al_x phases, it was found that the tritium diffusion pathway is affected by the Al vacancy concentrations in the channels. Based on the calculated energy barriers, the diffusion coefficients for tritium in Fe-Al phases have been determined.

NUCL

Development of reductive methods for metal recovery relevant to nuclear material processing

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Most solvent extraction processes use a pH swing or reductive strip to recover actinides from the organic phase. The back extraction of iron as an actinide surrogate from solutions of Aliquat 336 (A336) in xylenes using chemical reductants in hydrochloric acid is reported. This approach is an improvement because it allows us to avoid kinetic issues that can arise within our system due to chemical reactions required at the liquid-liquid interface. Differences in metal recovery, relative extraction kinetics, and O_2 sensitivity are explored with L-ascorbic acid, hydroquinone, oxalic acid, hydroxylamine, and hydrazine via batch extraction studies under variable concentrations of hydrochloric acid and A336. These studies suggest L-ascorbic acid is the most promising chemical additive for recovery of Fe from these solutions, with 96±1% recovery after five successive contacts. Further, spectroscopic studies of L-ascorbic acid in the system gave us insight into how to design the process for implementation in industrial scale applications. These initial results have given us a blueprint for designing reductive back extractions for other metal ions relevant to nuclear material processing.

NUCL

Applications of list-mode time-stamp data from an HPGe gamma spectrometer

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Several commercially available multi-channel analyzers (MCAs) utilized for HPGe spectral acquisition now offer the ability to save data in a list-mode time-stamp format. While the utility of this type of data format is well established for multi-detector configurations for coincidence or anti-coincidence counting applications, we are also looking at how this data format could be used in a single HPGe configuration.

NUCL

High-temperature reactions of simulated uranium oxide pellets doped with cesium and iodide matrices

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SimFuels are synthetic UO_2 materials that contain specific radionuclides or non-radioactive analogs that can be used to conduct research in the absence of irradiated fuel like spent nuclear fuel (SNF). For this research, uranium oxide pellets are pressed and doped with cesium and iodide and heat-treated under various stimuli to examine the chemical behavior of the defects with respect to the uranium oxide chemistry. Cesium-137 is a high-yielding, high-energy gamma emitter with a half-life of about 30 years, often present as a mixed oxide or dissolved inside the [U,Pu] fuel matrix, while Ioide-131 is a short-lived, high yielding fission gas. We hypothesize the possibility of CsI forming in spent fuel in small quantities, and while there hasn’t been any physical proof of CsI in spent fuel, this research aims at providing evidence that CsI can exist in the fuel matrix. The UO_2 pellets are pressed with various concentrations of CsI and heated under various stimuli, including high temperatures and in different atmospheres. We further reduce the concentration of CsI to try to mimic SNF to the best of our ability. Another important aspect of this research is the use of density functional theory (DFT) to help validate experimental findings. DFT has confirmed that CsI is stable in a UO_2 matrix, but this doesn’t explain how it can be formed. Further analysis is required, but the data collected so far, both experimentally and via DFT, are going to be used to help support a machine learning program we are creating that utilizes Bayesian probability, where the goal of the program is to provide a probability to a hypothesis given prior probabilities, i.e., those gathered from experiment and theory.

NUCL

Synthesis of N-[4(2’-[18F]fluoroethyloxybenzoyl)]pyrrolidine-2one by ELIXSY flex/chem automation system

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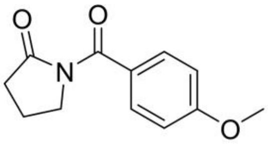
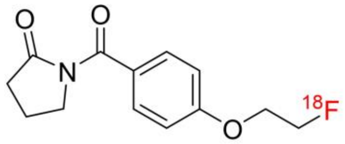
Aniracetam belongs to a family of compounds known as racetams. These compounds have been shown to be capable of binding to neuroreceptors and have been applied as treatments for central nervous system disorders. However, the exact mode of action of these compounds has not been elucidated. Development of racetam/ racetam derivative radiotracers would enable *in vivo* study of these compounds. The safe synthesis of radiotracers necessitates reagents be manipulated inside a hot cell to mitigate human exposure to radiation. This has been accomplished through manual mechanical manipulators, microfluidics, and other automation systems. A potential radiotracer for brain imaging, based on aniracetam, had previously been reported using a microfluidic system. We wish to report the synthesis of the title compound on the automated synthetic platform Elixys Flex/Chem. This alternative automated system is cassette based and uses a robotic arm. The product was obtained with a radiochemical yield of 21% (non-decay corrected), as determined by radio-TLC. Furthermore, the synthesis of the radiotracer precursor was improved. Application of a guanidine base during a deprotection step afforded a phenol intermediate with a yield of 90%. This was a 50% increase in yield, compared to the established deprotection method.



aniracetam



N-[4(2'-[18F]fluoroethyloxybenzoyl)]pyrrolidine-2one

21% RCY (non-decay corrected)

NUCL

Improving radioisotope production and purification in small research reactors: The Szilard-Chalmers process

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As the United States strives to produce more radioisotopes for domestic research and clinical applications, small nuclear research reactors can serve as development resources for improved production of neutron-created isotopes. The Szilard-Chalmers process with high surface area materials is being pursued at the Penn State Breazeale Reactor to develop higher specific activity isotopes. Additional purification efforts such as microfluidic solvent extraction methods are also being investigated in parallel with the Szilard-Chalmers process. Szilard-Chalmers recoil atoms can be harvested via a number of methods, but the simplest uses a solid target matrix and a liquid capture matrix. Emerging materials such as metal-organic frameworks and nanoparticles with high surface areas offer a potential opportunity for increasing the specific activity as the bulk of the captured recoil atoms are from the material surface. As a proof of concept, ^{64}Cu is produced through the (n, γ) reaction from novel natural copper targets and tested with a variety of capture matrices. Microfluidic solvent extraction (SX) separation methods are relatively new and offer many advantages over conventional separation methods.

NUCL

Piezoelectric nebulizer

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In a molten salt reactor, being able to quantitatively know what is in the molten salt mixture is important to monitor corrosion. Generating molten salt aerosol is a unique sampling method that allows for isotopic analysis of a molten salt mixture using various analytical techniques. It is important to keep as much radioactive material inside of the reactor as possible in order to maintain a safe environment. Developing a piezoelectric nebulizer will allow molten salt to stay in the reactor with only a small portion of salt coming out as an aerosol. This research can produce an aerosol from the molten salt in the loop and further analyze its components. In order to use the piezoelectric device, a function generator is needed to generate a vibrational frequency in the piezoelectric device. An oscilloscope is needed to measure the voltage and frequency circulating into the system. A metal mesh disc with micrometer-sized holes is needed in the center to produce an aerosol. Molten salt aerosol has been generated using a piezoelectric nebulizer and a low-temperature nitrate salt mixture using a specific frequency and voltage to operate the piezoelectric nebulizer at optimal conditions.

NUCL

Implementation of FAIR data principles for nuclear spectrometry and related data

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In 2013 the White House Office of Science and Technology Policy (OSTP) issued a policy memorandum, “Increasing Access to the Results of Federally Funded Scientific Research”, directing federal agencies to develop policies to make the publications and data resulting from funded research freely available to the public. In 2016, the ‘FAIR Guiding Principles for scientific data management and stewardship’ were published in *Scientific Data* (2016 Mar 15; 3:160018. doi: 10.1038/sdata.2016.18.). The authors of that work intended to provide guidelines to improve the Findability, Accessibility, Interoperability, and Reuse (FAIR) of digital assets. The U.S. Department of Energy has adopted a Public Access Plan and a number of DOE program offices require Data Management Plans for funded research efforts. We will provide information on the way we have made nuclear spectrometry and related data publicly available in compliance with the FAIR principles.

NUCL

Mechanochemical synthesis of uranyl peroxides: Implications for nuclear fuel reprocessing

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As the world is moving away from traditional fossil-fuel-based energy sources, nuclear power emerges as a promising alternative due to recent advancements in small modular reactors (SMRs) that afford numerous energetic, economic, and environmental benefits. The increase in SMRs technology leads towards a demand for better separations and reprocessing of spent nuclear fuel. Current reprocessing efforts, such as PUREX process, rely on dissolution of solid nuclear fuel in concentrated acids with numerous subsequent solvent extractions, that require sophisticated infrastructure and strict process control. Such approach not only generates large volumes of caustic radioactive liquid waste that is expensive to dispose, but also is not economically viable as we are moving to modular nuclear power. Green alternatives to wet reprocessing could include mechanochemical methods, which have been underexplored within actinide chemistry as a tool to enhance chemical reactivity for reprocessing. Herein, we explore the mechanochemistry of solid uranium dioxide $U(IV)O_2$ and uranium trioxide $U(VI)O_3$ with the range of alkali/alkali-earth metal peroxides to probe the chemistry of uranium in the solid state. We utilized single-crystal X-ray diffraction, powder X-ray diffraction, Raman and IR spectroscopy, as well as, SEM imaging to characterize the resulting product. Mechanochemical grinding of uranium oxides with metal peroxides results in the formation of uranyl triperoxide phases and induces the formation of superoxide anion, which in turn, captures carbon under ambient conditions resulting in alkali metal/uranyl carbonate phases. As a result, mechanochemistry is a solvent-free pathway toward water soluble uranyl peroxide and carbonate phases offering a green alternative to traditional acid digestion of spent nuclear fuels.

NUCL

Effect of ligands on the stability of studtite ($UO_2O_2 \bullet 4H_2O$) under repository and environmental conditions

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Spent nuclear fuel (SNF), currently housed in repositories across the U.S., includes large amounts of uranium, which is a major risk driving contaminant for the environment in the case of leakage. Understanding the solubility of the different uranium phases in SNF, and therefore uranium mobility, is critical. In SNF, uranium has been reported to form studtite ($UO_2O_2 \bullet 4H_2O$), a U(VI)-peroxide structure, through a redox reaction with H_2O_2, formed from the alpha radiolysis of water. SNF is a very complex waste mixture, which usually includes a variety of ligands and chelating agents, used in different processing stages, such as EDTA, NTA and HEDTA among others, which could affect the stability of studtite by contributing to its dissolution and subsequent release of U(VI) in the aqueous phase.

This study investigates the impact of these chelating agents on the stability of studtite as a function of ligand concentration, pH and the presence of oxygen. Preliminary results showed enhanced dissolution of studtite due to the presence of EDTA under circumneutral conditions and a positive correlation between U(VI) release and EDTA concentration under aerobic conditions. On the other hand, at pH 3 and 11 the dissolution of uranium is independent of the concentration of EDTA. These preliminary results show that the presence of EDTA is a liability for studtite stability, specifically at circumneutral pHs, but further study is needed under anaerobic conditions and in the presence of high ionic strength in order to understand the phenomenon better.

NUCL

Thermodynamic and kinetic analysis of uranyl peroxide precipitation via *In-Situ* transmission electron microscopy

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One of the main foci of nuclear forensics is to identify the processing history and potential origin of unknown nuclear materials. Understanding and predicting the morphology of Uranium ore concentrates (UOCs) is emerging as one of the main signatures for identifying the process history. Nonetheless, for morphology to advance, the underlying mechanisms involved in producing the morphological signatures need to be determined. Here, we use the relatively recently developed transmission electron microscopy (TEM) analysis technique, *in situ* liquid phase TEM, to see in real-time the formation of Uranyl Peroxide. To do this, three starting solutions of Uranyl Nitrate Hexahydrate (UNH), Uranyl Chloride (UCl), and Uranyl Phosphate (UPh) are used to precipitate Uranyl Peroxide via radiolysis. That is, using the dose from the electron beam, hydrogen peroxide is produced via hydroxide radicals. Then the hydrogen peroxide reacts with the UNH/UCl/UPh resulting in the formation and rapid onset precipitation of Uranyl Peroxide. Energy dispersive spectroscopy (EDS/EDX) and postmortem High resolution TEM (HR-TEM) lattice fringe imaging are used to confirm the presence of Uranyl Peroxide. Analysis focusing on electron dose, local concentration gradients, and angular dependent growth is used to explain the thermodynamic and kinetic interplay between free energy, pH, and concentration resulting in stable nucleation and eventual growth, as well as the observed features being manifested throughout the *in situ* experiment. Results from this study aid in the evaluation of the thermodynamics and kinetics governing particle nucleation and growth and subsequently the morphology signature on nuclear forensics.

NUCL

Mild and stable chelation strategies for small rare earth radiometals

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The recent US Food and Drug Administration (FDA) approval of numerous ^{68}Ga/ ^{177}Lu-based radiopharmaceuticals underscores the potential of radiometals in diagnostic and therapeutic nuclear medicine. However, $^{68}Ga^{3+}$ and $^{177}Lu^{3+}$ complexes possess disparate coordination chemistry and in vivo behavior, leading to discrepancies where the diagnostic tracer does not accurately predict the distribution and behavior of the radiotherapeutic. This shortcoming can be addressed if both radioisotopes are of the same chemical element (e.g., $^{86/90}$Y, $^{44/47}$Sc) or exhibit chemical homology (^{44}Sc/ ^{90}Y/ ^{177}Lu) and therefore possess matched coordination chemistry and in vivo behavior. Such matched pairs represent a powerful tool to non-invasively identify target expression, stratify patients for subsequent therapeutic intervention, and monitor therapeutic response.
The ^{44}Sc/ ^{47}Sc/ ^{90}Y/ ^{177}Lu isotope tetrad of small rare earth radiometals share similarities in ionic radii and coordination preference yet chemical approaches to utilize these isotopes under mild conditions compatible with a wide range of targeting vectors is critically lacking. To address this gap, we rationally designed a triaza-macrocycle derived chelator, H_4mphospatcn, that is well-matched to the ionic radii and coordination preferences of Sc(III), Y(III) and Lu(III), as supported by computational studies and pH-dependent speciation. Preliminary studies indicate that H_4mphospatcn enables low-temperature (< 40°C) radiolabeling and retains complex inertness with ^{44}Sc, ^{86}Y, and ^{177}Lu. Here, we explore four different strategies to produce a bifunctional derivative that maintains the favorable radiolabeling properties and kinetic inertness of H_4mphospatcn to enable ^{44}Sc-imaging and ^{47}Sc/ ^{90}Y/ ^{177}Lu-therapy applications.

NUCL

Effects of high ionizing radiation on organic solid-state materials

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Cocrystals are a promising class of materials for the future of functional material design and use in electronics and coatings. Herein we report the effects of gamma radiation on both single component- and co-crystalline organic materials. Radiation damage was

evaluated via single crystal- and powder- X-ray diffraction, Raman spectroscopy, differential scanning calorimetry, and DFT surface calculations. After irradiation with 11 kGy dose, both single- and multi-component materials were analyzed and compared to their pre-irradiated forms. One of the single components, 1,4-dibromotetrafluorobenzene (1,4-$C_6Br_2F_4$), underwent enhancement of physical properties affording its sublimation within an hour of exposure to air post-irradiation, attributed to impurities adsorbed to the chemical's surface. Surface changes are reported for 1,2-bis(4-pyridyl)ethylene (4,4'-bpe) via Raman spectroscopy with drastic change in peak intensities pre- and post-irradiation. Throughout the study, the cocrystal (4,4'-bpe-1,4-$C_6Br_2F_4$) affords little changes from radiation exposure, thus supporting the rational design of organic materials afford competitive alternatives to traditionally used inorganic materials for radiation damage resistance.

NUCL

Actinium-225 purification via membrane adsorbers with covalently tethered diglycolamide ligands

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Actinium-225 is an accelerator-produced, alpha-emitting isotope that shows promise for targeted alpha therapy, an emerging cancer treatment. A thorium target is irradiated and then, after production, microgram quantities of Ac-225 must be purified from residual thorium and byproducts (e.g. lanthanides). Current purifications rely on DGA resin (diglycolamide ligands physisorbed in an acrylic resin). Transport of ions to binding sites in resin-packed columns is governed by diffusion, so they must be operated at low flowrates (< 1 mL/min). This leads to long purification times (> 6 hours). Membrane adsorbers are an alternative to resins in which ion transport is governed by convection; therefore, they have the potential to perform the same separation in < 1 minute. In contrast to liquid-supported membranes, membrane adsorbers contain covalently bound ligands, preventing ligands from leaching at high flowrates. This contribution describes our efforts to 1) synthesize new, acid-stable membrane materials via electrospinning and 2) synthesize and covalently attach DGA ligands to those membranes. Membranes are synthesized by electrospinning solutions of poly(styrene-*co*-chloromethyl styrene) or poly(styrene)/poly(chloromethyl styrene) to create fiber mats. Membranes are cross-linked after electrospinning to increase the stability in organic solvents needed for grafting. Membrane surface area is measured by nitrogen adsorption experiments, permeability by pure water flux experiments and porosity by non-wetting solvent absorption. DGA derivatives are synthesized with reactive end groups (amines or alkenes) to bind to membranes. In initial experiments, lanthanum (a surrogate for actinium) is used in batch adsorption experiments to determine the binding capacity and kinetics of the DGA-functionalized membranes in hydrochloric acid. The results of this research are paving the way for faster separations in radiochemistry.

NUCL

Investigations into separation of molybdenum from other fission fragments using a phase transfer catalyst

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The Nuclear Energy eXperimental Testing Laboratory (NEXT Lab) seeks to provide global solutions to its most critical needs: clean energy, access to clean water, and access to useful radiomedicine. In order to do so, the NEXT Lab is assembling a fluoride molten salt research reactor. One of the teams working within NEXT Lab is the Isotope Extraction and Purification team (IEP). The team seeks to study chemical methods to identify and purify useful radioisotopes that are products of fission and corrosion reactions. Current efforts are aimed at non-destructive elemental identification including known fission and corrosion products such as iron, molybdenum, and chromium. It is known those elements will be present as the reaction is ongoing. These products have been made evident in molten salt, and corrosion samples, as well as analysis of their respective aqueous solutions. The aqueous solutions potentially produced from the reactor will hold hundreds of fission fragments, therefore a critical step is to selectively capture elements among other fragments. The focus of this research is in molybdenum isolation with the aid of long-chained quaternary ammonium molecules that serve as phase transfer catalysts. The catalyst is dissolved in an organic solvent of choice, and then the organic layer is placed on top of an aqueous one that contains molybdate. In this bilayer system, the catalyst was found to be able to interact with molybdate and pull it to the organic phase. Characterization of the phases with infrared and UV-Visible spectroscopy confirms the migration of molybdate into the organic phase, as well as evidence of a complex produced with the catalyst.

NUCL

Optimization and development of a calibration curve for a molybdenum indicator

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The Nuclear Energy eXperimental Testing Laboratory (NEXT Lab) is seeking to provide global solutions to the world’s most critical needs in energy, water, and access to medicinal radioisotopes. In order to accomplish this objective, the NEXT Lab is developing a fluoride molten salt research reactor. Among the byproducts of a nuclear reaction, there will be hundreds of different types of fission fragments produced. These isotopes are found in the molten salt and its gaseous headspace. One of NEXT Lab’s research interests is to isolate and identify these radioisotopes. The focus of this

research is the quantification of molybdenum, which is one of the fission fragments and also a component in steel. During processing, the presence and quantity of molybdenum in our reactor salt samples need to be confirmed. Colorimetric indicators are used to test for the presence of specific elements and compounds. In this research, an indicator method using KSCN that has a long shelf life and a specific consistent color reaction was tested. A calibration curve was created based on Ellis and Olson's research which described the KSCN indicator method (Ellis and Olson). In this work, several parameters were studied in order to find the best conditions for the KSCN indicator method. The final calibration curve was made using the KSCN indicator method as modified by experimental data produced in this work.

NUCL

Production and purification of ^{48}V from alpha-irradiated ^{nat}Sc foil

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Recently, there has been an interest in acquiring more accurate nuclear reaction data by performing direct neutron reaction measurements with targets of radioactive nuclei to improve computational models used in nuclear validation applications and to predict the outcomes of astrophysical phenomena such as stellar nucleosynthesis. ^{48}V ($t_{1/2}$ = 15.9735 d) has been identified as an isotope that requires improved nuclear data for the Stockpile Stewardship program. One possible method to produce ^{48}V in the required high isotopic purity for accurate nuclear reaction measurements is via the ^{45}Sc(α, n)^{48}V reaction. However, the lack of experimental data for the ^{45}Sc(α, γ)^{49}V reaction impedes the ability to accurately predict the attainable purity. Therefore, we set out to irradiate two ^{nat}Sc foil stacks with 24.3 MeV alpha particles at the Institute for Structure and Nuclear Astrophysics at the University of Notre Dame. Upon returning to Michigan State University, one of the foil stacks was used to optimize the radiochemical separation method for V and Sc. There were two separation methods we examined: one involving the use of a single large N,N,N',N'-tetra-n-octyldiglycolamide (DGA) column and the other involving the use of an AG 1-X8 anion exchange column in the hydroxide form and a small DGA column (An^-+DGA) sequentially. In both cases, we successfully separated ^{48}V from ^{nat}Sc, achieving ^{48}V recoveries of 96(5)% and 92(4)% for DGA and An^-+DGA respectively. The method utilizing only one DGA column yielded more favorable recovery yields with faster separation times, so we used it to extract radiovanadium from the other foil stack. Fractions containing ^{48}V/^{49}V from this last foil stack were used to produce samples for liquid scintillation counting to determine the actual ^{48}V/^{49}V ratio and the viability of this production method to produce radioisotopically pure ^{48}V.

NUCL

Impact of siderophores on actinide mobility in the environment: Eu interaction with manganese oxides in the presence of desferrioxamine B (DFOB)

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Manganese oxides participate in a variety of geochemical reactions that affect ground and surface water chemistry as well as soil composition. Their high sorption and scavenging capacities as well as their capability to influence chemical processes more significantly than their concentrations would suggest has made them a species of interest in environmental research. Due to past practices and accidental releases of nuclear waste into the environment, it has become increasingly important to find ways of influencing the fate and transport of actinides such as Americium, begging the question as to how manganese oxides interact with said contaminants. In the present study, Europium was used as a non-radioactive surrogate of Americium and its sorption on manganese oxide substrates in the presence and absence of the siderophore DFOB was studied. Siderophores are biologically produced organic ligands that strongly complex with Fe (III) but can also form strong complexes with other metals such as Mo, Mn, Co, and Ni. Batch experiments were conducted where Eu was brought into contact with pyrolusite, bixbyite and manganite in the presence and absence of DFOB in a 6-8 pH range and at varying substrate concentrations. Results show that the presence of DFOB does not play a significant role on Eu sorption at pH 6 when in contact with manganese oxides as the average percent Eu sorption is above 60% for all samples. At pH 8 the speciation diagram of the contaminant confirms that it precipitates, and results show that the presence of the ligand does not hinder its precipitation. For bixbyite, results show that Eu sorption increases with increasing substrate concentrations. Future studies aim to further clarify the mechanism behind these interactions by observing the behavior of DFOB derivative DFOD.

NUCL

Spectrophotometric study of Pu(VI)-oxalate speciation and the impact of pH

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Available literature related to hexavalent plutonium in the presence of oxalate ($C_2O_4^{2-}$) is severely limited, primarily due to the reduction of Pu(VI) to lower oxidation states and the low solubility of the resulting Pu-oxalate complexes. The low solubility of tri- and tetravalent plutonium oxalates has been utilized as a means to purify plutonium on an industrial scale for decades. However, the presence of the slightly more soluble

hexavalent plutonium oxalate should not be ruled out due to the possibility of incomplete reduction of Pu(VI) in Pu-oxalate systems.

A spectrophotometric study was performed to investigate the aqueous behavior of Pu(VI) in the presence of oxalate as a function of pH (1, 3, >6), metal-to-ligand (M:L) ratio (1:10 – 10:1), and time. Solutions containing oxalate were pH adjusted and then were spiked with a Pu(VI) stock solution to reach the desired M:L ratio. The reaction mixture was subsequently analyzed by ultraviolet-visible near-infrared (UV-vis-NIR) spectroscopy and compared to Pu(VI) in the absence of oxalate at the same pH. Solutions were sampled as a function of time to monitor the reduction of plutonium. Preliminary thermodynamic calculations were performed to determine formation constants for possible Pu(VI)-oxalate complexes.

Two wavelength ranges (820-870 and 900-1050 nm) in the NIR spectrum were observed to contain absorption bands indicative of Pu(VI)-oxalate complexation. These absorption bands, identified in systems at pH 1, 3, and >6, were sensitive to changes in pH and M:L ratio, resulting in isosbestic points that indicate the presence of at least two Pu(VI)-oxalate complexes in solution. UV-vis-NIR data coupled with thermodynamic calculations have provided more insight into the behavior of Pu(VI) in the presence of oxalate.

NUCL

Interaction and complexation of uranium with EDTA under environmentally-relevant conditions

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The interactions of uranium (VI) and uranium (IV) with EDTA were investigated under anoxic conditions, in the pH range of 2-12, and at low ionic strength. These data help define the redox effects of EDTA on the speciation of uranium and target its high pH speciation (pH > 8) under environmentally-relevant conditions. EDTA is a strong complexant, but it also potentially affects the oxidation state distribution of multivalent actinides. Uranium (VI), formed stable complexes with EDTA at near-neutral conditions (pH ~ 6-8) but the precipitation of hydroxide phases were observed at higher pH even when EDTA was present. At pH <6, an EDTA phase was precipitated and some reduction to U(IV) was also noted. Uranium (IV) formed stable complexes with EDTA under the range of conditions investigated confirming the high stability of this complex as well as the lack of redox effects seen elsewhere. A 1:1 U-EDTA complex predominated at pH < 8, but further hydrolysis was noted at higher pH. This higher-pH speciation is often missing in the environmental chemistry models of uranium and is likely relevant when pH > 8 (e.g. many repository project conditions) are present in the environment. A re-estimation of the 1:1 formation constant and a proposed higher-pH speciation model for the uranium(IV) speciation is provided and discussed. These data

help provide a greater understanding of the effects of organic complexants on the behavior of multivalent actinides in the environment.

NUCL

Spectrophotometric determination of americium-EDTA complexation in perchlorate media at elevated temperature

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Americium (z = 95) is a manmade radioactive element generated by the bombardment of uranium or plutonium by neutrons in a nuclear reactor. In terms of inventory at the Waste Isolation Pilot Plant (WIPP) (i.e., the world's only currently-operating deep geologic repository for the disposal of defense-related transuranic waste), the radioactivity of Am-241 is of comparable concern to that of plutonium (> 1,000,000 Ci) and, with a half-life of 432 years, poses a radiological risk for thousands of years. Ethylenediamenetetraacetic acid (EDTA) is an organic complexant commonly used to produce, process, and separate actinide elements or decontaminate items contaminated with actinides, and is thus co-disposed with Am at the WIPP. In this work, we used UV-vis-NIR spectrophotometry to study the effect of elevated temperature on Am-EDTA complexation. Samples were prepared in an anoxic glovebox with 10^{-5} M Am-243 and H-Na-EDTA salt (with H and Na ranging from 0–4, depending on the desired pH) in 0.1 m $NaClO_4$ as a function of pH (1–13), temperature (25–90°C), and time (0–60 days). At each time point, the pH of the sample was measured and spectra were acquired using a Varian Cary 5000 UV-Vis-NIR spectrophotometer equipped with a temperature controller. Samples were then filtered through 10 kDa filters and measured by ICP-MS to determine concentration, so as to check for precipitation and normalize spectral measurements. The resulting stability constants contribute to a growing actinide thermodynamic database and can be used to determine the extent and likelihood of Am mobility in the environment.

NUCL

Technetium complexation with multidentate carboxylate-containing ligands: A combined solubility, spectroscopic, and theoretical study

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^{99}Tc is a low energy beta emitter with a high fission yield from both ^{235}U (~6.1%) and ^{239}Pu (~5.9%), making it a radionuclide of particular interest in the context of nuclear

waste disposal. Tc has 9 oxidation states; Tc(IV) and Tc(VII) are the most common. Notably, Tc(VII), which exists predominantly as pertechnetate (TcO_4^-), is considered soluble and mobile, while Tc(IV) forms sparingly soluble TcO_2(s) and is characterized by strong sorption. Many small organic molecules capable of strong aqueous complexation interactions may be present in scenarios where Tc is disposed, and these interactions can increase the solubility and mobility of Tc. For these reasons, it is essential to understand the impact of complexing organic ligands on the solubility, speciation, and redox distribution of Tc to determine the fate and transport of Tc under relevant boundary conditions. Within this contribution, we performed a series of over- and undersaturation solubility studies under reducing, anoxic conditions coupled with advanced spectroscopic measurements and theoretical calculations. Five organic ligands (L) with environmental and repository relevance were investigated: L = ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citrate, oxalate, or phthalate. Tc, added to the experiments either as $Tc^{IV}O_2$(am,hyd) or as a $NaTc^{VII}O_4$ solution, was reacted with experimental solutions at constant pH (9, 11, or 13), ionic strength (0.7 M NaCl-NaOH-Na_xL), and ligand concentration (0, 12, or 100 mM). Experiments with TcO_2(am,hyd) were all performed in the presence of $SnCl_2$ as a redox buffer, while experiments with TcO_4^- were performed in both the presence and absence of $SnCl_2$. Solutions were analyzed with pH and E_h measurements, liquid scintillation counting for aqueous Tc concentrations, selected UV-Vis-NIR spectrophotometric measurements, and Tc K- and L_3-edge X-ray absorption spectroscopy. Additionally, Tc L_3-edge spectra were complemented with multiconfigurational relativistic *ab initio* calculations. Data was interpreted in the context of oxidation state determination, speciation identification, structural elucidation, and thermochemical model generation, thus providing further necessary thermodynamic information for the determination of the fate and transport of Tc in the context of waste disposal.

NUCL

Technetium dioxide solubility at elevated temperatures

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To understand the risks associated with deep geologic storage of nuclear waste over geologic time frames, thermodynamic constants describing the equilibrium behavior of solubility-controlling radionuclide phases are needed, particularly for the elevated temperature conditions expected in repository environments. Specifically, this work seeks to quantify the solubility of technetium dioxide ($Tc^{IV}O_2$) at elevated temperatures (up to 80 °C) and to define the variable temperature Tc^{IV} hydrolysis constants over the pH range 1–11.5. Additional solubility experiments conducted from oversaturation of TcO_2 at variable ionic strengths will further provide a means to quantify ion interaction coefficients appropriate for activity corrections using the specific ion interaction theory (SIT) or the Pitzer model. Preliminary TcO_2 solubility data collected under anoxic conditions are in good agreement with Tc^{IV} solubility simulations generated using the

geochemical code PHREEQC v.3.7 and the thermodynamic constants currently available in the LLNL.v8.r6+ database. This work will increase the accuracy of predictive models of Tc solubility and transport in elevated temperature and ionic strength environments, providing a means to better assess the specific risks associated with the storage of technetium in deep geologic repositories.

NUCL

Environmental fate of actinide-siderophore complexes: The case of desferrioxamine B-actinide-manganese oxide ternary system

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Anthropogenic activiites related to the nuclear fuel cycle have produced large volumes of nuclear waste, that always include uranium and trivalent actinides as part of their composition. Poor past waste management practices have resulted in the release of actinides in the soil and groundwater with adverse effects in the environment and the biosphere. There is a need for a btter understanding of the factors that govern the fate and transport of contaminants, especially the ability of naturally ocurring ligands to promote or hinder the adsorption of radionuclides to minerals, which is a potential pathway for natural remediation however.

The current work examines the complexation of U(VI) and Eu(III), as a non-radioactive surrogate for trivalent actinides, with desferrioxamine B (DFOB - a hydroxamate type siderophore), and the interactions of this complex with common manganese minerals. Manganese oxides were selected as representative natural substrates due to their well known high adsorption and redox capacity. Sorption experiments with U(VI)-DFOB complex were performed at circumenutral conditions and revealed that DFOB promotes the sorption U(VI) on manganese oxides. On the other hand, europium sorption in the presence of DFOB under slightly acidic conditions remain unaffected, but DFOB creates a stable soluble complex with europoum at pH 8, where free europium is not encountered. These results indicate that uranium sorption is heavily influenced by the presence of siderophores, which can assist in natural attenuation, decreasing uranium mobility in the environment, whereas in the case of trivalent actinides,ophore presence promotes contaminant proliferation.

NUCL

Trends of adsorption and desorption of rare earth elements on uranium oxide minerals

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Rare earth element (REE) signatures are used in nuclear forensics to understand the origins of uranium minerals. Most naturally occurring uranium ores have REEs in their structure that are geogenic in origin and, hence, constitute a unique signature that depends upon which geologic deposit the mineral was extracted from. Given that REEs are essential to several modern industries and that anthropogenic inputs to environmental systems are increasing, it is important to understand how REEs behave at the uranium mineral–water interface and whether they can influence the geogenic REE signatures of uranium minerals. We used batch sorption experiments to examine the competitive sorption of REEs on $UO_{2(s)}$ and $U_3O_{8(s)}$ under oxic conditions as a function of time, pH (5–7), and ionic strength (0.002 M, 0.25 M, 0.5 M). Typical S-shaped sorption edge were observed at steady-state and were attributed to inner-sphere complex formation when the solid phase was U_3O_8, and both outer- and inner-sphere complexation when the solid phase was UO_2. REE fractionation (i.e., preferred adsorption of light REEs (LREEs) onto the uranium mineral surface as compared to the heavy REEs (HREEs)) was observed in all systems, but was more apparent when the solid phase was U_3O_8 and less apparent at higher ionic strengths. At high ionic strength, a strong tetrad pattern was identified across the LREEs. Dissolution of uranium oxides at the end of batch sorption experiments revealed unique REE signatures, even at low pH when the fraction of sorbed REE was low. Batch desorption experiments and X-ray absorption analyses were also performed in order to help elucidate the nature of the surface complexes formed at the uranium mineral–water interface. Future expansion of this work to “aged” uranium oxide minerals will lead to a better understanding of the effects of the environment on alteration of REE signatures in uranium minerals.

NUCL

Impact of crystal orientation on sorption uptake and surface speciation of Y(III) on orthoclase

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Trivalent minor actinides, An(III), pose a high environmental risk in the long-term storage of spent nuclear fuel in deep geological repositories. Their environmental fate can be controlled by interactions with minerals of repository’s host rocks. One host rock considered in the US is a plutonic igneous rock enriched with feldspars. Therefore, a fundamental understanding of retention of An(III) by feldspar surfaces contributes to a reliable risk assessment of repository sites. Typically, sorption behavior is studied using mineral powders, in which information about crystallographic effects on sorption processes are not accessible.
Here, we study adsorption of Y(III), a rare earth analogue for An(III), on two different

crystal orientations, (001) and (010), of orthoclase, the K-endmember feldspar mineral, using surface X-ray diffraction (SXRD). We identify a bidentate inner-sphere species at a distance of ~1-2 Å from the top surface oxygens with a coverage of < 0.2 Y^{3+}/A_{UC} (A_{UC}: area of the unit cell; $A_{UC,(001)} = 55.53$ Å^2, $A_{UC,(010)} = 30.82$ Å^2). Outer-sphere and extended outer-sphere sorption complexes are found at distances of > 4 Å with coverages of > 0.2 Y^{3+}/A_{UC}, depending on pH and concentration of Y^{3+}. Uptake of Y(III) increases generally with increasing [Y(III)] and pH, in good agreement with results reported for mineral powders.

The comparison of the reactivity of the two crystal facets shows that the molecular structure of the adsorbed complexes on the two crystal orientations appears similar. However, the quantitative contributions of the species differ presumably because of a different surface charge density of the two investigated crystallographic planes. These observations emphasize the importance of understanding facet-dependent reactivities to enable the development of more reliable predictive thermodynamic models of the mobility of contaminants in the environment.

NUCL

Role of mineral particle size on the sorption behavior and redox chemistry of plutonium

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Plutonium is present in the environment due nuclear weapons production and testing and poses an extensive threat to public health because of its radiological toxicity and long half-lives (e.g., $t_{1/2,\ Pu\text{-}239} = 24,100$ years). The primary factor in determining the mobility of plutonium in the subsurface environment is oxidation state. While Pu(IV) is generally assumed to be the least mobile oxidation state and Pu(V) the most mobile oxidation state, certain caveats exist, such as the potential for nanoparticle-facilitated transport. Previous studies report that decreasing the diameter of nanoparticles can impact the chemical behavior of metal due to the increase of chemical reactivity and surface area at smaller sizes. Thus, we hypothesize that nanoparticles may influence the sorption and reduction of Pu due to the presence of more undercoordinated and defective sites at the nanoparticle surface. To test this hypothesis, we conducted batch sorption experiments with hematite (α-$Fe^{III}_2O_3$) and magnetite ($Fe^{II}Fe^{III}_2O_4$) nanoparticles as a function of nanoparticle diameter under environmental conditions (e.g., constant ionic strength of 0.1 M NaCl and pH 8). Preliminary sorption data shows that Pu sorption to nano-magnetite is faster than Pu sorption to nano-hematite. However, nano-hematite shows more Pu(V) reduction than nano-magnetite. Further research is needed determine if this behavior is due to the presence of Fe(II) in the magnetite structure or the smaller particle size of nano-magnetite (8 nm) as compared to nano-hematite (40 nm). The results of these experiments will lead to an understanding of how changes in particle size affect the rate and extent of Pu sorption and reduction and, ultimately, how these effects impact the chemical behavior of Pu at the mineral-water interface.

NUCL

Sorption and reduction behavior of plutonium on Al-substituted hematite (α-Fe_2O_3) and goethite (α-FeOOH)

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The ability to predict the mobility of plutonium (Pu) in geologic and engineered environments requires geochemical understanding and modeling approaches that can describe the redox behavior of plutonium in the presence of complex mineral assemblages. Metal substitution (i.e., the presence of impurities) in minerals occurs naturally due to geologic and anthropogenic processes. Iron oxides (such as hematite (α-Fe_2O_3) and goethite (α-FeOOH)) are some of the most abundant and sorption-reactive mineral phases in surface and subsurface environments, and commonly contain up to 15% aluminum (Al). Iron oxides are also an integral part of determining the ultimate performance of a generic geologic repository (e.g., granite, clay, salt) for used nuclear fuel and of influencing contaminant fate and transport in the environment. We hypothesize that estimates that fail to account for impurities in mineral assemblages result in inaccurate projections of Pu redox behavior and mobility in the environment. To test this hypothesis, we combine the application of (i) macroscopic batch sorption experiments with synthetic Al-substituted minerals and (ii) synchrotron-based X-ray absorption spectroscopy (XAS) to develop a more comprehensive understanding of plutonium sorption and reduction as a function of mineral complexity. XAS reveals that Pu sorption to Al-substituted iron oxides leads to different coordination environments compared to sorption to their Al-free counterparts. Determining the oxidation state distribution, speciation, and bonding environment of Pu associated with the solid phase will help us improve our understanding of surface-mediated reduction and immobilization of Pu in the environment.

NUCL

Detection of pertechnetate using anodic stripping voltammetry on carbon electrodes

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Technetium-99 (99Tc) is a primary fission product of 235U, 233U, and 239Pu and is a major constituent of radioactive waste. 99Tc is commonly found as pertechnetate

(TcO4-), an anion that does not readily adsorb to natural sediment and is extremely mobile in environmental water systems. With concerns that radioactive waste may be leaking from sub-surface storage tanks and potentially reaching groundwater, developing detection methods for TcO4- is important. Square wave anodic stripping voltammetry (SWASV) is a simple electrochemical technique that has yet to be investigated for pertechnetate due to the high potential required to form solid TcO2. In this work, we use SWASV with a variety of carbon electrodes to determine the optimal conditions for the detection of TcO4- in a variety of solutions including acid, basic and neutral pH. Carbon electrodes such as glassy carbon, boron-doped diamond, and nitrogen-doped tetrahedral amorphous carbon were examined. Carbon electrodes are ideal for the detection of pertechnetate due to their robust nature, low background current, and wide windows when compared to metal electrodes. Control studies included optimization of the deposition potential and time. In addition, calibration curves were created for each solution’s optimized parameters. Several analytical figures of merit such as the sensitivity, limit of detection, and limit of quantification were determined. This work expands upon the use of carbon electrodes for trace detection of environmentally relevant analytes.

NUCL

Oxygen isotope ratios of uranium oxides during precipitation and reduction to uranium dioxide

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Oxygen isotope ratios of nuclear materials are of great interest to the nuclear forensics community. With high fidelity in the measurements and a fundamental understanding of reactions altering $^{18}O/^{16}O$ ratios, these signatures could help elucidate the production history and production location of unidentified nuclear materials. One commonly studied nuclear material is uranium dioxide (UO_2) as it is the main fuel used within power reactors. UO_2 is commonly produced by precipitating uranium from a nitric acid solution as a uranium ore concentrate (UOC) followed by reduction in a hydrogen furnace. The initial precipitation reaction can impart unique oxygen isotope ratios based on the water and chemical environment (i.e., pH, complexants, etc.) present in solution. Those $^{18}O/^{16}O$ ratios will likely also be altered during the high temperature reduction to UO_2. To fully probe these phenomena, sodium diuranate (SDU) and magnesium diuranate (MDU) were precipitated from three individual waters containing a low, neutral, and high $^{18}O/^{18}O$ ratio. All of these materials were then reduced to UO_2 in a hydrogen furnace with and without steam present. The reductions without steam will enable us to identify oxygen isotope fractionation at the elevated temperatures while the reductions with steam will allow us to probe oxygen isotope exchange between the U-oxides and water vapor. Finally, the morphology of the synthesized materials will be quantified using scanning electron microscopy (SEM). It is hypothesized that differences in the starting

morphology of the SDU and MDU will affect the $\delta^{18}O$ ratios of the resultant UO_2 and affect the rate at which the materials are reduced.

NUCL

Shaped radiation resistant materials: A Step forward in the nuclear waste management industry

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The emission of volatile radionuclides, which must be captured and subsequently stored, significantly complicates the process of recycling spent nuclear fuel. Solid adsorbents, particularly ultramicroporous metal-organic frameworks (MOFs), could be effective at capturing these volatile radionuclides, such as ^{85}Kr. MOFs, on the other hand, are shown to be more Xe-philic than Kr and to have a comparable affinity for Kr and N2. Additionally, the adsorbent must be radiation stable. To address these concerns, we developed radiation-resistant materials with high selectivity for Kr over Xe and N_2, resulting in a significant reduction in nuclear waste volume. The stability of the materials against gamma and beta irradiation has been thoroughly investigated, demonstrating that the metal center and coordinating groups of the organic linker are crucial for the MOF's radiation resistance. The high-performance materials were processed into monoliths and membranes for practical applications utilizing a facile and highly scalable synthetic technique.

NUCL

NiO_x modified cotton fabric: Technical textiles towards Uranium removal from water

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In this present work, nickel oxide (NiO_x) nanoparticles were coated over cotton cloth for U^{6+} removal under various environmentally relevant conditions. Characterization of the NiO_x-coated cotton cloth showed a nanoflower-structured morphology over the cotton fabric, with poly-crystalline $Ni(OH)_2.2H_2O$ and microcrystalline cellulose on the surface. XRF analysis of the cloth revealed the presence of 87% of Ni as NiO, while XPS analysis indicated that the Ni present on the cloth was in the form of $Ni^{2+}2p_{3/2}$ and $Ni^{3+}2p_{1/2}$. The NiO_x-coated cotton cloth exhibited excellent U^{6+} immobilization with 93.5% removal within 6 minutes. The sorption capacity was determined to be 12.05 mg/g, and equilibrium studies indicated favorable monolayer adsorption. Solution pH having a significant effect on U^{6+} sorption on NiO_x-coated cotton cloth, with maximum immobilization occurring at pH 6. Sorption kinetics was best explained using pseudo-second order kinetics and indicated a combination of chemisorption at acidic to neutral

pH conditions, and U^{6+} intra-particle diffusion into the chrysanthemum flower-like nanostructured pores. Post-sorption XPS of U^{6+} sorbed NiO_x modified cotton cloth revealed only U^{6+} with no reduced forms, suggesting a pure adsorption-based immobilization mechanism. The superior performance even in the presence of competing ions$^-$demonstrated that the NiO_x-coated cotton cloth is a low-cost, effective material for U^{6+} removal.

NUCL

Actinide silica colloids in high ionic strength environments

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Colloids increase the mobility of actinides in the environment. These colloids can be formed intrinsically, as is well known for the hydrolysis of many actinides, or through interactions with mineral fragments. Understanding the colloidal behavior of the many components of nuclear waste is useful for calculating release scenarios in deep geological repositories such as the Waste Isolation Pilot Plant (WIPP). Silica is a prevalent component of nuclear waste and is known to form colloids with many actinides in low ionic strength environments [1,2]. These studies were extended to high ionic strength environments (I = 5 m) and a wide pH range (pH = 2-12). The studies focused on U(IV), Np(IV), and Nd (III) as an analog for Pu(III) and Pu(IV) behavior under these conditions.

NUCL

Plutonium transport in sediments from the Hanford site, USA

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Beginning with the Manhattan Project in 1943, 1.85×10^{15} Bq (200 kg) of plutonium (Pu) were released into over 80 unlined cribs, trenches, and field tiles at the Hanford Site, Washington, USA. Specifically, the Z-9 trench received over 4 million liters of Pu-laden reprocessing waste, containing an estimated 50-140 kg Pu, between 1955 and 1962. Approximately 90% of the waste deposited in the trench consisted of high ionic strength (~5 M nitrate, ~ 0.6 M Al), acidic (pH ~ 2.5) aqueous solutions, while the rest of the waste consisted of organic solvents including tributyl phosphate (TBP) and its degradation products, carbon tetrachloride (CCl_4), kerosene, and lard oil. The majority of the Pu was observed to precipitate in the first several centimeters beneath the trench, but a small fraction of the Pu was detected in the vadose zone at depths of 37 meters.

The exact mechanisms controlling Pu mobility beneath the trench are unknown, but Pu migration is likely driven by weak sorption of aqueous Pu under low pH conditions as well as the formation of Pu-TBP-nitrate complexes in the organic phase.
In this study, the reactive transport of Pu in uncontaminated Hanford Site sediments was investigated using column experiments. The sediments were first thoroughly characterized then loaded into glass columns. Pu-bearing aqueous solutions ([Pu] = 1 x 10^{-8} M, [NaNO3] = 5 M, pH 1 – 2.5) were pumped through the sediments at a rate of 0.022 mL/min using a piston pump. The pH of the effluent was measured and analyzed by liquid scintillation counting and ion chromatography. Pu-bearing 15% TBP in dodecane ([Pu] = 1 x 10^{-8} M) was also pumped through select sediment columns. Pu transport in the aqueous and the organic sediment columns was compared and modeled.

NUCL

Variation of air radiation dose rates from March 04 to 29 2022 in suburbs of Tokyo, Japan

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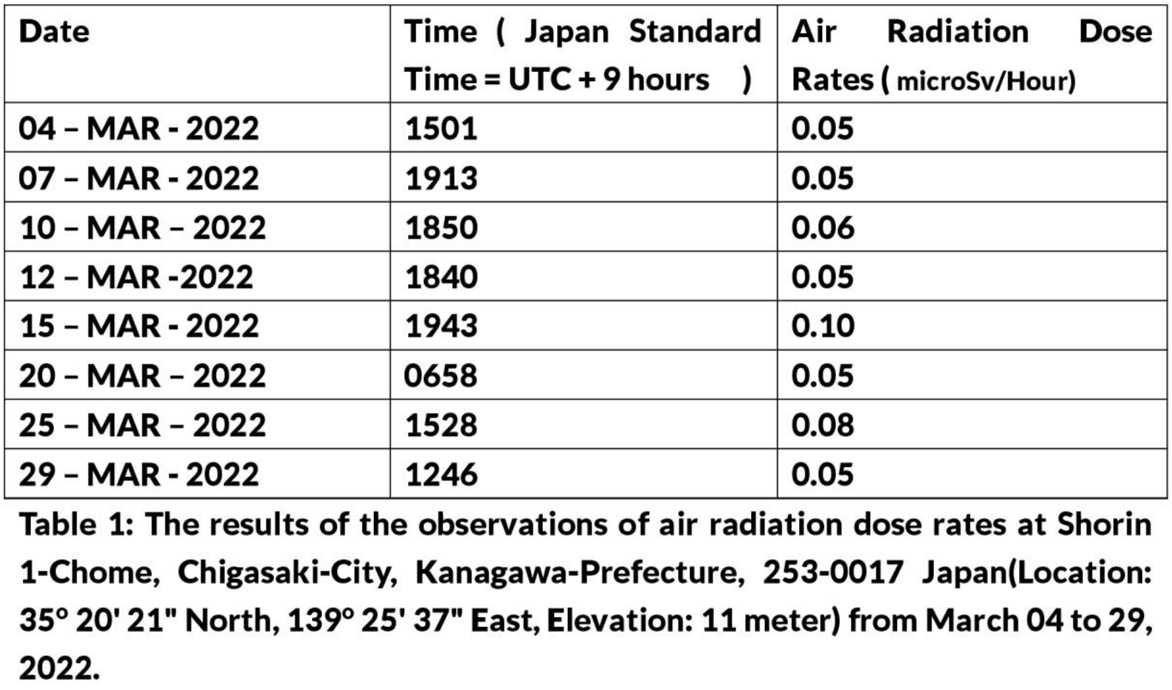
The results of the observations of air radiation dose rates at Shorin 1-Chome, Chigasaki-City, Kanagawa-Prefecture, 253-0017 Japan(Location: 35° 20' 21" North, 139° 25' 37" East, Elevation: 11 meter; About 50 km Southwest of form Central Tokyo) from March 04 to 29, 2022 are as follows(Table 1) by S. T. Corporation Air Counter S. It has peak air radiation dose rates on March 15, 2022 When atomic reactor was destoroyed on April 26, 1986 in Chernobyl, Ukraine, it had higher air radiation dose rates in Japan.



Date	Time (Japan Standard Time = UTC + 9 hours)	Air Radiation Dose Rates (microSv/Hour)
04 – MAR - 2022	1501	0.05
07 – MAR - 2022	1913	0.05
10 – MAR – 2022	1850	0.06
12 – MAR -2022	1840	0.05
15 – MAR - 2022	1943	0.10
20 – MAR – 2022	0658	0.05
25 – MAR – 2022	1528	0.08
29 – MAR - 2022	1246	0.05

Table 1: The results of the observations of air radiation dose rates at Shorin 1-Chome, Chigasaki-City, Kanagawa-Prefecture, 253-0017 Japan(Location: 35° 20' 21" North, 139° 25' 37" East, Elevation: 11 meter) from March 04 to 29, 2022.

NUCL

Exploitation of existing radiation in the Bolivian highlands

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Bolivia is a Mediterranean country located in the heart of South America, which has great natural wealth in which we can highlight its variety of minerals. One of the elements present in Bolivian soils is uranium. This element has radioactive properties, which can be used in various processes that depend on nuclear energy. For example, its use as fuel in power plants. In the Bolivian highlands, the element gives off radiation due to its long exposure to the sun (which is stronger than in other parts of the world due to the altitude of the area) which causes it to be activated, thus demonstrating the energy potential necessary to take advantage of it without harming the health of people and animals.

These soils, although they present a great economic benefit for Bolivia, unfortunately, they are not used, because the Bolivian government has never conducted an in-depth study of the subject. This work intends to make known the utility of these soils, so that the Bolivian population can benefit from them.

The uranium present in the soils of the Bolivian highlands has shown interesting phenomena, but the one we want to point out is that there is a relationship between the radiation of the soils and their fertility. This observation has been made from the relationship of native flora in highland regions with uranium concentrations. This can be affirmed by observing the localities near the Cotaje mine (department of Oruro) in spite of being located in the middle of the highland (known for its arid and infertile geography due to the conditions of pressure and climate) has similar characteristics to those of a valley where the flora abounds throughout the year, This characteristic is shared by several highland zones in Bolivia, but the concentration of uranium in particular is related to the Cordillera de los Frailes, which includes part of the departments of Oruro and Potosi and where the Cotaje mine is located.

As future prospects it is planned to take advantage of this radiation so that it can be spread throughout the highland helping native localities which suffer for decades the drought of the country due to the geographical conditions of the highland where they live, thus motivating the national agriculture. Also, by studying uranium concentrations in greater depth, this would not only be used for this purpose, but also as a source of energy with the possibility of providing water and electricity service in the localities that require it.

NUCL

We’re just messing with U: strategies for engaging actinyl oxo atoms in the solid state

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Actinyl (AnO_2^{2+}) cations are near-linear species with the oxo groups typically remaining uncoordinated in solid state compounds. Engaging these nominally terminal groups, however, is of interest for a variety of reasons. From a structural perspective, axial coordination promotes connectivity in another dimension and thus promotes structural diversity. From a properties perspective, oxo coordination has been shown to influence redox behavior and electronic structure. Over the past few years, we have developed a number of strategies for engaging oxo groups via controlled hydrogen- or halogen-bonding motifs or incorporation of metal ions. Presented will be a structural survey of compounds prepared with these interactions in mind, and the influences thereof on Raman and luminescence spectra. Moreover, a computational treatment involving density functional theory based natural bonding orbital (NBO) analysis and quantum theory of atoms in molecules (QTAIM) will provide a description of the orbital level ‘response’ to oxo engagement.

NUCL

Electrochemical activation and functionalization of the uranyl ion: Electrophiles, reduction potentials, and solid-state structural chemistry

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A fundamental challenge in uranium chemistry is the design of rational pathways for activation of the very strong and usually quite inert U–O bonds in the uranyl(VI) dication [UO_2^{2+}]. Prior work has demonstrated that uranyl(V) monocations [UO_2^+] can be formed by one-electron reduction of [UO_2^{2+}], a reaction that has been shown to increase the Lewis basicity of the oxo groups and promote interaction(s) with exogeneous electrophilic reagents. Here, we report a new activation scheme for the uranyl ion that can be achieved either chemically or electrochemically using moderately electrophilic borane reagents. The first step in our process is the clean formation of a metastable U^V species, supported by both NMR spectroscopy and spectroelectrochemical experiments. Electrokinetic monitoring of the functionalization process provides a tantalizing glimpse into the kinetics of the uranyl oxo functionalization chemistry, a multistep process that follows fast one-electron reduction and involves formation of both mono- and bis-borylated species that are themselves redox active. Our most recent efforts will be discussed, including solid-state structural studies of the oxo-functionalized species and comparison of these to related derivatives.

NUCL

Paired synthetic and computational efforts exploring hydrogen bonding effects on formation enthalpies of uranyl chloride solids

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Within the United States, an open nuclear fuel cycle leads to the formation radioactive waste containing uranium and transuranic elements, which are currently destined for long term storage facilities. Some of the planned repositories (e.g., Waste Isolation Pilot Plant in New Mexico) are located on within salt bed formations, which will impart different speciation than what is expected in other geologic units. Water within salt formations will form ionic brines and uranium is expected to exist as uranyl (UO_2^{2+}) chlorides ($[UO_2Cl_3(H_2O)]^–$, $[UO_2Cl_4]^{2–}$, $[UO_2Cl_4(H_2O)]^{2–}$, $[UO_2Cl_5]^{3–}$). In this study, we are interested in how intermolecular interactions like hydrogen bonding can influence the formation enthalpies of the uranyl solid-state products in presence of high Cl^- concentrations. We focused on $[UO_2Cl_4]^{2–}$ and $[UO_2Cl_4(H_2O)]^{2-}$species as they offer simple molecular complexes that can participate in charge assisted hydrogen bonding when paired with heterocyclic hydrogen donors. These two uranyl systems enable us to further evaluate how systematic variation in the coordination environment around uranyl cation impacts hydrogen bonding networks and energetics. Slow evaporation of solutions with high ionic strength yields crystalline materials composed of uranyl chlorides and with various heterocyclic counter ions. These crystalline materials were analyzed by Raman spectroscopy, single crystal X-Ray diffraction (SC-XRD) for structural information, and powder X-ray diffraction (P-XRD) for bulk characterization. Theoretical calculations were then performed using the refined crystallographic information. The enthalpy of formation of these uranyl systems are calculated using a newly developed Density Functional Theory + Thermodynamics approach, which is used to accurate incorporate the solvation energies in these reactions. All the DFT calculations were done using VASP (Vienna Ab initio Simulation Package), employing PBE functionals and Hubbard U corrections to properly model the uranium system. Overall, we report the synthesis and characterization of uranyl chloride salts that display varying degrees of hydrogen bonding networks and intermolecular interactions, and computation results suggest hydrogen bonding plays a role in the formation of these uranyl chloride complexes.

NUCL

Tetravalent actinide solid-state structural chemistry

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Actinide solid-state structural chemistry has played an important role in our understanding of the chemical and physical behavior of the actinides. As an example, isomorphism in the AnO_2 series of compounds along with the systematic decrease in ionic radii was one of the factors upon which G. T. Seaborg proposed the “actinide concept.” Still today, actinide solid-state structural chemistry continues to highlight important differences in the chemistry of the 4f and 5f elements, inform our understanding of variations that arise from trends in periodicity, and uncover fundamental insight that is critical to understanding the bonding and reactivity of heavy elements. Motivated by both the utility of structural chemistry and ongoing needs to control and predict the behavior of actinides under chemically complex conditions, our group has sought to further elucidate the factors that govern the formation and precipitation of actinide complexes and clusters from aqueous solution. In this talk, the role that solution conditions, ligand complexation, and counter-ion identity have on tetravalent actinide species formation, stability, and reactivity will be discussed.

NUCL

Reactions of neptunium in alkali metal hydroxides

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The chemistry of neptunium(V) and neptunium(VI) was investigated in aqueous solutions of alkali metal hydroxides including LiOH, NaOH, KOH, RbOH, and CsOH. The focus of these studies was the exploration of the phase space in concentrated hydroxide solutions that are known to stabilize higher oxidation states of the actinide elements. As well, these conditions mimic those that are encountered in high-level waste tanks where the solid phase speciation of the actinides, in particular neptunium is poorly defined. A variety of solid phases were synthesized including ternary neptunium oxides and hydroxides, that included both Np(V) and Np(VI) products. In a number of

structures, cation-cation interactions were observed. The results of our structural studies suggest that the dimensionality of the neptunium hydroxide phases could be influenced by the chemistry of the alkali metal cation. Additionally, where single crystal ternary oxide phases were synthesized, we demonstrated that much lower temperature routes in aqueous solutions could be used to synthesize single crystal phases of materials typically synthesized at much higher temperatures using traditional solid-state synthesis techniques. The resulting structures as determined by single crystal X-ray diffraction, underlying neptunium chemistry, and our spectroscopic characterization of these materials using vibrational spectroscopy will be presented.

NUCL

Removal of CO2 and sequestration of carbonate using a recyclable uranyl triperoxide system

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Uranyl peroxides already have uses in the nuclear fuel cycle, such as uranium precipitation after *in situ* leach mining, but applications of this class of materials is not well understood. Uranyl triperoxide, $[UO_2(O_2)_3]^{4-}$, was synthesized as the lithium, sodium, and potassium salts. These solids were found to significantly increase the conversion of CO_2 into carbonate in aqueous solutions. The uranyl triperoxide salts were studied under a continuous flow of nitrogen with 300 ppm CO_2 at a relative humidity ranging from 40-85%. The lithium salt was found to adsorb water to the surface and likely alters to a carbonate phase through a solid-state transformation. The sodium and potassium salts adsorb water until they dissolve and convert to a series of carbonate species before recrystallizing. The sodium salt produced crystals of tri-sodium hydrogen (bis)carbonate dihydrate separating the carbonate and uranium phases. Higher relative humidity led to more complex speciation and structures. Samples were analyzed using single crystal and powder X-ray diffraction, Raman and IR spectroscopy, and electrospray ionization mass spectrometry.

NUCL

Exploration of neptunium(V) chemistry via synthesis of metal–organic frameworks

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Neptunium exhibits rich redox and coordination chemistry, that is relatively unexplored due to its radioactivity and limited supplies. A thorough understanding of neptunium chemistry is essential for discernment of the 5*f* electron contribution to bonding and developing appropriate techniques for nuclear waste stewardship. The prevalence of pentavalent neptunium promotes rare bonding motifs called actinyl-actinyl interactions (AAIs) that result in unique connectivity patterns. We explore the coordination chemistry of neptunium using metal–organic frameworks (MOFs) to understand interactions between neptunium and organic species. Here we report a neptunium MOF structure consisting of anionic neptunyl sheets dominated by AAIs, bridged by 1,4-napthalene dicarboxylic acid. Using X-ray diffraction, Raman spectroscopy, infra-red spectroscopy, and thermal gravimetric analysis, we examine the bonding patterns and properties of the structure gain a better understanding of fundamental neptunium (V) chemistry.

NUCL

Mechanochemical synthesis and applications of actinide nanoclusters

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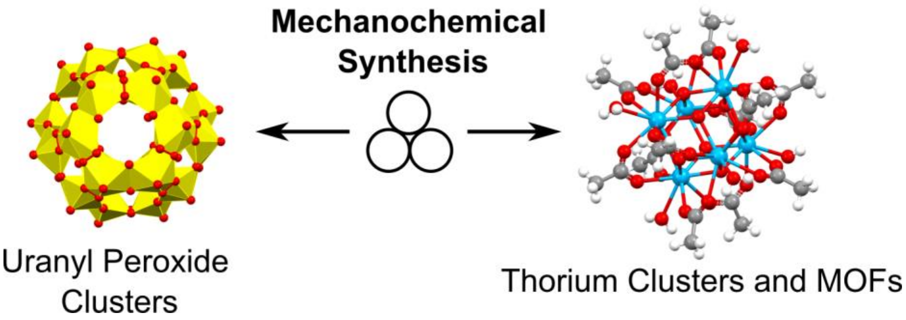
Mechanochemistry is emerging as a more sustainable approach for conducting actinide chemistry by reducing the volume, environmental impact, and cost of solvent and therefore waste produced by reactions. In this work, ball milling was used to explore the formation of uranyl peroxide nanoclusters from insoluble uranium precursors such as uranium dioxide (UO_2) or the uranyl peroxide mineral studtite $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$. These reactions are of fundamental importance for understanding uranium processing, potential transformations in nuclear waste, and the environmental transport of radionuclides. In addition, a mechanochemical synthesis of the $Th_6O_4(OH)_4(H_2O)_6(R\text{-}CO_2)_{12}$ cluster was used to develop a one-pot, rapid, efficient, and scalable liquid assisted grinding synthesis of a family of robust and highly porous metal organic frameworks such as Th-UiO-66, with comparable properties to those reported from solution syntheses.



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Expanding uranyl peroxide cluster chemistry via new synthetic routes and the introduction of free radicals

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Uranyl peroxide clusters (UPCs) are a subclass of polyoxometalates (POMs) that have grown substantially since the first structure was reported in 2005. These complexes are known to self-assemble in solution and have potential for applications in the nuclear fuel cycle; however, synthetic routes to produce these materials have thus far been limited. Understanding and expanding the synthetic toolbox for producing these unique metal assemblies presents a rich set of scientific challenges and our experimental approach uses a combination of inorganic and in situ methods to access and characterize new peroxide cluster species, including kinetic intermediates. Results thus far include the largest UPC containing only uranyl ions and peroxide and hydroxide ligands as well as a whole family of clusters that are produced photochemically, with topologies that vary based on the identity of the charge balancing alkali metal cation. Additionally, dioxygen radicals are known as important radiolysis products, and here we describe the first example of a UPC that includes an oxygen radical species. All clusters have been characterized via single crystal X-ray diffraction (XRD) and vibrational spectroscopy, with EPR spectroscopy also used to definitively confirm and understand the behavior of the oxo radical included in the uranyl peroxide cluster.

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Nanoscale uranium oxide: Correlating synthetic parameters with structure at the atomic and nanometer length scale

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Actinide oxides at the nanoscale are underexplored compared with their lighter-element counterparts. Further investigations are required, however, due to the relevance of nanoscale actinide particles to corrosion in nuclear fuels, their potential as new accident-tolerant fuel materials, and their tendency towards proliferation through environmental systems. Correlating structure/property relationships within these materials requires 1) methods to control size and morphology of actinide oxide nanoparticles with high precision and 2) comprehensive characterization at the atomic and nanometer length scale. Towards this end, approaches to the synthesis and characterization of uranium oxide at the nanoscale will be described. Colloidal-based methods have been used to control both the size and morphology of uranium oxide nanoparticles through varying solvent and molecular ligand chemistry. In particular, anisotropic “nanoflower” particles have been synthesized and the mechanism behind their preferential formation interrogated. Hard-template based approaches using Zr-MOFs have also been pursued and used to control resulting nanoparticle size and

surface binding species. Results show that choice of template, precursor and decomposition conditions affect the structure of the resulting nanoscale constructs. Synthesized nanoparticles were characterized using X-ray focused approaches- primarily using X-ray scattering and X-ray spectroscopy. Atomic and nanometer scale structure will be correlated back to synthetic chemistry and provide insight into differences in structural arrangements at the nanoscale in comparison to what is observed in conventional bulk counterparts.

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Optical vibrational spectra of δ-UO_3

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At least 6 structural modifications of UO_3 are known. For many of these UO3 polymorphs, structural attributes and spectroscopic details have been reported. δ-UO_3 possesses the highest symmetry of any UO_3 polymorph (U (VI) in octahedral coordination, *Pm-3m*, Z = 1). The structural simplicity of this polymorph lends a high degree of computational tractability that has resulted in numerous theoretical studies involving this phase, however no Raman spectra are available for δ-UO_3. To further understanding of the UO_3 phase space, we have synthesized and characterized δ-UO_3 and report Raman and infrared spectroscopic data for this phase. Results from density functional perturbation theory (DFPT) were used to guide our interpretation of optical vibrational spectra and correlate structural features with unexpected spectroscopic observables for δ-UO_3. Based upon symmetry analysis of phonon modes predicted from density functional perturbation theory, δ-UO_3 should possess two IR-active and no Raman active vibrational modes. However, several vibrational modes are observed in the Raman spectrum of this phase that appear to correlate with DFPT predictions. IR spectra collected for δ-UO_3 are consistent with literature reports and DFPT-predicted phonon modes. After confirming phase purity via PXRD and collecting a depth profile using conofocal Raman spectroscopy, we hypothesize that there is additional complexity present in δ-UO_3 arising from subtle structural distortions in our synthesized material.

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Electronic structure of actinide compounds: Evidence from core-level spectroscopies

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The covalent character of bonds in actinide compounds, especially oxides, are important factors that help to determine the chemical and physical properties of the compounds. However, the assignment of this character, and its separation into contributions from different frontier orbitals, is difficult on the basis of commonly used theoretical methods. In particular, Mulliken populations, often used in connection with cluster models of the compounds, have uncertainties that may rather large. The features of core-level spectra obtained with X-Ray Photoelectron Spectroscopy, XPS, and X-Ray Absorption Spectroscopy, XAS, can provide invaluable information about the properties and the chemical bonding in actinide compounds. However, it is necessary to properly interpret these features in terms of the bonding in the compound. Here, we demonstrate how XPS and XAS can show the covalent character of the bonding in different compounds and the contributions to this bonding of different atomic shells of the actinide. We will examine oxides with different oxidation states for an individual actinide and we will examine actinides with different 5f shell occupations; in particular, the series of U, Np, and Pu. The XPS and XAS spectra obtained for isolated actinide cations will be compared with the spectra obtained for cluster models of the oxides. We will also compare $L_{2,3}$ XAS edges with $M_{4,5}$ edges to show the difference between the involvement of the actinide 5f and 6d orbitals in the bonding. The results presented are based on the properties of atomic and cluster model wavefunctions which include scalar and spin-orbit relativistic effects.

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Phase stability of actinide-bearing hollandite waste forms from first-principles calculations

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Hollandites are titanate-based materials that have been shown to effectively immobilize radioactive cesium. Their general formula is $A_{1.33}(Ti^{4+}, B)_8O_{16}$, where A is an alkali/alkaline earth element and B is a metal. Due to the beta decay of Cs-137 in a prospective hollandite waste form, the structure must be energetically stable containing the decay product barium. We have thus investigated the structural stability of actinide-bearing hollandites where actinide atoms occupy a fraction of the titanium-containing B-sites to allow consideration of waste form that can host both actinides and alkali radionuclides. Specifically, we studied uranium, neptunium, and plutonium in hollandite structures and the effect of cesium and barium A-sites occupancies on formation enthalpy using density functional theory (DFT) calculations. It was observed that structures with low actinide concentrations are stable as they exhibit values of enthalpy of formation more negative than those not containing actinides, as those phases had been previously synthesized.

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How does the inner-valence electron correlation affect covalency in heavy-element complexes?

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The computational modeling of heavy-element complexes requires an accurate treatment of spin-orbit and electron correlation effects to fully understand the physical underpinnings of their chemical properties. Our recent studies using many-body multireference methods suggest that there is a significant correlation effect of inner-valence electrons in heavy-element complexes. Ignoring this effect could lead to inaccurate descriptions of molecular properties, such as covalency, bonding, and spectroscopic response. In this talk, we will carefully examine how the correlation effect of inner-valence electrons is manifested in molecular properties with a focus on the covalency in heavy-element complexes.

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Which relativistic approximations are necessary and when for modeling the X-ray spectroscopy of actinides?

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The need for relativistic Hamiltonians in the calculation of the electronic structure of heavy elements is already well established. For calculating X-ray spectroscopies, such as absorption (XAS) and emission (XES), these effects are even more pronounced due to the participation of core electrons. A variety of approximations have been made to treat relativistic effects more cheaply than the full 4-component Dirac equation, including effective core potentials, all-electron scalar relativistic, and all-electron spin-orbit calculations. These methods can then be combined with a variety of approaches, including density functional theory (DFT), coupled-cluster theory, or configuration interaction to include electron correlation and model the relevant excited states. In this talk I will be presenting calculations using several different levels of relativistic theory on uranium and other actinide complexes to better understand the role of these approximations on the expected accuracy of computed X-ray spectra. An assessment of the differences between computed and experimental spectra shows that while sometime spin-orbit calculations may be required for even qualitative agreement, for other cases there is little quantitative difference with a simpler scalar relativistic approach. This is due not only to the specific complex of interest, but also the selection rules governing the transitions for the X-ray edge of interest.

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Surface properties of actinide dioxides; crystal growth and catalysis

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Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. The behavior of these materials under different conditions dictate aspects from crystal growth to disposal of spent fuels, and much of those properties start at the surface. In that way, catalytic reactions that can lead to unstable storage conditions stem from surface interactions with environmental species. Similarly, the morphology of crystal growth conditions is dictated by the stabilization or destabilization of different surfaces by ligands present in the solution environment. We have recently been focusing on surface properties induced by the presence of surface defects and surface interactions with environmental and non-environmental molecules. In this talk we present results of these studies for a series of actinide dioxides (AnO_2). We show how, under predicted conditions, one can control the morphology of growth, starting from nanoparticles to solids. The effect of surface defects is also analyzed as they can significantly affect the outcome, not only in morphology but also on the catalytic properties of the different exposed surfaces.

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Ab initio spectroscopy study of the low-lying electronic states of ThBr, UBr, and their cations

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Spectroscopic constants (T_e, r_e, B_0, ω_e, and $\omega_e x_e$) have been calculated for the low-lying electronic states of ThBr, $ThBr^+$, UBr, and UBr^+ using complete active space 2nd-order perturbation theory (CASPT2) with a series of correlation consistent basis sets. The latter included those based on both pseudopotential (PP) and all-electron Douglas-Kroll-Hess Hamiltonians. Spin orbit (SO) effects were included *a posteriori* using the state interacting method using both PP and Breit Pauli (BP) operators. Complete basis set (CBS) limits were obtained by extrapolation where possible and the PP and BP calculations were compared at their respective CBS limits. The present results will be compared to previous results in the literature for the analogous F and Cl molecules.

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Computational approaches to the study the structure and dynamics of heavy elements in condensed phase

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The 4f and 5f block elements exhibit interesting chemistries that open up a wide range of potential applications. Computational modeling of these elements in the condensed phase is largely impacted by time and length scales that need to be accessed. In this presentation, we will briefly summarize our recent contributions in the study of these elements in condensed phase: (i) the development of condensed phase lanthanide and actinide bases sets and companion pseudopotentials [1, 2] for ab initio molecular dynamics (AIMD); and (ii) an adaptive-learning algorithm that enables the location of multiple low-energy minima in high-dimensional spaces, and which allows us to resolve local structure in these highly dynamic environments [3]. As a first example we will report the computed of aqua-lanthanide pKa's, that are notoriously difficult to measure [4]. In a second example, we show the ability of AIMD combined with data analytics, based on the Smooth Overlap of Atomic Positions (SOAP) descriptors, to distinguish structural fingerprints of actinides in molten salts [5].

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Hydrolysis of uranium hexafluoride: Mechanism, spectroscopy, and thermochemical kinetics

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Depleted uranium hexafluoride (UF_6), a stockpiled byproduct of the nuclear fuel cycle, reacts readily with atmospheric humidity, but the mechanism is poorly understood. Seeking agreement with a recently measured rate law[1], we traced out a network of elementary steps connecting UF_6 and water to the observed *solid* uranyl fluoride (UO_2F_2)[2]. Barrier heights were obtained using an *ab initio* composite method incorporating complete-basis-extrapolated CCSD(T) energies, and the resulting barrier heights were entered into a master equation solver. Our predicted rate constants are in good agreement with those measured by Richards *et al*. We also report the first benchmark study assessing the performance of double-hybrid density functional theory (DH-DFT) for describing U(VI)-containing chemical reactions. DH-DFT was subsequently used to explore the potential energy surface beyond the UF_6 hydrolysis initiation step. The corresponding mechanism is predicted to proceed by intermolecular hydrogen-transfer within van der Waals complexes involving UF_5OH and UOF_4, followed by formation of a previously unappreciated dihydroxide intermediate, $UF_4(OH)_2$. Unlike the higher-energy pathway leading to *molecular* UO_2F_2, the dihydroxide is predicted to form spontaneously under both kinetic and thermo-dynamic

control, in agreement with observation. Finally, harmonic and anharmonic vibrational simulations were performed to reinterpret literature infrared spectroscopy in light of newly identified species.

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Thermal properties of intrinsic defects in CeO_2: A density functional theory study

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Cerium dioxide (CeO_2, ceria) is used in multiple sustainable technologies, such as catalysis (three-way catalyst, TWC), energy generation (the electrolyte in solid oxide fuel cells, SOFCs) and as a surrogate material for actinide oxides in mix oxide fuel (MOX). By 2050, the UK has set a net zero greenhouse gas emission target, and as such nuclear power, which is carbon neutral, will have a major role in achieving this goal. A shift from fossil fuels to carbon neutral energy supplies is vital and CeO_2 will play an essential role in this transition.

Historically CeO_2 has been used as a surrogate for PuO_2 but also used in CeO_2-UO_2 solid solutions. Therefore, the thermophysical properties of CeO_2 in these MOX fuels is of interest for the nuclear community. For example, the thermal conductivity of CeO_2 is comparable to that of PuO_2 and UO_2 suggesting only small differences in thermal transport. Even computationally, it is much easier to deal with CeO_2 than PuO_2 and UO_2 and as such we have employed this material in our study. We use Density Functional Theory (DFT) calculations to study the impact of Schottky, anion Frenkel and cation Frenkel defects in CeO_2. We find that the presence of these defects affects the thermophysical properties of the material. In particular, we identify the characteristic spectral signature of these intrinsic defects in the phonon dispersions and infrared (IR) spectra. Finally, we employ an approximation to assess the impact of these defects on the thermal conductivity, all of which impose a significant reduction. Our methodology is transferable to any nuclear materials and allows for the characterisation of transport properties at the atomistic level.

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Amidoxime-functionalized graphene-like nanosheets as electrocatalysts for the recovery of actinides

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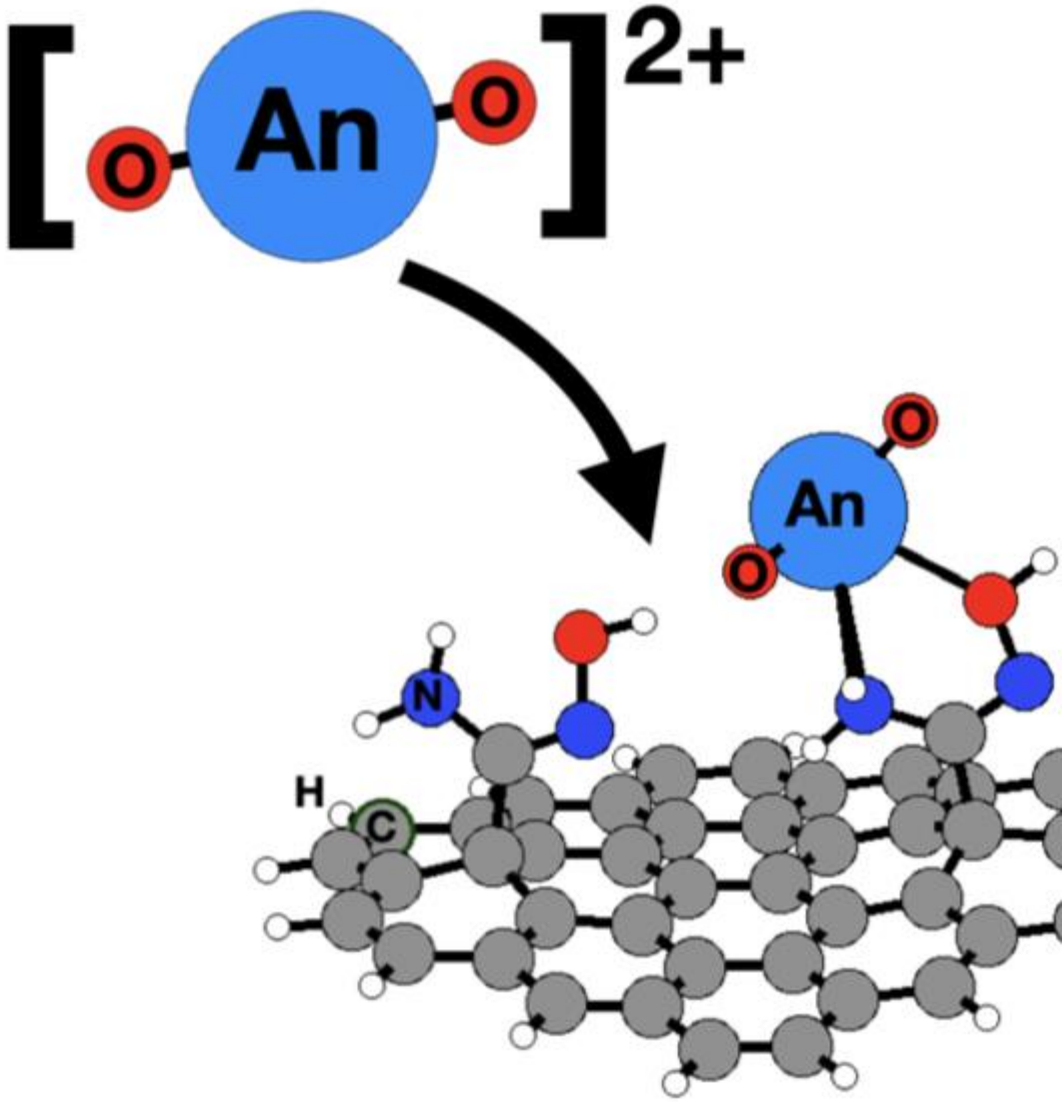
Actinyl ions, e.g., UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, AmO_2^{2+}, are receiving major attention due to their large geographical mobility and radioactive behavior, which increase the background radiation in the environment and genetic variations in biological systems. Moreover, they are primary sources for nuclear power, medical diagnosis, and several applications which necessitate the use of radionuclides. Several materials such as metal-organic framework (MOFs), polymers, and graphene-like materials have been employed as scavengers, electrodes, and catalysts, often functionalized with organic groups such as amidoxime groups, to selectively uptake and reduce actinyls in the environment.

Therefore, it is important to understand how these various materials adsorb actinides and their oxide forms in order to understand their chemical behavior in the environment. I will present our theoretical findings based on density functional theory calculations that illustrate how actinyl ions are adsorbed on amidoxime functionalized graphene-like nanosheets. Our studies additionally examine the reduction of AnO_2^{2+} (An=Actinide) to their more stable and insoluble form of neutral oxides, AnO_2, which are necessary for safe transportation and utilization of these radio nuclear chemicals. The nanosheet acts as an electrocatalyst in this reduction process. Hence, this study aims to understand the adsorption and redox properties of a sample of actinyl ions on a functionalized carbonaceous material.



Adsorption and reduction of an actinyl (An=U, Np, Pu or Am) on amidoxime functionalized graphene-like nanosheet.

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Lanthanide-selective lixiviants: A computational view of optimizing binding constants

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Conventional recovery of rare earth elements requires brute-force mineral dissolution using strong acids and bases, followed by many rounds of solvent extraction to separate the lanthanides based on their size differences. These processes render lanthanide recovery expensive, hazardous, and inefficient. The goal of our project, Dissolution by design: selective leaching of rare earth elements using SMART lixiviants, is to create a ligand that selectively coordinates between the lanthanides. Macrocycles have been investigated to fulfill this role, and several ligands have shown significant prospects. The current focus of this project is testing the capability of acyclic versions of the macrocyclic ligands experimentally tested to show selectivity. Running calculations with NWChem, we use density functional theory (DFT) to optimize the geometry of potential ligands for each lanthanide. After running a frequency calculation to confirm the optimized structure is a minimum energy conformation, we then run a solvent phase energy calculation. In addition, single point energy calculations are run with a larger basis set to get a more accurate energy. Through these calculations, we are able to compare the energy stabilities of light and heavy lanthanides with these lixiviant ligands. This talk will cover the in depth methods we use to run these calculations, and the results we have obtained so far. These ligands' potential selectivity between the lanthanides would bring a cost effective lixiviant to the American rare earth element industry.

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Data-driven DFTB for improved aqueous americium reaction energies

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While nuclear reactors provide a safe and abundant source of energy, processing the spent nuclear fuel remains a fundamental issue. Major actinides can be removed from the waste through various processes, but the remaining minor actinides complicate storage due to their high radioactivity. A greater understanding of the chemistry of these actinides in solution is required to improve the separation process. However, low availability and necessary safety precautions cause this to be a slow endeavor in the laboratory. In this talk, I will (1) discuss how the chemistry of americium, a minor

actinide, in aqueous solution can be understood through reaction energies, (2) show that a data driven approach to fitting density functional tight-binding parameters can accurately reproduce trends in these reaction energies, and (3) that augmenting this theory with a machine learning model improves the accuracy of the method and reduces total training time. These advances provide the groundwork for further studies of the reaction kinetics that would not be possible without the computational efficiency and accuracy afforded by this method.

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High Performance Computing Applications in Modeling Rare Earth Elements and Actinides in 2022

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Modeling Rare Earth Elements (REEs) and actinides is critical in nuclear and radiochemical applications. REEs and actinides are essential in national security and societal needs, including green energy, technology, defense, and medical applications. High Performance Computing (HPC) has been vital in advances in modeling these elements. However, challenges from a hardware-software ecosystem out-of-balance limit efficiency in modeling performance since the software needed for molecular modeling has not advanced at the same rapid pace as hardware. Strategies for efficient modeling as we enter the HPC Exascale era will be shown with mapping efforts applied to separations of REEs and actinides from data obtained with ab initio methods and machine learning. An update on the state-of-the-art HPC global resources in 2022 will be discussed, including the latest rankings from the Top500 List, resources distribution, and performance of the latest HPC systems.

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Prediction of stability constants of metal-ligand complexes by machine learning and the role of ab-initio, force-field, and experimental properties

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Extraction of rare earth elements by different separation processes is of great importance for the US economy. Stability constants, logK values, estimate the binding strength of a metal ion to a particular ligand. Comparison of logK's provides insight into the ability of a ligand to separate and extract target metals. The directed message passing neural network (D-MPNN) approach of machine learning (ML) was applied to predict the logK's of metal-ligand complexes. The ML algorithms were trained on reliable experimental data extracted from a legacy NIST database based on the multi-volume work of R. M. Smith and A. E. Martell "Critical Stability Constants" and the

IUPAC database. Complementary to the experimental logK databases, a substantial number of atomic, molecular, and molecular-fragment properties were obtained by ab-initio calculations that were facilitated by workflow automation. In addition, properties that are calculated by classical force fields and experimental properties were gathered. The role of ab-initio, force-field, and experimental properties on the quality of the logK predictions was elucidated.

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Learning actinide-ligand binding motifs and structure from organometallic structural databases

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Organometallic actinide compounds are critical for applications ranging from nuclear waste treatment to rare earth separations. Due to the relative complexity in synthesis and electronic structure of organometallic actinide compounds compared to organic compounds, atomistic-level and experimental data for actinide complexes has lagged organic chemistry. Here, we leverage mononuclear organometallic compounds chemical structures derived from the Cambridge Structure Database (CSD) to develop machine-learning predictors targeted towards determining binding sites on ligands and metal-center geometries for actinide chemistries. In combination with generalized 3D structure-generation routines using recent accelerated ab-initio methods, we enable accurate ab-initio screening of large swaths of underexplored actinide chemistries. In total, we present tools for high-throughput computational exploration of actinide-ligand chemical space towards enhanced actinide separation chemistries.

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Decoding the drivers of chemical separations by chemistry-informed data science

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Hydrometallurgical processes underlie several chemical separations including radiochemical separations for nuclear fuel cycles and nuclear medicine. Despite decades of technological advances in the field, the fundamental drivers of separations remain ill understood. From a thermodynamic viewpoint, the challenges stem from the multiphase, multicomponent nature of the separation processes involving high thermodynamic degrees of freedom and non-ideal solution behaviors. There is a need

to understand and model this complex multidimensional energy landscape to enable efficient and sustainable chemical separation processes. Our approach is to obtain descriptors of structure and energetics of the phases by applying chemistry-informed data science tools. The input to data science based prediction models will be multiplexed vibrational spectroscopies and X-ray scattering data, spanning the compositional simplex. We will focus on chemical speciation of the components as a key descriptor. Chemistry inputs to the models will be supplied by defining spectroscopic regions of interest, as determined by domain knowledge, and by incorporating mass conservations in speciation predictions. We will be presenting the results obtained on a representative system of three component mixture relevant to chemical separations and discuss the role of noise on model quality and interpretability. Addressing the challenges in precise data collection and analysis using tools from data science will be broadly applicable to the field of cheminformatics and specifically to the critical subject of chemical separations.

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Developing Computational Protocols for Lanthanide and Actinide Systems with Molecular and
Data Modeling Techniques

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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 using molecular modeling methods, like ab initio and DFT, have been
popular to simulate binding interactions. Using modern data modeling methods, like Artificial Intelligence
techniques, such as Machine and Deep Learning, can be insightful to understanding binding selectivity
properties.

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AI Optimization coupled with meta-heuristic for Neutron Spectra Tailoring

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There is an increasing need in many fields of nuclear engineering to accurately tailor neutron source energy spectra to specific applications due to the scarcity of isotope sources. For example, diverse neutron sources are needed that meet the requirements for producing synthetic debris and fission products (FPs) for nuclear forensics, detector calibrations, study of radiation damage to different materials, cross section measurements, materials science, design of targets for the production of medical isotopes, or medical applications, which often do not exist. Each of these applications has widely varying neutron spectrum and intensity requirements, making progress in one area difficult to apply to other areas using the current set of tools and literature basis. Dramatic increases in simulation capabilities and computational methods could assist nuclear engineers in designing and optimizing nuclear engineering systems with drastically improved performance, safety, and efficiency. The objective of this research is, therefore, to create a novel, high fidelity, more efficient method for Energy Tuning Assembly (ETAs) to tailor neutron spectra, by developing an autonomous Artificial Intelligence (AI) based algorithm trained on data generated by metaheuristic algorithms. The optimization tools being developed are used to generate ETA for automated neutron beam spectral tailoring based on a set of pre- determined constraints and objective function, and include Gnowee, a general-purpose metaheuristic optimization algorithm, and Coues v3.0, a framework that couples Gnowee to a radiation transport solver and the integration of AI. The innovation of the proposed method is here presented in terms of simulated evaluations performance, running time, and the use of the advanced optimization objectives and constraints used in the design process: inclusion of the radiation damage minimization of the materials used for modifying the neutron spectra; the quantification and accounting of nuclear data uncertainties; and the exploration of complex geometries.

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FFT Computation for Exascale Applications

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In this talk, we present heFFTe, a library for the computation of distributed FFT on upcoming Exascale supercomputers, and currently the only one supporting GPU accelerators from NVIDIA, AMD, and Intel. Besides supporting state-of-the-art features, heFFTe provides unique novel features such as:
- Batched 2-D and 3-D FFTs, very useful for applications in particle and micro-mechanical simulations.
- FFT Convolutions for digital processing.
- Sine and Cosine transforms for wave propagation phenomena.

We show experiments on scalability on over 1 million CPU cores and 6,000 GPUs using the world’s most powerful supercomputers. We analyze the effect of different algorithmic settings, such as tuned processor grids and sizes. Finally, we analyze the

well-known communication bottleneck using mathematical and experimental models to study parallel efficiency by leveraging Infiniband, NIC and NVLINK interconnections.

NUCL

Black-box optimization of expensive functions through ML models

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Black-box optimization is the problem of finding the value of the parameters that minimizes a certain objective function where no analytical formulation of this function nor its derivative are available as their evaluation is only possible through a costly run of an application.

Several algorithms exist in the literature that target this problem, among which are the surrogate-based black-box optimization algorithms.
Their main idea is to build a cheap to evaluate model of the objective function and try to optimize this model instead of the original function.

Our work is a generalization of such methods. Instead of tuning an application on a given problem, we aim at tuning it on possibly any problem it can encounter.
To this end, we rely on the multitask learning and transfer learning frameworks, as they have proven to be useful in the field of machine learning when additional knowledge is available to help a prediction task.

We show comparative results with state-of-the-art autotuning techniques for the tuning of computer applications.
We explain how our approaches can be more suitable than some state-of-the-art autotuners for the tuning of applications in general and of expensive exascale applications in particular.

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Careers at a national laboratory: Through the lens of a postdoctoral researcher

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Careers at a national laboratory, such as the Pacific Northwest National Laboratory, are accompanied by unique opportunities to conduct groundbreaking and innovative research as well as opportunities to diversify one’s scientific and leadership abilities. This can include opportunities like working on diverse project teams and/or leading one’s own project by applying for internal funding such as the Linus Pauling Distinguished Postdoctoral Fellowship. In addition, national laboratories are one of the few facilities equipped for the handling and characterization of highly radioactive

transuranic elements, such as plutonium and americium. This enables us to work on both fundamental and applied actinide chemistry research. The focus of this talk will be career development and the pathway to transition from a Ph.D. student to a Pauling Postdoctoral Fellow. In addition, preliminary results from my Pauling postdoctoral work will be presented on the intersection of solution and solid-state actinide oxide nanocluster chemistry. The goal of this work is to use actinide oxide nanoclusters as a model to study periodic trends in the electronic and coordination environment, and the physical and chemical properties of the actinides in efforts to advance fundamental actinide chemistry.

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From fundamental measurements to applications: Actinide materials research at Los Alamos National Laboratory

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Nuclear research at Los Alamos National Laboratory (LANL) is very diverse revolving around its core National Security mission. Department of Energy's National Nuclear Security Administration (DOE-NNSA) Weapons Programs funds over two-thirds of LANL's programmatic portfolio, but research spans a broad swathe of topic areas across DOE, the Department of Defense (DoD), the Intelligence Community (IC), Department of Homeland Security (DHS), and more. This talk will focus on ongoing actinide materials work in the Materials Synthesis and Integrated Devices group (MPA-11) within the Physical Sciences directorate. Specific points of interest relate to stockpile stewardship activities, synthesis of actinide materials for understanding of bonding, and fundamental and applied separations of actinides and lanthanides.

NUCL

National laboratories' research and development experience opportunities for diverse scholars

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Under the umbrella of the U.S. Department of Energy (DOE), 17 National Laboratories located throughout the United States drive critical scientific and technological advances that solve our nation's strategic needs. These distinguished federal facilities are equipped with state-of-the-art equipment and facilities that enable the brightest scientific and engineering minds to develop and implement innovative ideas, ensuring America's homeland security and continued prosperity. National Laboratories sponsor a myriad of STEM literacy programs and positively influence the development of a diverse scientific community while focusing on a common vision of advancement in the STEM fields. As

we continue through the 21st century, it is essential to diversify our perspectives in STEM related fields to ensure our progress toward solving many of mankind's scientific mysteries. In this talk, I will present a number of science and literacy programs, including internships, fellowships, postdoctoral research opportunities, grants, trainings, etc., offered for diverse scholars within the DOE Complex.

NUCL

Fundamental actinide science: An avenue to Foster Research and Career Development

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The environment at Pacific Northwest National Laboratory (PNNL) is scientifically entrepreneurial, collaborative, and creates a forum to mature as an early career scientist through the controlled exposure to both multi-disciplinary, team-based science and self-directed research. These opportunities can manifest for staff members and student interns alike via numerous mechanisms, ranging from internships, fellowships, and general solicitations for funding, all of which foster cutting edge science, technology, and innovation. This framework has allowed me to traverse the path from a graduate student research fellow at PNNL to staff scientist while establishing a research program that includes fundamental 4f- and 5f- element chemistry, functional material design, and uranium metallurgy. This presentation will provide a brief overview of several nuclear-related project areas and highlight instances where the scope of work intersects both fundamental and practical applications. A specific focus on lanthanide and actinide containing metal-organic frameworks (MOFs) will be covered and framed within the context of the expanding heavy element chemistry program at PNNL. Research relevant to lanthanide containing frameworks and actinide sequestration will be discussed while the utility of MOFs to function as a construct for probing actinide bonding and photophysical properties will be introduced. Vehicles designed to support student opportunities at PNNL will be highlighted along the way.

NUCL

Nanoscale interactions of neptunium and plutonium with uranyl peroxide nanoclusters

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Polyoxometalates (POMs) are metal oxide clusters truncated by doubly- or triply-bonded O atoms. Whereas transition-metal POMs have been extensively studied, uranyl-based POMs, also known as uranyl peroxide nanoclusters, have been known for approximately a decade. In contrast to most transition-metal POMs, the uranyl peroxide nanoclusters can form cages that encapsulate cations. They are stable in aqueous

solution and their very large surface-to-volume ratios ensure that liquid-“solid” interfaces can be probed at the nanoscale. This work describes the nanoscale interactions of the uranyl peroxide nanoclusters LiNa-U_{24} ($Li_{23}Na[UO_2O_2OH]_{24}*58H_2O$) and $U_{24}Pp_{12}$ ($Li_{24}Na_{24}[(UO_2O_2)_{24}(P_2O_7)_{12}]$) with plutonium(VI) and neptunium(V). Ultra-small angle X-ray scattering (USAXS), small angle X-ray scattering (SAXS), and dynamic light scattering (DLS) were used to describe the aggregation of individual nanoclusters into secondary and tertiary structures in solution, whereas UV-vis-NIR spectroscopy was used to monitor for redox changes. Understanding redox chemistry and aggregation is essential for the consideration of actinide separation schemes via size filtration, which could potentially lead to new approaches to the reprocessing of used nuclear fuel.

NUCL

Investigating the degradation of uranyl peroxide clusters under ionizing radiation

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Although uranyl peroxide cage clusters have been studied extensively since their discovery in 2005, there has been limited research on their behavior in high ionizing radiation fields. Conditions favorable for uranyl peroxide cluster formation exist in high radiation environments. It is imperative to investigate how these materials change when exposed to doses of ionizing radiation in the MGy range. A tandem Van de Graaff particle accelerator was used to generate 5 MeV He^{2+}-ions to simulate alpha particles, where doses of up to 50 MGy have been achieved. Both pristine and irradiated $Li_{28}[UO_2(O_2)_{1.5}]_{28}$ (Li-U_{28}) and $Li_{24}[UO_2O_2OH]_{24}$ (Li-U_{24}) cage clusters in the solid state were characterized using Raman, infrared, and X-ray photoelectron spectroscopy to describe alteration within the material. Irradiated clusters exhibit amorphization due to broadening of spectroscopic features, and new signals in the IR spectra indicate evidence for carbonate formation.

NUCL

Synthesis of the first actinide borosulfate series and establishing an unconventional structural hierarchy

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The first actinide borosulfate, $(UO_2)_2[B_2O(SO_3OH)_2(SO_4)_3]$ (Z=4 *a:* 10.8722(10) Å, *b:* 11.831(11) Å, *c:* 14.8118(14) Å, *β:* 92.4810(10)°), is also the first borosulfate to exhibit

an isolated zero dimensional unconventional anionic substructure that translates to one and two dimensional connectivity reported previously in the borosulfate literature. This unit consists of one sulfate tetrahedron vertex sharing with two B-O-B bridged borate tetrahedra that each share a vertex with two sulfate tetrahedra. As this structure does not conform to current sorting methods, a graphical structural hierarchy was constructed to better understand unconventional borosulfate substructure and dimensionality. Additionally, another actinide borosulfate, $(UO_2)[B(SO_4)_2(SO_3OH)]$ (Z=2 *a:* 5.4476(10) Å, *b:* 7.0210(12) Å, *c:* 13.522(2) Å, *α:* 92.248(2)°, *β*: 95.347(2)°, *γ:* 101.987(2)°), was synthesized and the crystal structure is only partially consistent with the established conventional hierarchy. This is due to the inert oxygen atoms of the uranyl cation $(UO_2)^{2+}$ that limit coordination to the equatorial plane. The resulting uranyl pentagonal bipyramid limits the anionic network linkages and isolates sulfate tetrahedra within the anionic network. Therefore, the classical one-dimensional chain established in the hierarchy does not fully describe the structure. Thus, a new graphical notation for the anionic structural hierarchy is proposed. This work reports the first expansion into the actinide series for borosulfates as well as key structural unit coordination similarities across the field.

NUCL

Synthesis and characterization of anhydrous actinide fluorides

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Actinide fluorides are important nuclear fuel cycle materials (e.g., UF_4 and PuF_4 are common intermediates in the production of uranium and plutonium metal), yet much remains to be learned about the fundamental properties of these materials, including the effects of aging on their chemical and physical properties. Such studies are challenging because standard production techniques involve the manipulation of large quantities of hydrogen fluoride at high temperatures and there are radiological hazards associated with handling actinide materials. In contrast, the synthesis and characterization of lanthanide fluorides via ionic liquids is well established and provides an appealing alternative route to the production of actinide fluorides. This work explores an approach in which the ionic liquid 1-Butyl-3-methylimidzalium hexafluorophosphate ([BMIM][PF6]) is used to fluorinate actinide dioxides (AnO_2) and produce anhydrous actinide fluorides (AnF_3, AnF_4). Powder X-ray diffraction, electron microscopy, thermogravimetric analysis, inductively-coupled plasma optical emission spectroscopy, vibrational spectroscopy, and high temperature oxide melt solution calorimetry were used to characterize the resulting actinide fluorides. The latter technique allows us to determine the heats of formation for each product and can be used to comment on trends across the actinide series. Such baseline thermodynamic information is necessary for future studies directed at understanding the environmental chemistry of these materials.

NUCL

Careers in nuclear chemistry at Los Alamos National Laboratory (LANL)

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Nuclear chemistry and technology are central to a very wide range of activities, ranging from fundamental basic research to applied national security. In this presentation, we will introduce some of the career opportunities available at Los Alamos National Laboratory (LANL), primarily focusing on chemistry, nuclear forensics, theory, nano, and surface chemistry, and discuss how these activities contribute to national security. We will also discuss how the G.T. Seaborg Institute serves as a bridge between academia and LANL in order to favor exchanges of knowledge and expertise and present the various opportunities it offers to scientists at various stages in their careers.

NUCL

Nuclear science career opportunities at Lawrence Livermore National Laboratory

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As a premier research and innovation laboratory, Lawrence Livermore National Laboratory's (LLNL's) workforce is our most important asset. LLNL's vision is to be recognized as a workplace for innovating science and technology (S&T). Our mission is to educate, engage, encourage, and empower every employee and visitor to contribute to building and supporting a community that contributes to our S&T mission. We are committed to building a high-performing workforce by recruiting from a diverse talent pool, creating a culture that promotes inclusivity, and engaging diverse and marginalized communities through a broad range of outreach activities. LLNL's Institutes and Centers play a critical role in LLNL's outreach goals, supporting education and training of the next generation of scientists, and providing a pipeline for staffing the national laboratories. For example, the Seaborg Institute engages with scientists from around the world to work on diverse research including super heavy element discovery, nuclear forensics and attribution, fundamental actinide chemistry, and environmental radiochemistry. Visiting scientists and staff are able to take advantage of the state-of-the-art analytical capabilities available at LLNL, such as nano-secondary ionization mass spectrometry, accelerator mass spectrometry, nuclear magnetic resonance, resonance ionization mass spectrometry, and transmission electron microscopy. In this presentation, we will discuss career opportunities at LLNL, provide insight into the hiring process, and discuss research growth areas in nuclear science.

NUCL

Nuclear energy research at Idaho National Laboratory

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This invited talk will present an overview of the nuclear energy related research at Idaho National Laboratory (INL) including that performed through the INL Glenn T. Seaborg Institute (GTSI). INL has a long 80+ year history in nuclear energy research and development (R&D), is the lead national laboratory for nuclear energy R&D in the US, and is the only national laboratory sponsored by the DOE Office of Nuclear Energy. The nuclear programs and initiatives at INL offer opportunities for a wide range of chemistry professionals including but not limited to those interested in solution chemistry (aqueous, non-aqueous, molten salt), solid state chemistry and physics, forensics and trace element analysis, and materials science. Nuclear fuel development efforts supporting the operational extension of existing reactors as well as advanced reactor designs, microreactors, and small modular reactors are investigating metallic alloys, ceramics, composites, and dissolved fuel. A number of these efforts are studied for integration into hydrogen production, clean water generation, and industrial and new chemical processes. Processing and reprocessing work at INL associated with nuclear energy systems offers opportunities in advanced manufacturing, chemical and electrochemical separations (particularly for the actinides and lanthanides), off-gas capture, and radiation chemistry, the latter addressing also corrosion and interfacial chemistries. The research at INL is supported by some of the most advanced instrumentation available for the study of both radioactive and non-radioactive systems and INL hosts its own nuclear test reactor for neutron irradiation studies (the Advanced Test Reactor – ATR). To complement the experimental scope, INL is a leader in the application of advanced atomic-, meso-, and continuum-scale computational research to understanding the complexities of nuclear energy systems as well as the application of machine learning and artificial intelligence to the accelerated discovery of nuclear materials. Nuclear research at INL covers both applied and fundamental areas wherein researchers execute a full spectrum of collaborations with industry and academic researchers. Specific to the realm of basic research, the INL Glenn T. Seaborg Institute is focused on the actinides and their fundamental solution chemistry and separations, solid state chemistry and physics, and forensics and standards in its post-doctoral program.

NUCL

Characterizing radioactive waste chemistry and sediment interactions at the US Department of Energy's Hanford site

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The nuclear weapons fuel cycle consists of front-end steps to produce, extract, purify, and engineer plutonium, and back-end steps to safely manage, prepare, and dispose of radioactive wastes. The Hanford site, which produced plutonium for the US Department of Energy's weapons program, is the most contaminated nuclear site in the nation and its largest environmental clean-up activity. During weapons production, 200 million liters of liquid waste (sludge, salt cake, and supernatant), with 170 million Curies of radioactivity and 240,000 tons of complex chemicals, was generated. Comprising a major environmental contamination risk, the waste is destined for processing into a glass form for stabilization, to allow its radioactivity to safely dissipate over hundreds to thousands of years. Uncertainty associated with this unprecedented task can be mitigated by: (i) characterizing waste chemistry; and (ii) understanding contaminant reactions both in the waste form and with environment.

A key issue of Hanford tank waste processing and disposal is that, although radionuclides such as technetium are risk drivers, it is 'benign' dominant elements such as aluminum that dictate processing limits and uncertainties, given that tank waste is removed on a volume basis. Safe, cost-effective, and efficient waste processing thus depends on a fundamental understanding of aluminum chemistry in complex high ionic strength, highly alkaline solutions. Basic research by the Interfacial Dynamics in Radioactive Environments and Materials (IDREAM) Energy Frontier Research Center (EFRC) has focused on leveraging national user facilities to unravel complex ion coordination, solvation, pairing with other ions, and cluster formation in these highly concentrated chemical environments.

The tank waste must be processed into a stable waste form because it represents a radioactive source term to the environment. One third of the tanks are suspected of having leaked waste, resulting in contaminated groundwater that migrates toward the Columbia River. Here, spectroscopic characterization of plutonium, technetium, and uranium speciation in unsaturated, vadose zone sediments at Hanford will also be presented. These results are being used to understand radionuclide migration, and to develop improved long-term remediation strategies that are most likely to succeed during field application, through stimulation of conditions that enhance radionuclide attenuation.

NUCL

High-pressure spectroscopy and diffraction of Uranium compounds

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Uranium dioxide (UO_2) is the most common fuel for nuclear reactors and, thus, a major component of the generated waste. Under some geologic repository conditions, alpha-radiolysis of water can lead to the formation of hydrogen peroxide, which contributes to the formation of studtite through oxidative dissolution of UO_2. Under alkaline conditions, studtite dissolves and can form uranyl peroxide nanoclusters. In this work, the structural behavior and electronic structure of UO2 and the pyrophosphate-functionalized uranyl peroxide nanocluster $U_{24}Pp_{12}$ ($Li_{24}Na_{24}[(UO_2)_{24}(O_2)_{24}(P_2O_7)_{12}]x120H_2O$) were probed up to approximately 16 GPa in diamond anvil cells. X-ray diffraction coupled with Rietveld analysis was used to determine the bulk modulus and changes in long-range order for each material, whereas synchrotron-based U-LIII edge X-ray absorption spectroscopy was used to determine average changes in bond distances between uranium and its neighboring atoms and changes in coordination number of these neighboring atoms. Results indicate, on average, a shortening of axial and equatorial uranium-oxygen bond distances and an increase in coordination number of neighboring atoms. Such information is essential when trying to predict the behavior of uranium materials far from equilibrium.

NUCL

Interrogating the Fe/UO_{2+x} interface through nanoparticle synthesis and characterization

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The colloidal behavior and properties of actinides, specifically uranium, is currently an under-studied but important phenomenon with far-reaching applications ranging from next generation fuels to environmental remediation. Colloid formation is a known threat to long-term nuclear storage sites and has been shown to contribute to far-field transport from sites of environmental release. The specific case of iron/uranium oxide colloids is a highly relevant system to study when considering transport in multiphasic environments, as (1) colloids of this composition have been detected in the field and shown to aid far-field transport and (2) bulk adsorption onto iron minerals is known to immobilize aqueous uranium, and nanoscale systems offer the unique opportunity to study the surface chemistry of said interface.

We have developed an organic synthetic system in which monodisperse iron nanoparticles are formed in air-free conditions ranging from 3-10 nm in diameter and a layer of uranium oxide can be subsequently overgrown. This system allows tight control and study of factors dictating uranium uptake, like oxidation state, iron colloid size, and concentration, and can be cleanly isolated enabling precise characterization. Initial results have shown that a thin uranium oxide shell grows regardless of the concentration of overgrowth solution or iron core size. Advanced X-ray techniques such

as small-angle X-ray scattering (SAXS) and X-ray absorption fine structure (XAFS) are being pursued both in-house and at synchrotron sources, to discern the connectivity, coordination environment, atomic scale distribution, and oxidation state of both elements. At the nanoscale, a heightened proportion of atoms are surface atoms, thus these characterization methods will be directly interrogating the iron/uranium interface. This rigorous characterization will contribute not only to our understanding of multi-phasic transport, but more broadly to the field of actinide colloidal behavior with implications for next generation fuel and separations technology, to name a few.

NUCL

Role of metal selection in the radiation stability of isostructural M-UiO-66 metal–organic frameworks

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Robust and versatile metal–organic frameworks (MOFs) have emerged as a sophisticated scaffold to meet the critical needs of the nuclear community (e.g., fission product capture, radiation detection, and actinide/lanthanide separations). The performance of MOF materials in such applications, however, is inextricably linked to their structural integrity under ionizing radiation, and this key property is relatively underexplored. In this presentation, we identify the contributions of the selected metal node in the radiation stability of the isostructural M-UiO-66 series (where M = Ce, Hf, Th, and Pu). MOF samples were irradiated via gamma and He^{2+} ion methodologies to obtain doses up to 3 MGy and 85 MGy, respectively, the latter strikingly higher than that obtained in most other studies. Appreciable self-irradiation constituted the total absorbed doses of the isotopically weapons-grade Pu-UiO-66 samples. Structural degradation was ascertained by powder X-ray diffraction, vibrational spectroscopy, and where possible, N_2 physisorption isotherms. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) probed atomic-level mechanistic insight to reveal the node-linker connection was most susceptible to radiation damage. Density functional theory (DFT) truncated cluster models were optimized to evaluate the binding affinity of linkers to each metal node. While the isostructures disclosed the same breakdown

signatures, distinct radiation sensitivity as a function of metal selection was evident. We hope these endeavors will contribute to the rational design of radiation-resistant materials for targeted applications.

NUCL

Modeling for nuclear waste disposal: From materials to minerals

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Long-duration nuclear waste disposal requires a comprehensive understanding of the storage environment, engineered packaging, and the waste form material. Here, overviews of multiple ongoing projects at Sandia National Laboratories will be presented that focus on developing a fundamental scientific understanding of the properties of materials and minerals that is necessary for safe and secure nuclear waste disposal. For example, material design can enable selective radioactive material capture. Through the use of grand canonical monte carlo (GCMC) simulations we have enabled design of metal-organic frameworks for capture of volatile iodine, as a gaseous fission product. Materials for nuclear waste disposal, for example filler materials for moderator exclusion are needed to enable an option for direct disposal of dual-purpose containers (DPCs). We have applied peridynamic continuum scale modeling to evaluate cementitious materials for use in DPCs, identifying the role of porosity in controlling fracturing during setting which is unfavorable for successful containment. Finally, the packaged nuclear waste is disposed of in subsurface geologic repositories, such as the salt formation that hosts the Waste Isolation Pilot Plant (WIPP) in Carlsbad, NM (a low-level waste repository). The stability of the salt in the presence of mixed brines was analyzed via classical molecular dynamics (MD) to evaluate the changing salt-bring interface stability as a function of pressure and temperature, which controls the stability of the salt dome. Through these exemplars, the depth and breadth of SNL’s modeling research on materials and minerals critical to successful long-term nuclear waste disposal will be highlighted.

NUCL

Nuclear chemistry opportunities in radioisotope production at Oak Ridge National Laboratory

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Oak Ridge National Laboratory (ORNL) executes the largest radioisotope production and research portfolio within the Department of Energy (DOE) Office of Science for Isotope R&D and Production, as well as extensive isotope production programs for the DOE Office of Nuclear Energy and National Nuclear Safety Administration. This mission is enabled by the unique facilities at ORNL, including the High Flux Isotope Reactor (HFIR) and the Radiochemical Engineering Development Center (REDC).

The staff within the Isotope Science and Engineering Directorate (ISED) produce a variety of important medical, scientific, and industrial radioisotopes. These include several alpha/beta emitting radioisotopes either deployed or under clinical trial for treatment of cancer (e.g., Ac-225, Ac-227, Ra-224/Pb-212, and W-188); heavy actinides Bk-249, Es-254, and Fm-257 for fundamental chemistry research and new element discovery; Cf-252 for neutron emitting applications; Pu-238 for space exploration; and Ni-63 and Pm-147 for industrial applications. This work is often performed within hot cells, caves, and gloveboxes.

ORNL employs a broad mix of radiochemists, chemical engineers, materials scientists, nuclear engineers, mechanical engineers, chemical technicians, and quality assurance representatives throughout all stages of their careers to execute this research, development, and production portfolio. The laboratory is open to postdoctoral scholars, as well as graduate and undergraduate interns. In this talk we will provide an overview of the radioisotope programs at ORNL and discuss the careers available supporting this highly critical and fulfilling mission.

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HIPPO: A path to a career in isotope production

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There are a diversity of careers within the field of radionuclide production. Many different individuals with a variety of talents are necessary to be able to supply the nation with the critical isotopes that are needed to drive our nation's medical, industrial and scientific infrastructure. The DOE Isotope Program is sponsoring *the Horizon-broadening Isotope Production Pipeline Opportunities (HIPPO)* program to bring together faculty, staff, and resources from seventeen institutions to develop this much needed future workforce. In addition to developing a pipeline for PhD level scientists to contribute to future research efforts, HIPPO is vital for attracting students to fill opportunities at the bachelor and master's levels. Skilled and knowledgeable technicians with backgrounds in chemistry, physics, and engineering are highly sought after to fill positions as operators for accelerator and reactor production sites, to conduct isotope processing, quality control functions, and maintenance of the complex equipment required in the field of radionuclide production. HIPPO has been designed to attract and expose a diverse set of students to these exciting careers. Students from many universities, especially institutions without a strong nuclear science program, may not even realize that their more "traditional" science education can be successfully applied to a career in isotope production and processing. By exposing students to both research and production facilities, the door will be opened to have students apply their expertise in a variety of essential functions for isotope production and research areas. The inaugural cohort of students participated in research experiences at universities and national laboratories as well as HIPPO campuses, which are week-long workshops focused on various aspects of isotope production. The summer experiences were capped off by a week-long exposure to a national lab production site, for 2022 this was at Los Alamos National Laboratory.

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How it's made: Plutonium edition

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Chemical processing of plutonium is one of the greatest chemistry and engineering feats of the last hundred years. Scaling up from the first experiments to plant scale was a factor of 1 billion and completed in a few short years. The plants for processing material were built before the process was even decided upon. In the end, a flowsheet was developed to separate and purify the ~100 ppm of plutonium present in spent nuclear fuel at an efficiency of 99.9% and decontamination factor of 10^8. In this talk we will discuss those first processes to separate and recover plutonium as well as how they led to the modern PUREX process. We will also highlight the finishing processes that are still performed at the lab today, which engineering typically refers to as "just run it through a column". Since the end of the cold war and arms race there has been a significant decline in the demand for new plutonium. As such the complex has responded with further innovation. Today, the majority of “new” plutonium comes from a pyrochemical process. This entire pyrochemical flowsheet is capable of recovering and purifying plutonium utilizing just two reactants and a single solvent throughout the entire process. This talk will also give an overview of pyrochemical processing which is currently performed at LLNL at two different scales.

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High pressure studies of uranyl compounds to enhance understanding of *5f*-orbital bonding

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Compared to other parts of the periodic table, relatively little is known about the role of *5f* electrons in bonding and the impact of orbital overlap between the *5f*, *6d*, and *7s* orbitals in actinides. Studies of actinide materials in extreme conditions such as high pressure probe the complex bonding of the actinides. Uranium is of particular interest due to its prevalence in nuclear energy and nonproliferation programs. The goal of this project is to further elucidate the nature of U(VI) bonding through pressure-induced structural changes in uranyl compounds relevant to nuclear waste and mineralogical environments. High (gigapascal (GPa) range) pressures were achieved experimentally using a diamond anvil cell (DAC). Raman spectroscopy and X-ray diffraction were used to probe the short- and long-range structure of materials, respectively, at high pressures. Preliminary results indicate reversible pressure-induced bond shortening and sheet compression in boltwoodite ($K,Na[(UO_2)(SiO_3OH)]1.5H_2O$).

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Thermal decomposition and mechanistic discernment of uranyl compounds within different solvent systems

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UO_2 is the fuel of most commercial nuclear reactors. Thin films of UO_2 are also used as target materials for nuclear science measurements. Solution combustion synthesis has been shown to successfully produce uniform thin films for nuclear physics measurements to aid such studies. This work investigates the combustion synthesis mechanisms of uranium oxides in uranyl nitrate – acetylacetone – solvent systems. We

investigate the effects of three solvents (water, dimethylformamide and 2-methoxyethanol) and reactant ratios on the formation and decomposition of intermediate uranyl compounds. Five intermediate compounds have been isolated and examined by single crystal and powder X-ray diffraction methods, Raman spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and mass spectrometry. Results show the formation of structures containing the uranyl moiety with varying numbers of solvent and acetylacetonate ligands. Thermal decomposition pathways and total energy release of intermediate compounds are compared to that of corresponding combustible solutions to examine the contribution of the compounds to the overall combustion process. Establishing links between intermediate compounds and decomposition trends and oxide formation is key in better predicting combustion systems. The current work has shown how deviations in structures within even the same solvent system can result in differences to the energy release mechanism of the material.

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High temperature calorimetric study of synthetic actinide oxalate minerals and materials

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In the many, now-closed, uranium mines, exposure of the uranium minerals to air and moisture has resulted in the formation and subsequent discovery of many new uranium minerals – more than 22 have been discovered out of a single mine. Uroxite ($[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]\ H_2O$) and metauroxite ($\alpha$-$[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$), were reported in 2020 and are the first uranyl oxalate minerals. In addition to being minerals, actinide oxalates are important in the nuclear fuel cycle and environmental transport of actinides. It is important to understand the formation and mobility of actinide oxalate complexes in aqueous systems. Thermodynamic data is needed for prediction of environmental speciation and migration of actinide oxalate complexes, however, this data currently exists only for very few actinide oxalates. Several actinide oxalates were prepared, including synthetic analogues of the two uranyl oxalate minerals. High-temperature oxide-melt drop-solution calorimetry was performed with a Setaram AlexSYS calorimeter to determine the enthalpies of formation from elements of these compounds. This data can be used to aid in predicting the speciation and migration of actinide oxalate compounds. It can also be used to investigate trends of stability across compounds with different actinides, oxidation states, counter cations, oxalate chelation, and crystallographic structure.

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Transformations of a uranyl oxy-hydroxide phase: Probing alteration behavior through humidity and ionizing radiation

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The fundamental chemistry of uranium minerals and their associated alteration phases is important for nuclear waste storage and the environmental mobility of uranium. Of the possible transformations at mineral surfaces, buildup of peroxide and formation of uranyl peroxides has been reported on spent fuel and depleted uranium-containing projectiles. The uranyl peroxide phase studtite, $[(UO_2)O_2(H_2O)_2](H_2O)_2$, is a secondary mineral that can form by incorporating radiation-produced peroxide at a mineral-water interface of an existing uranium-bearing mineral. Recent reports of studtite formation via alpha radiolysis are inconsistent with the existing understanding of the water-uranium-radiolysis system. Irradiating samples using an external source of radiation is therefore useful as a controlled dose can be delivered to a well-characterized specimen to study alteration products. Here we focus on the irradiation and subsequent alteration of a uranyl oxy-hydroxide hydrate phase, metaschoepite, in an effort to better probe the interfacial properties of this system.