NUCL 4504767

Machine learning in tritium production

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To address the complexity of hydrogen isotope processing, distinguishing protium, deuterium, and tritium, advanced analytical and computational methods are required to parse overlapping spectral features and dynamic process signatures. Before isotopes can be efficiently separated, chemical impurities such as water , ammonia, and methane must be detected, quantified, and either removed or recycled to minimize interference with separation efficiency. The spectral fingerprints of these molecules often overlap with those of hydrogen isotopologues, necessitating multivariate statistical tools like chemometrics to disentangle signals. Layered on top of this, radiological environments that limit high-dimensional feature extraction from continuous sensor data are still possible with modern classification methods for pattern recognition and anomaly detection without prior labeling. By combining impurity identification with isotope-specific signal separation, chemometric workflows provide a comprehensive framework for both pre-separation purification and high-resolution isotope analysis, ultimately optimizing recovery, minimizing loss, and improving real-time decision making.

NUCL 4512363

Probing interfacial actinide reactivity with (resonant) X-ray reflectivity

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Solid–liquid interfaces play a central role across nuclear science and technology, governing actinide behavior in environmental transport, nuclear waste disposal, advanced reactor systems, and fuel recycling. At these interfaces, molecular-scale actinide speciation, solvation, and surface interactions control key processes such as radionuclide mobility, corrosion and passivation, colloid formation, and separation efficiency. Despite their importance, the buried nature of solid–liquid interfaces severely limits direct experimental access to actinide interfacial reactivity, creating a need for in-situ approaches to shed light on the molecular mechanisms governing actinide reactions at interfaces.
Here, I present an interface-specific synchrotron technique that combines high-resolution specular X-ray reflectivity (XR) with resonant anomalous X-ray reflectivity (RAXR) through energy tuning near metal absorption edges, and demonstrate its utility for elucidating actinide interfacial reactivity. XR and RAXR enable the extraction of (element-specific) electron density profiles along the surface-normal direction at buried interfaces with sub-Å resolution, providing direct insight into interfacial actinide ion distributions, including ion coverages and metal coordination environments.
I illustrate the power of XR and RAXR using two of my recent studies. First, pH-

dependent changes in uranyl adsorption on aluminum oxide single-crystal surfaces were investigated, revealing how solution chemistry controls the interfacial distribution and hydration environment of U(VI) species. Second, XR, RAXR, and complementary atomic force microscopy to study the interfacial formation of Th(IV) nanoparticles on the muscovite (001) basal plane. Variations in background electrolyte composition (Li^+, Na^+, K^+) lead to pronounced differences in Th uptake, with RAXR providing direct evidence for discrete Th-rich particle layers extending tens of Å from the surface, consistent with interfacial nucleation and growth rather than simple ionic sorption.
Together, these examples highlight how electrolyte composition governs actinide interfacial reactivity, from ion adsorption to nanoparticle nucleation, and demonstrate the unique capabilities of synchrotron user facilities to resolve complex actinide interfacial phenomena with chemical specificity and sub-Å-level resolution.

NUCL 4513904

Towards an automated process for the dissolution of particles

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At Pacific Northwest National Laboratory (PNNL) the nuclear forensics transformational innovation (NFTI) has been working to change how nuclear materials are processed and analyzed. Specifically, the initiative is interested in utilizing micro sampling and analysis. Towards that end, the microdissolution team has been working on the automation of large numbers of particle dissolutions. This is primarily being accomplished through the use of a commercial off-the-shelf liquid handling device originally intended for biological and medical applications. We present here some of our work on dissolution and analysis of sol-gels obtained from Idaho National Laboratory. Two different types of particles were obtained and analyzed. The first were larger in size, around 1 mm in diameter, and contained weapons grade plutonium (WGPu) at 10 parts per billion (ppb) with fission products produced in April of 2025. The second set of particles were smaller in size, around 50 micrometers in diameter, and contained fission products that were produced in July of 2024. The particles produced from this material were pure silica and collected on a Whatman filter paper.
Both sets of particles were placed into well plates and dissolved by adding 15 µL of nitric acid, 10 µL of hydrochloric acid, and 10 µL of hydrofluoric acid. The large particles were then heated at 100°C and shaken at 1000 rpm on a Hamilton heater-shaker until dry. The small particles were placed under a heat lamp until dry. Both sets were brought up in 3 M HNO_3 + 10% H_2O_2, processed through a UTEVA column, and analyzed on a Neoma MS/MS multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS).

NUCL 4515777

Structural investigation of UO_3 polymorphs via neutron scattering

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In recent years, significant progress has been made in understanding the structure-property relationships of the uranium trioxide (UO_3) polymorphs. UO_3 crystallizes in at least 6 distinct structural modifications in addition to an amorphous phase. The consistent stoichiometry and variable structure of these materials make the UO_3 polymorphs an ideal system for exploring optical vibrational spectroscopic signatures and the structural origins thereof. The diversity of UO_3 can be attributed to variations in precursor materials, synthesis parameters, and resultingly, mechanisms of phase transition from precursor to oxide. Three polymorphs (α-, δ-, and ε-UO_3) are of particular importance to both basic actinide science and applied nuclear fuel cycle chemistry. α- and ε-UO_3 possess similar but distinct crystallographic structures, and additional insight into the local U coordination environment is needed to fully resolve the structural distinctions therebetween. δ- UO_3, despite having a high-symmetry cubic crystal structure and no Raman-active vibrational modes based on symmetry shows intense

Raman scattering. To this end, we employ powder neutron diffraction to elucidate features in the crystal structures of α-, δ-, and ε-UO_3 not detectible using X-ray crystallography that may give rise to unique optical vibrational spectroscopic signatures observed experimentally for these phases.

NUCL 4521548

Streamlining access to theranostics of mixed element pairs using a trifunctional amino acid linker

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Theranostic radiopharmaceuticals are emerging as a cornerstone of oncological intervention, with mixed element theranostic pairs offering the flexibility to combine radioisotopes with compatible decay characteristics for optimised imaging and therapy. These pairs often use inorganic radioisotopes that require highly selective, stable chelators to ensure accurate and safe delivery of radiotherapeutic dose to target tissue. However, divergent coordination preferences between radiometals can compromise metal ligand stability. Dual chelation within a single ligand scaffold can address this, but broad chelator selectivity reduces chelator choice due to risk of cross coordination across binding centres.

In this work, click chemistry was employed to facilitate a modular assembly of a series of radiopharmaceuticals, aimed to overcome these potential selectivity issues, providing a theranostic ligand platform that can be used with any desired pairing of radiometal isotopes. A lysine amino acid backbone was functionalised to introduce a trans cyclooctene (*t*CO) and dibenzocyclooctyne (DBCO) moiety, allowing orthogonal click reactions with target groups that possess an azide or tetrazine moiety. The terminal amine of the amino acid backbone could be further functionalized to attach a chelator or targeting molecule through thiourea or amide chemistry. This scaffold provided great flexibility, allowing the ‘clicking’ of pre labelled azide/tetrazine functionalised chelators for theranostics or multiplexed imaging with up to three unique radioisotopes. Further potential applications include bispecific imaging, or pre targeted administration of the radiopharmaceutical.

Preliminary results have focused on the successful radiolabelling of multiple radioisotopes, the production of radiopharmaceuticals with bispecific targeting groups and the application of these constructs in *in vitro* settings.

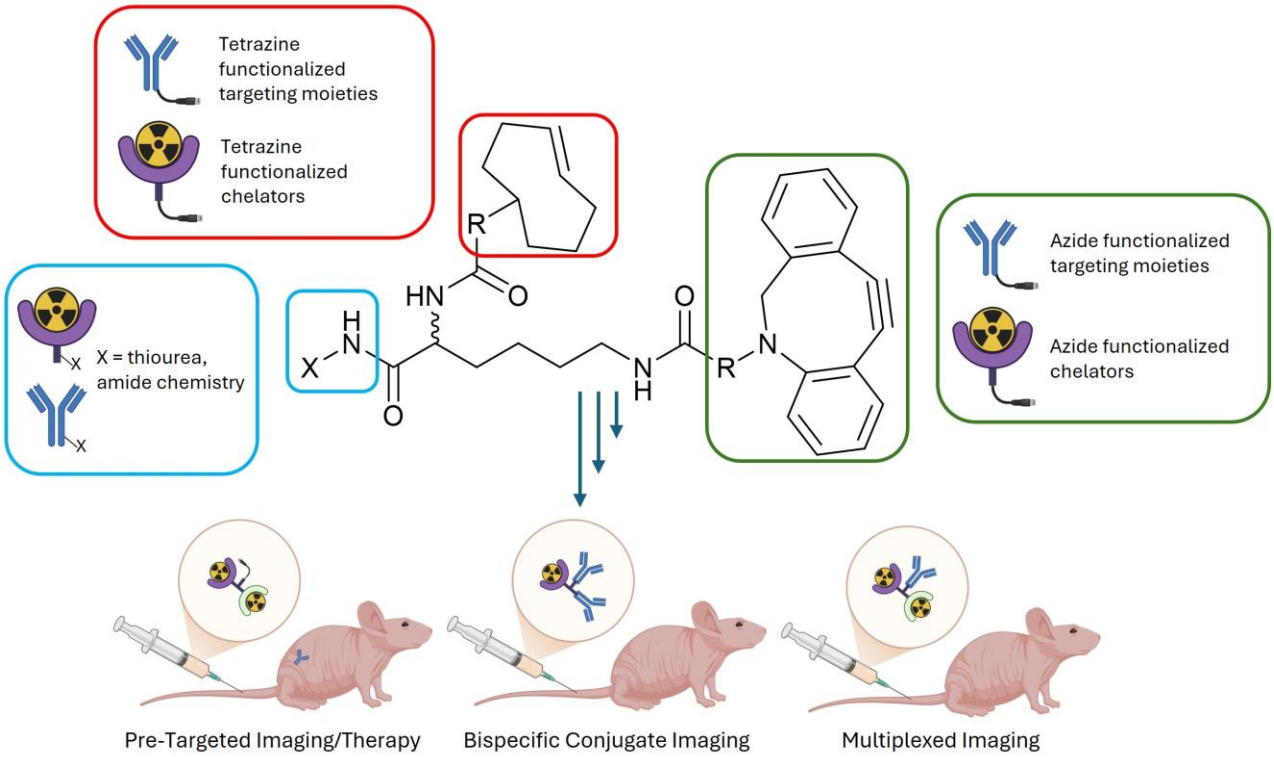

Figure 1. Modular system that incorporates two click handles for selective radiolabelling of mutliple radiometals, pre-targeted imaging/therapy, bispecific conjugate imaging and muliplexed imaging.

NUCL 4522653

Identification and characterization of insoluble high-level waste solids in the tank 14H annulus at the Savannah River Site

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At the Savannah River Site, approximately thirty-three million gallons of high-level radioactive waste, generated from used nuclear fuel reprocessing, are stored in the H and F Tank Farms. The Tank Farms consist of a total of fifty-one carbon steel waste tanks of which eight have been operationally closed. The waste treatment process involves bulk waste removal where the insoluble sludge solids and salt-bearing liquid supernatant are transferred to facilities where the high and low-level waste streams are eventually immobilized through vitrification and grouting, respectively. Tanks that have completed bulk waste removal are subject to cleaning and heel removal, after which a declaration of preliminary cease waste removal (PCWR) may be reached where waste removal efforts are complete and no further waste transfers are made in or out of the

tanks. Finally, tanks are operationally closed. There are four types of waste tanks in the Tank Farms; three out of the four types are doubly contained with an annulus between the two walls. Tank 14H, a double-shelled Type II tank with a carbon steel primary wall and annulus pan, experienced leaks of salt supernatant through the primary wall into the annulus. The supernatant dried and formed water insoluble solids, creating a significant challenge for annulus cleaning due to safety basis requirements only permitting water utilization for cleaning purposes. In this work, the water insoluble solids were identified to be primarily gibbsite and characterized for their radiochemical composition for PCWR purposes. The radiochemical findings facilitated the cessation of annulus cleaning efforts and progression toward primary tank PCWR operations.

NUCL 4523298 - Withdrawn

NUCL 4523302

3-Substituted derivatives of 7-Methoxy-2,3,4,5-tetrahydro-1*H*-benzo[d]azepin-1-ol generate radioligands for imaging brain GluN2B in vivo

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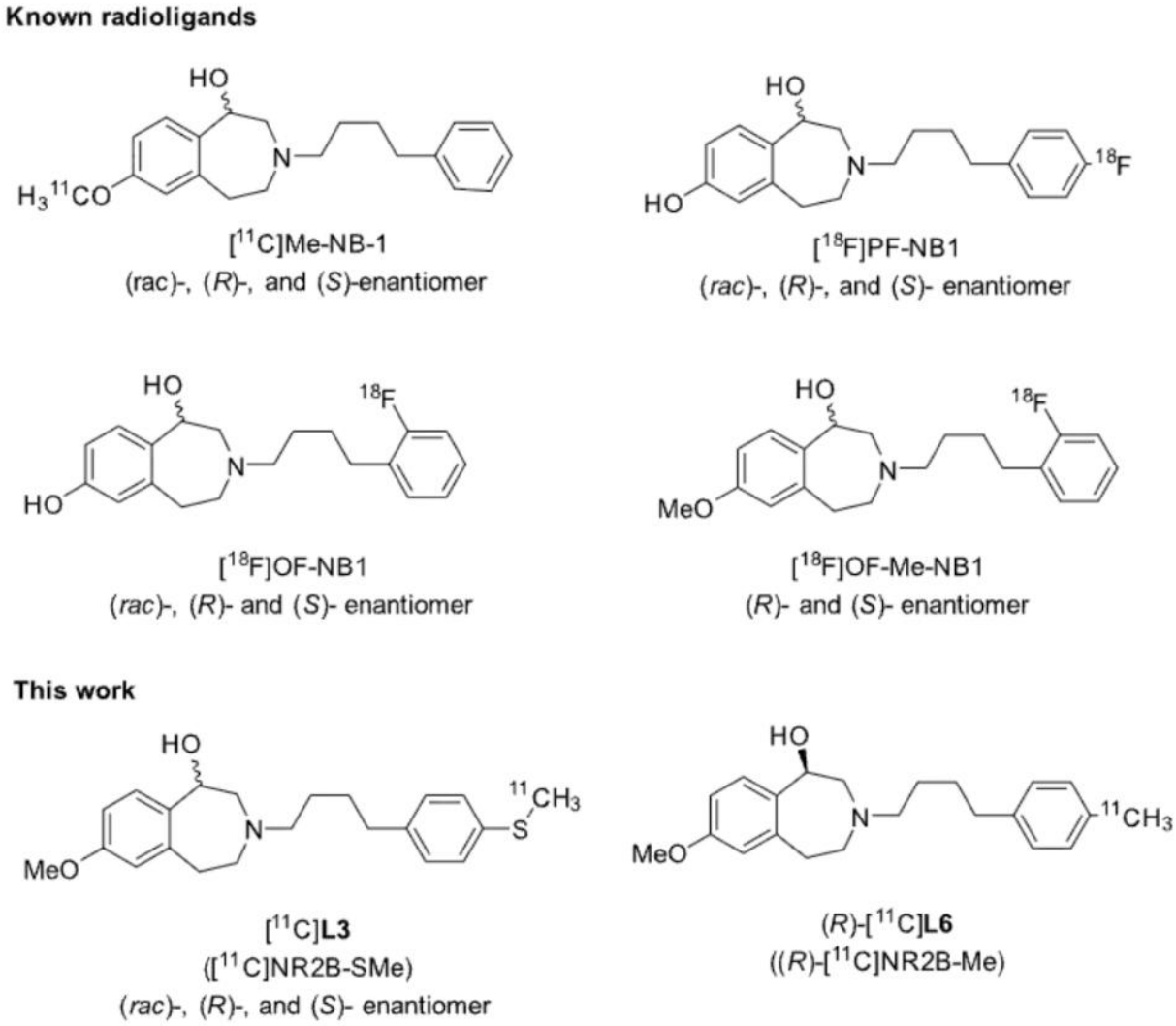
Background: *N*-Methyl-D-aspartate (NMDA) receptors containing the GluN2B subunit are therapeutic targets for neurologic disorders such as Alzheimer's. Yet, few PET radioligands provide robust, displaceable in vivo signals at this site. We designed and synthesized 3-alkylaryl derivatives of 7-methoxy-2,3,4,5-tetrahydro-1*H*-benzo[d]azepin-1-ol to explore structure–activity relationships (SAR) and identify candidates ideal for carbon-11 labeling (t1/2 = 20.4 min) as PET radioligands.
Methods: Nineteen ligands and selected enantiomers were prepared via alkylation with substituted alkyl tosylates. Binding affinity was evaluated in rat brain homogenate competition assays versus [3H]ifenprodil and screened through the NIMH Psychoactive Drug Screening Program. Variations included para-substitution, linker length (3–5 carbons), heteroaryl substitution, and unsaturation. Configuration was established by vibrational circular dichroism and infrared spectroscopy, and GluN2B ligand docking was performed. Selected compounds were labeled with C-11 for PET imaging in rats and rhesus monkeys.
Results: SAR showed minimal sensitivity to para effects and tolerance for bulky hydrophobic substituents, whereas hydrogen bond acceptors reduced affinity. A four-carbon tether was preferred. No correlation was observed between lipophilicity and binding affinity ($r^2 \approx 0.03$). L3 and L6 enantiomers displayed nanomolar GluN2B affinity, moderate lipophilicity, and low σ1/σ2 binding liability. Docking elucidated binding interactions. PET studies showed [11C]L3 produced strong displaceable binding in rat brains, and [11C]L6 showed high binding potential in monkeys relative to other GluN2B radioligands.
Conclusion: These studies define key structural determinants for high-affinity GluN2B

binding. [11C]L3 and [11C]L6 demonstrate favorable in vivo characteristics, supporting further GluN2B-selective PET radioligand development for clinical imaging.



NUCL 4524328

Effect of citrate on the solubility of uranium (VI) in synthetic WIPP brines across variable pC_H^+ conditions

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The Waste Isolation Pilot Plant (WIPP) is the only operational deep geological repository in the United States for the disposal of defense-related transuranic (TRU) waste. Solubility studies are essential for predicting radionuclide behavior and long-term repository performance, in the unlikely event of a brine intrusion. WIPP brine is chemically complex, which complicates the radionuclide solubility studies as compared to simpler aqueous systems.
Organic compounds in WIPP waste, primarily EDTA, citrate, oxalate, and acetate, can complex with metals and actinides, significantly affecting actinide solubility. In WIPP performance assessment, U(VI) is the only significant An(VI) actinide, as Np(VI) and Pu(VI) are excluded under the strongly reducing conditions expected in the repository. Previous work demonstrated that citrate increases uranium solubility in pC_H^+ 9 synthetic WIPP brine. However, these earlier studies were limited to a single pC_H^+. In the next phase of the study, experiments were conducted over a pC_H^+ range (7, 9, and 11), in synthetic WIPP brines as well as 5 M NaCl, in the presence and absence of all organics and with citrate alone, under anoxic conditions, and over 123 days using an under-saturation approach. The results confirmed that citrate increases U(VI) solubility.
In the synthetic brine at pC_H^+ 9, uranium solubility reached ~10^{-6} M both when all organic complexants were present and when citrate was present alone. The solubility at pC_H^+ 11 was slightly lower than at pC_H^+ 9, while the highest solubility was observed at pC_H^+ 7. Similarly, citrate showed the greatest impact on uranium solubility among the tested organic complexants. Additionally, experiments in 5 M NaCl exhibited uranium solubility approximately one order of magnitude higher than in WIPP- brine at pC_H^+ 9, highlighting the influence of brine composition and ionic strength on actinide behavior. The results provide important screening data to support thermodynamic modeling and long-term performance assessment calculations for the repository.

NUCL 4524351

Characterization of synthetic ianthinite and synthetic schoepite: Implications for uranium oxide alteration

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Natural weathering of uraninite, UO_{2+x} where x = 0–0.25, is analogous to what is expected for used nuclear fuel (UNF) in a geological repository. This alteration is characterized by oxidation-hydration corrosion and the formation of uranyl oxyhydroxide phases including ianthinite $[U^{4+}_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$, schoepite $[(UO_2)_4O(OH)_6](H_2O)_6$, and metaschoepite $[(UO_2)_4O(OH)_6](H_2O)_5$ along with a host of U(VI) structures influenced by collocated ionic species. Synthesis of pure-phase analogs of ianthinite and schoepite has remained elusive, however, our efforts have successfully produced crystalline powder and single crystal products matching these mineral phases. Identity is confirmed using X-ray diffraction techniques with excellent agreement with the natural mineral structures. Local uranium bonding environments within polymeric sheets are explored using Raman and infrared spectroscopy with a

particular emphasis on the proposed U(IV) octahedral site of ianthinite. Additionally, the mixed-valent nature of ianthinite is revisited using X-ray photoelectron, diffuse reflectance, and solid-state UV-Vis spectroscopies with preliminary results indicating a mixture of U(IV/VI) in agreement with structural calculations. The interconversion of these phases induced by atmospheric alteration and thermal degradation is explored and experimentally visits previously hypothesized pathways starting from pure phase components. The successful synthesis of these minerals and a renewed understanding of their interrelations support our understanding of both natural and synthetic UO_2 alteration in the environment with further implications for UNF storage, resource recovery, and radionuclide mobility.

NUCL 4524708

Inelastic neutron scattering for studying materials in the nuclear fuel cycle

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Inelastic neutron scattering (INS), a vibrational spectroscopic technique using neutrons as the excitation source, was used to study several materials relevant to the nuclear fuel cycle including actinide(IV) oxalate phases and radioiodine sorbents. Actinide(IV) oxalate hydrates are important intermediates in the purification of actinides and the formation of actinide oxides by calcination in the fuel cycle. An improved understanding of the water molecule environments and the effect of these water molecules on the structures and properties of the actinide oxalate phases is important to the nuclear fuel cycle. Thus, we used INS to study the hexa- and dihydrates of U(IV) and Th oxalates. This technique, coupled with infrared spectroscopy, revealed vibrational modes related to water molecules that had not previously been assigned to such. The results of this work contribute to an improved understanding of not only the U(IV) and Th oxalate phases, but the structurally analogous Pu(IV) and Np(IV) phases as well. Highlighting the diversity of INS applications for investigation of nuclear fuel cycle materials, radioiodine sorption was also examined using this technique. The capture of radioiodine, a fission product of interest due to its mobility and the long half life of iodine-129 (~15 million years), is an important consideration for nuclear fuel recycling. Solid sorbents with metallic iodine getters, such as Ag, Cu, or Bi, have demonstrated some success in the capture of iodine. Since iodine capture in a fuel recycling flowsheet will occur in a nonideal environment, with temperature, humidity, and competing gaseous components affecting the performance of these sorbents, understanding how

these variables affect the sorbent materials is important in selecting the sorbent best suited to the capture environment. We used INS to probe the changes in vibrational modes of three sorbents (Ag-mordenite, Cu_2S-polyacrylonitrile, and Bi_2S_3-polyacrylonitrile) related to their exposure to environments of I_2, NO_2, and a mixture of I_2, NO_2, and H_2O. In the latter environment, the oxidation of the Cu getter was observed along with a change in the vibrational modes related to the polyacrylonitrile scaffolding. No similar change was observed in the Bi sample. These results provide insight into the mechanisms that affect the performance of these sorbents under different environments.

NUCL 4525233

Analysis of Mo isotopes and ^{90}Sr in smear samples collected at the Fukushima Daiichi Nuclear Power Station

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The fission yields of the Mo isotopes (^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, ^{100}Mo) and ^{90}Sr are relatively high, and Mo tends to be released from fuel under oxidizing conditions, whereas ^{90}Sr is more readily released under reducing conditions. Therefore, these nuclides in the smear samples collected inside the reactor buildings of Unit 1, 2, and 3 at the Fukushima Daiichi Nuclear Power Station (FDNPS) were analyzed to estimate the oxidation–reduction state of the core atmosphere during the core-degradation process.
Smear sample was cut into 4 or 5 pieces, and one fragment was applied to acid digestion. Mo was purified using TEVA resin and Mo isotopes were measured using ICP-MS/MS with oxygen dynamic reaction. ^{90}Sr was analyzed using β-ray spectrometry or using liquid scintillation counter after chemical separation. ^{137}Cs were measured using a high-purity Germanium semiconductor.
The mole of Mo or ^{90}Sr were plotted against the mole of ^{137}Cs in Fig. 1 a and b. Solid lines indicate the ratios of Mo/^{137}Cs or ^{90}Sr/^{137}Cs in the reactor core. All of the samples collected from Unit 1 showed no detectable fission-derived Mo. Because of low activity of ^{137}Cs for Unit 1 samples, the Mo amount is also relatively low, and it may not have been detected. In Unit 2, Mo/^{137}Cs levels from the first to fourth floors were comparable to those in the reactor core but tended to be higher on the fifth floor. The results imply existence of the oxidizing atmosphere. The ^{90}Sr/^{137}Cs ratio was about two orders of magnitude lower in Unit 2 and about two to four orders of magnitude lower in Units 1 and 3.

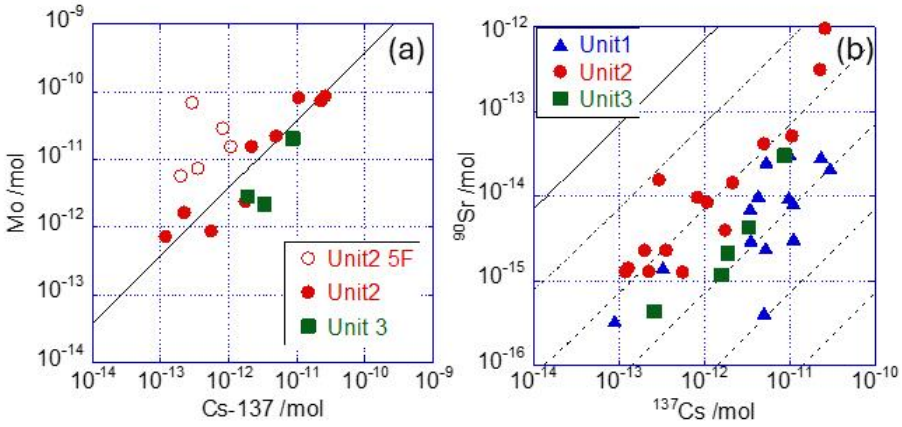

Fig.1 Relationship between ^{137}Cs and (a) Mo or (b) ^{90}Sr

NUCL 4527042

Plutonium Chloride speciation as a function of pH, temperature, and ionic strength

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Plutonium (Pu) is present in the environment as a direct consequence of nuclear energy production and weapons development. Although underground nuclear weapons testing has ceased, long-term safety assessments and remediation planning remain essential due to the continued storage and disposal of transuranic waste and the potential for accidental release. In the United States, the Waste Isolation Pilot Plant (WIPP) – the only operating deep geologic repository for transuranic waste – is hosted in the Salado Formation of southern New Mexico, a salt bed system where Pu has also been

introduced through legacy nuclear activities. Predictive modeling of Pu transport and retention in such environments depends critically on accurate descriptions of Pu(VI) aqueous speciation under variable pH, temperature, and salinity conditions.
This work will describe Pu(VI) speciation in NaCl and $MgCl_2$ solutions (0.1–10m) as a function of pH (2–11) and temperature (25–95 °C) using Ultraviolet–Visible–Near Infrared (UV–Vis–NIR) absorption spectroscopy. Experiments were conducted under oxic conditions to allow hydrolysis and potential carbonate uptake, reflecting realistic environmental and repository scenarios. Spectral evolution was used to assess transitions from the uncomplexed plutonyl ion (PuO_2^{2+}) to chloride coordinated species and identify the formation of other mixed chloro–hydxo and chloro–carbonato complexes.
Comparisons between NaCl and $MgCl_2$ systems provide insight into how background electrolyte composition and ionic strength influence ligand competition and Pu(VI) coordination geometry. The resulting spectroscopic results will be interpreted in the context of established actinide ligand-affinity trends and prior studies of Pu(VI) hydrolysis and stability in saline systems.
This study aims to generate useful thermodynamic data relevant to the aqueous speciation of Pu(VI) under coupled pH, temperature, and salinity conditions, strengthening the mechanistic basis for predicting plutonium behavior in salt-based nuclear waste disposal environments.

NUCL 4528303

Effects of redox conditions and temperature on diffusion of 99Tc and 237Np

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Understanding the transport of radionuclides through clay buffer materials is key to risk assessment for the burial of spent nuclear fuel in deep geologic repositories (DGRs). In such a scenario, tight packing of the clay buffer is expected to limit advective flow such that diffusion is the main mass transport mechanism. Transport behavior will also be affected by retardation mechanisms such as sorption and precipitation which are in turn influenced by the oxidation state of the radionuclide. For redox sensitive radionuclides such as Tc, Np, and Pu, redox states can have a profound impact on diffusion rates. For example, under oxidizing conditions 99Tc(VII) will exist as the aqueous pertechnetate oxyanion which is expected to diffuse quickly due to low affinity for mineral surfaces while under reducing conditions at environmentally relevant pH values, formation of sparsely soluble and strongly sorbing Tc(IV) can limit Tc mobility. However, the impacts of temperature on Tc(IV) sorption and solubility are unknown.
We have investigated the diffusion behavior of 99Tc and 237Np through Na-montmorillonite at 25, 50, and 75 C under both atmospheric and reducing (2% H2 / 98% N2 anaerobic chamber) conditions. Stainless steel diffusion cells were set up with dry clay packed between 10 μm pore size stainless steel filters and saturated from the bottom up with 0.01 M NaCl in ultrapure DI H2O. Temperatures were set using resistive

heating coils fitted around the stainless steel clay housing cylinder. Diffusion experiments were performed by circulating a 10-7 M 99Tc/237Np solution through one of the porous filters while circulating a second, initially radionuclide-free solution through the opposite filter. Aliquots were periodically taken from the reservoirs to assess the extent of diffusion over time. At the end of the experiment, the clay was sliced and digested to determine the spatial distribution of the nuclides. The diffusion results show significant differences in the diffusion behavior for both 99Tc and 237Np between the benchtop and the anaerobic chamber, suggesting that Na-montmorillonite is facilitating reduction in the anaerobic chamber at elevated temperatures.

NUCL 4528318 - Withdrawn

NUCL 4529555

Energy generation from γ-rays via iron oxide-hydrogen peroxide electrochemical cells

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Historically, nuclear waste has been regarded as a negative asset; however, contemporary research is shifting toward its utilization as a resource. Most of these studies have investigated hydrogen production through water radiolysis as a primary means of energy recovery.
In our previous study, we investigated the reduction of iron in high-concentration of iron aqueous dispersions under γ-irradiation, and ^{60}Co was used for irradiation. Also, we successfully demonstrated electricity generation using an electrochemical cell with iron oxide particles (IOPs) and hydrogen peroxide for active materials. However, the direct electron exchange between IOPs and H_2O_2 was the cause of the low efficiency.
In the present study, we aim to enhance both the power output and Faradaic efficiency of these electrochemical cells. To improve electrochemical cells, we investigated the effects of electrode size and insertion of separator into electrochemical cells. In this experiment, IOPs (10–200 mg/mL) prepared by coprecipitation were irradiated at 359 Gy to analyze H_2 production and concentration of divalent iron. Using Fricke dosimetry for dose calculation and GC-MS for H_2 measurement, 100 mg/mL samples were tested in electrochemical cells immediately post-irradiation for direct energy harvesting.
As a result, we achieved significant improvements in electrochemical cell performance by expanding the electrode diameter from 1 cm to 8 cm and insertion of separator, which increased the power output from an initial 1 μW to 380 μW. During this process, the Faradaic efficiency also increased from 1 % to 28 %. Furthermore, these results underscore the critical roles of both electrode surface area and separator integration in

enhancing overall performance. Finally, we have successfully harvested 70 mJ from a 32 J of γ-ray dose.

NUCL 4530086

Achieving favorable kinetics in the low-temperature chlorination of Zircaloy cladding

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Variations in Zircaloy chlorination kinetics have been observed using low-temperature sulfur chloride solvents to process used nuclear fuel cladding. The reaction time is influenced by different batches of commercially obtained sulfur monochloride, the main chlorinating agent. Solvent impurities and in-situ solvent preparation methods have been investigated. We present purification techniques, Zircaloy chlorination results, and Raman spectroscopy characterization of the solvent's equilibrium with higher sulfur chloride species. Techniques to enhance reaction kinetics, including achieving higher temperatures, altering surface area to volume ratios, and using different Zircaloy types will also be discussed.

NUCL 4530526

Target and radiochemical separations development for (n,2n) cross-section measurements of ^{73}As at the National Ignition Facility

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The National Ignition Facility (NIF) at Lawrence Livermore National Laboratory enables inertial confinement fusion experiments that produce an intense, short pulse of 14.1 MeV neutrons during deuterium-tritium burn. These conditions allow nuclear reaction measurements on extremely small quantities (≈ 10^{13} atoms) of radioactive material, opening a new frontier for nuclear data measurements.

We are developing methods to measure neutron-induced reaction cross-section on arsenic-73 (^{73}As, $t_{1/2}$ = 80.3 d) at NIF. This effort is motivated in part by the use of stable arsenic (^{75}As) as a radiochemical neutron-fluence detector via production of ^{72,73,74}As activation products. Completing ^{73}As(n,2n) measurements requires doping ^{73}As into capsules with a 10 μm fill hole, which imposes stringent purity constraints because microgram-level salt residue can cause an obstruction. In NIF cross-section experiments, vanadium solid radiochemical collectors (SRCs) capture condensed implosion debris for post-shot analysis; SRCs also contain hohlraum-derived gold and depleted uranium activation and fission products that create gamma-ray backgrounds

which can obscure desired signals in direct gamma spectrometry.

In this work, we evaluate halide distillation as a volatility-based purification and separation strategy relevant to both capsule doping and SRC processing. Arsenic halides such as arsenic trichloride ($AsCl_3$; bp 130 °C) can be distilled from nonvolatile matrices, enabling inorganic salt removal and separation from nonvolatile impurities or radionuclides that drive high gamma background. No-carrier-added ^{73}As is predominantly present as As(V) in aqueous solution and does not readily volatilize as halides; we therefore implement *in-situ* reduction with hydrobromic acid (HBr) to form As(III) and enable As recovery by distillation. Inorganic salt removal from mixed HCl/HBr solutions achieved a > 99 % reduction in salt mass, while maintaining an overall ^{73}As recovery of 88.1 % (SD = 5.4 %, n = 2). We also apply halide distillation to SRC processing to separate ^{73}As from a simulated fission and activation product matrix. This presentation will describe these methods and their application to upcoming $^{73}As(n,2n)$ cross-section measurements.

NUCL 4531629

Effect of fast critical assembly discards on supernate solubility of plutonium and uranium in tank 51H at the Savannah River Site

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The Savannah River Site's H-Canyon is responsible for the dissolution and disposal of Fast Critical Assembly (FCA) material that was received from the Japan Atomic Energy Agency (JAEA). The most recent batch of material consisted of bundles of stainless steel (SS) clad plutonium and enriched uranium fuel that was chemically and electrolytically dissolved at the H-Canyon facility before being transferred to Tank 51H in the tank farm for interim waste storage and disposition. The Tank 51H supernate must fulfill Waste Acceptance Criteria (WAC) before being sent to the Salt Waste Processing Facility (SWPF). Additionally, controls for Tank Farm transfers require that a Plutonium solubility limit be adhered to allow transfers between waste tanks. It was a concern that this new disposal of FCA material could impact the processability of the supernate. A sample of the tank supernate was taken before and after this discard took place, so that the change in the amount of dissolved plutonium and uranium could be measured. This task served not only to determine the amount of soluble material present that may pose a current processing issue but also help predict the effects of future material disposals. It was found that the disposal of this additional FCA material did cause a noticeable increase in the amount of dissolved plutonium and uranium in the supernate. This increase did not cause, however, any concerns with regards to compliance with the SWPF WAC and internal Tank Farm limits. This work will discuss the results of the FCA discards and how other characteristics of the Tank 51H

environment can have an effect on the ability of plutonium and uranium to remain soluble in the supernate.

NUCL 4532286

Computational Insights into Iodine Capture by MOF-74 Frameworks

***Juliana Antonio**, jrodriguezantonio2@gmail.com, Elfi Kraka. Chemistry, Southern Methodist University, Dallas, Texas, United States*

The management of spent nuclear fuel requires effective capture of volatile fission products; notably iodine, which poses environmental and radiological risks due to its volatility and long-lived isotope (I-129). Metal-organic frameworks (MOFs) are promising materials for iodine (I_2) capture because of their high surface area, tunable chemistry, and accessible metal sites. Among these, the MOF-74 family offers well-defined one-dimensional channels and open metal-center sites.

In this work, periodic density functional theory calculations are used to investigate iodine capture in M-MOF-74 systems (M = Mg, Mn, Fe, Co, Ni, Cu, and Zn). Local mode analysis is employed to quantitatively characterize metal-iodine interactions, covalent I-I bonding within I_2 and noncovalent $I_2 \cdots I_2$ interactions that arise within the framework pores. For open-shell transition metals, both ferromagnetic and antiferromagnetic spin configurations are explicitly considered.

The results demonstrate that magnetic ordering has a significant impact on the nature and strength of metal-iodine, and iodine-iodine interactions, as reflected in local mode force constants and topological bonding descriptors. These findings highlight the importance of incorporating magnetism and local mode analysis in open-shell systems when modeling iodine capture in open-metal-site MOFs and provide design principles for developing improved materials for iodine capture in nuclear fuel cycle applications.

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NUCL 4532767

De novo design of radium-binding proteins

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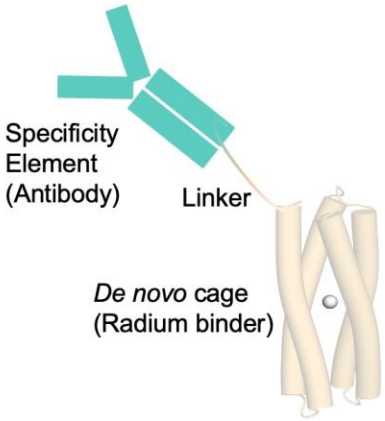
De novo protein design has emerged as a powerful strategy to design and engineer functional proteins from scratch for a broad range of applications from catalysis to pharmaceuticals. I chose to use de novo design to engineer proteins that can bind radium for radiopharmaceuticals. [223Ra]RaCl2 is the only clinically approved alpha particle-emitting drug, which is used to treat castrate-resistant prostate cancer bone metastases. However, this targeted alpha particle therapy (TAT) for the treatment of disseminated cancer is severely limited due to either failed radiolabeling or poor kinetic stability of the chelated complex. Metal ions in radiopharmaceuticals are generally attached to peptides or antibodies using small molecule chelators, such as ethylenediamine (EDA). However, Ra(II) has very weak affinity for known small molecule chelators. Thus, our aim was to design small, genetically encodable proteins, which can bind Ra(II) in such a way that it is trapped and does not dissociate for hours to days, thereby kinetically stabilizing Ra(II) for TAT. Since, the ionic radius of Ra(II) is only marginally larger than Ba(II), I planned to bind Ba(II) first as a non-radioactive analog of Ra(II). In this work, I designed de novo proteins guided by AI-based Ligand MPNN strategy, which could bind Ba(II) with high affinity. Considering the lack of biologically stable chelator complexes of 223Ra(II), I anticipate that our novel approach will open the path for cancer-targeted radiotherapies. Additionally, variants of our protein could be widely used to cage other alpha particle emitters, such as 225Ac, 213Bi, 227Th, 211At, and beta-emitting radionuclides, such as 153Sm for novel biomedical applications. Since it is genetically encodable, our proteins should provide a plug and play approach to production of fusion proteins, such as antibody-radionuclide complexes or, complexes with peptide hormones (e.g., somatostatin).



Fusing *de novo* radium binding-protein as a genetically encoded tag to antibody (or, peptide hormone (not shown)) to develop targeted radiopharmaceutical.

NUCL 4533303

Closure of Tank 9H - Annulus Characterization

***Hope Brown**, jhbrownprunty@gmail.com, Lawrence Oji. Savannah River National Laboratory, Aiken, South Carolina, United States*

Radioactive waste from the processing of spent nuclear fuel has been stored in underground waste tanks located on the Savannah River Site. The waste from these tanks must be removed to the maximum extent practical before the tanks may be removed from service and grouted in place. As part of this effort, residual material within the tanks must be analyzed to document radioactive and chemical constituents remaining at the time of closure. Three liquid samples, each containing approximately 200 mL of the annulus salt solution, were composited and analyzed for radionuclide, elemental, anions, and total mercury analysis by various methods. The primary alpha-emitting radionuclides and their concentrations were Pu-238, Am-241, Pu-239, Pu-240, and Cm-244. The primary beta-emitting radionuclides and their concentrations were Sr-90, Y-90, and Cs-137. The activities for uranium isotopes, which were above instrument detection limit, were U-234, U-235, U-236, and U-238. The data gave evidence that Tank 9H held minimal waste and would qualify to be removed from service and grouted.

NUCL 4533454

Evaluation of di methyl heptyl methyl phosphonate (DMHMP) for neptunium – plutonium separations

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Several countries' plans to develop isolated regions on Earth and in space have increased demand for radioisotope thermoelectric generators (RTGs) which harness the decay of radionuclides to produce heat sources. Production of ^{238}Pu, a primary fuel source in RTG systems, is achieved via irradiation of ^{237}Np targets. ^{238}Pu must be separated from the remaining ^{237}Np and any reaction byproducts for efficient energy conversion in RTG systems. Currently, purification of ^{238}Pu from ^{237}Np is performed by selective separation and redox control with 30% tributyl phosphate (TBP) via solvent extraction or ion exchange resins. However, multiple extraction cycles are required to achieve significant purity of the targeted actinides. A new extractant, di-1-methyl heptyl methyl phosphonate (DMHMP), which reports higher extraction of U(VI) and Th(IV) than TBP and other neutral organophosphorus extractants, has been synthesized. Experimental data on DMHMP extraction trends, the coordination of extracted DMHMP complexes, and thermodynamic data associated with DMHMP extraction of metals in all oxidation states have not been identified. We will present mechanistic and thermodynamic data for the extraction of Pu(III), Pu(IV), and chemical analogs Sm(III) and Th(IV) by DMHMP through solvent extraction and spectroscopic methods. The DMHMP data will be compared to TBP and an analogous phosphonate extractant, dibutyl butyl phosphonate (DBBP), to explain the extraction favorability across different organophosphorus extractants. We will present the stoichiometric parameters of the extraction reactions and associated thermodynamic parameters (ΔH, ΔS, ΔG). Spectroscopic techniques such as XANES, EXAFS, and FTIR provide the coordination environment of the extracted complex. Computational modeling driven by electronic structure theory calculations and artificial intelligence tools will allow for deriving binding preferences and coordination environments.

NUCL 4533540

Evaluation of modified amidophenolate ligands for redox reactivity at thorium centers

Andrew Mitchell*, drt788@gmail.com, Suzanne C. Bart, Matthias Zeller. James Tarpo Jr. and Margaret Tarpo Department of Chemistry, Purdue University, West Lafayette, Indiana, United States*

The redox restriction of thorium greatly limits its reactivity particularly when compared to uranium. In order for thorium to access the rich redox chemistry seen in other actinides, electrons must be provided from sources other than the metal center. One way this can be achieved is by storing electrons in redox active ligands around the metal. Electrons can then be accessed from the ligands to achieve redox reactivity at the metal. The 4,6-di-tert-butyl-N-(2,6-di-isopropylphenyl)-o-iminobenzoquinone (^{dipp}iq) ligand and particularly its doubly reduced amidophenolate form (^{dipp}ap^{2-}) have previously been used to provide the necessary electrons for the activation of dioxygen in dry air by thorium, forming a rare terminal thorium oxo species. Through this work and characterization of the thorium oxo complex, two challenges have become clear. First, the bulky di-isopropyl moieties provide steric protection to the oxo ligand, stabilizing it, but also inhibiting further functionalization. Second, the oxidation of the ligands reduces the ligand charge which in turn leads to weaker binding following the activation of dioxygen. In particular, full oxidation to the neutral iminoquinone ligands is accompanied by ligand dissociation in many cases. This presentation will discuss a ligand modification approach to addressing these steric issues including the impacts on structure, electronic properties, and reactivity that result from modifications to the ligand system.

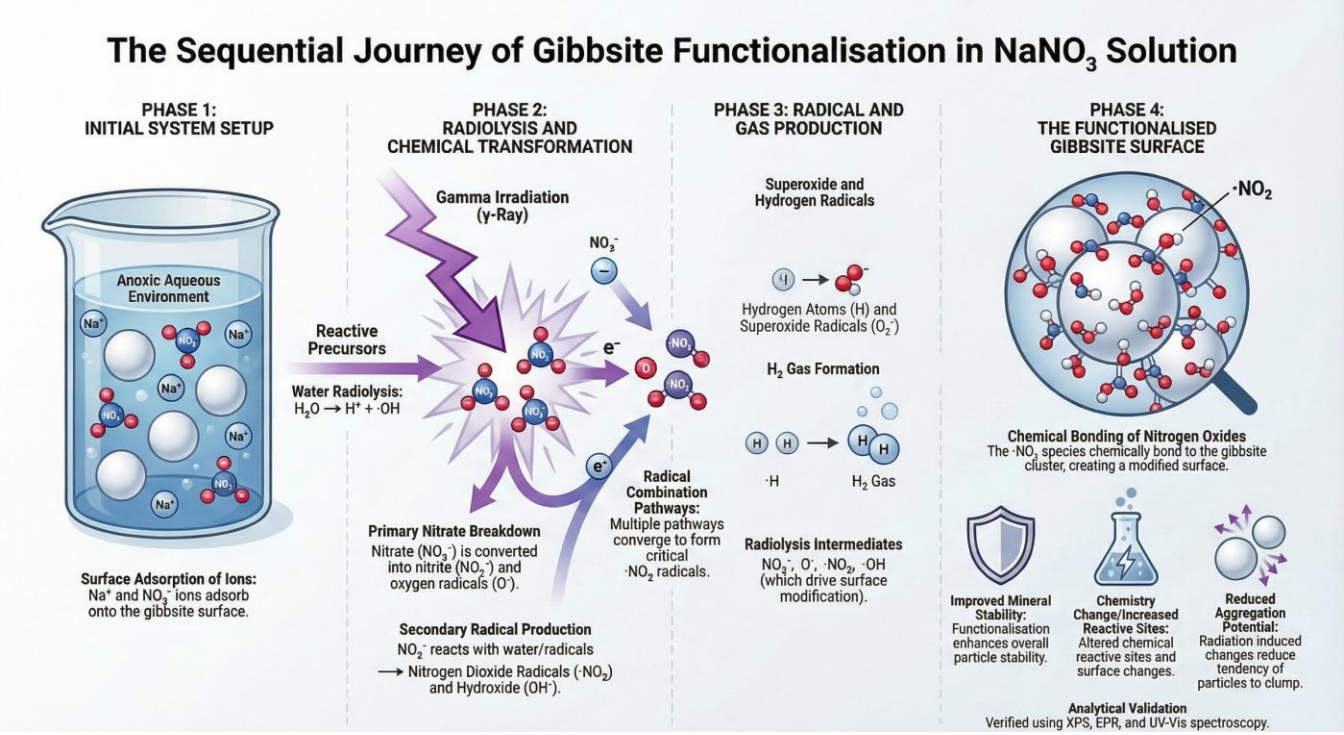
NUCL 4533709

Radiation-induced surface modification of gibbsite in $NaNO_3$ environments

Amita Bedar[1]*, bedar.amita@gmail.com, Hanna Hlushko*[2]*, Xin Zhang*[3]*, Kevin Rosso*[3]*, Carolyn Pearce*[3]*, Jay A. Laverne*[1,4]*. (1) Radiation Research Laboratory, University of Notre Dame, Notre Dame, Indiana, United States(2) Idaho National Laboratory, Idaho Falls, Idaho, United States(3) Pacific Northwest National Laboratory, Richland, Washington, United States(4) The Department of Physics and Astronomy, University of Notre Dame, Notre Dame, Indiana, United States*

Corrosion and dissolution of aluminum-based fuel cladding co-disposed with spent nuclear fuel promote the formation of aluminum (oxy)hydroxide minerals, primarily boehmite (AlOOH) and gibbsite ($Al(OH)_3$). Gibbsite is a dominant solid phase in legacy radioactive waste stored in underground tanks at the U.S. Department of Energy's Hanford site. In these environments, it persists in highly alkaline, nitrate-rich solutions under continuous ionizing radiation. Its stability, surface reactivity, and aggregation behavior strongly influence waste rheology, retrieval efficiency, and processing. Understanding radiation-driven mineral transformations under these coupled conditions is therefore essential for predicting long-term waste evolution.
Here, we examine the effect of γ-irradiation on the surface chemistry of gibbsite particles dispersed in anoxic aqueous $NaNO_3$ solutions. Samples before and after irradiation were characterized using diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and diffuse-reflectance UV–visible spectroscopy. Prior to irradiation, vibrational spectroscopies confirm adsorption of NO_3^- onto the gibbsite surface. Irradiation induces radiolytic decomposition of surface-associated nitrate species, accompanied by systematic modification of surface hydroxyl

coverage with increasing dose. XPS analysis shows reduced hydroxyl functionality alongside persistent nitrogen–oxygen surface species, indicating formation of nitrate-derived products.
Overall, γ-irradiation drives coupled nitrate radiolysis and surface hydroxyl restructuring on gibbsite, generating reactive oxygen and nitrogen intermediates that alter surface charge and particle interactions. These changes are expected to impact mineral stability, aggregation, and transport in high-level waste systems. The results provide mechanistic insight into radiation-induced mineral evolution and support predictive models for safer waste storage, retrieval, and processing.



NUCL 4533916

Functional integration of Boron Carbide in concrete materials for enhanced neutron shielding and reduced activation waste

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The safe management and long-term disposal of radioactive and hazardous waste require shielding materials that provide not only effective radiation attenuation but also long-term durability and sustainability. Concrete is widely used as a primary structural and shielding material in nuclear facilities due to its mechanical performance and economic advantages; however, its intrinsic neutron shielding capacity is limited and requires functional modification. Effective neutron shielding involves the moderation of fast neutrons followed by the absorption of thermal neutrons, for which boron-based materials are particularly effective due to their high neutron capture cross-section. Boron carbide (B_4C) is a promising neutron-absorbing additive that can significantly enhance shielding performance when incorporated into concrete. The use of B_4C enables the design of more efficient shielding systems, potentially reducing structural thickness and, consequently, the volume of activated concrete generated during operation and decommissioning. However, practical implementation is limited by the chemical incompatibility between B_4C and the cement matrix, which can lead to hydration retardation and deterioration of curing characteristics and early-age performance.

In this study, a surface modification strategy for B_4C is proposed to improve its compatibility with cementitious systems. The pre-treatment is designed to mitigate adverse chemical interactions with the cement matrix, thereby enabling stable curing behavior and improved material performance. The modified system is expected to provide enhanced neutron shielding efficiency while maintaining mechanical reliability and durability.

The results demonstrate that optimized incorporation of B_4C can simultaneously improve shielding performance and reduce the generation of radioactive concrete waste. This study provides a practical and sustainable approach for developing advanced shielding concrete applicable to nuclear waste handling, storage, and disposal infrastructures.

NUCL 4534224

Chemical and magnetic dynamics in Uranium oxides and Fluorides

***Andrew Miskowiec**, miskowiecaj@ornl.gov, Tyler L. Spano, Brodie Barth, Sara B. Isbill, Daniel Felton, Zachary Brubaker, Jennifer Neu. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Neutron scattering is a powerful technique for probing the properties of matter. For nuclear materials, neutrons are an attractive tool for studying hydrogenous samples, such as crystal hydrates, due to the relatively large cross-section of H, in contrast to X-ray scattering. Neutrons are also sensitive to magnetic interactions, which are of special interest for open-*f*-shell systems. Here, we will discuss a series of experiments on the uranium oxides, fluorides, and oxyfluoride phases using neutron diffraction and inelastic spectroscopy. We will show how neutrons are critical for understanding the magnetic structure and formation of crystal hydrates in UO_2, U_3O_8, UO_2F_2, and UF_4 phases. Of particular interest is the fluctuating uranium oxidation state in the mixed-oxidation-state

U_3O_8 compound. We show, by way of inelastic neutron scattering, that U valence in U_3O_8 is dynamic – a distinct combination of mixed and fluctuating valence.

NUCL 4535600

Real-time observation of metal oxalate precipitation kinetics using a rapid mixing flow cell for synchrotron X-ray scattering

***Anna G. Servis**, annagservis@outlook.com, Matthew I. Swindall, Ori Sullivan, Xiaobing Zuo, Derek McLain. Argonne National Laboratory, Lemont, Illinois, United States*

Oxalate precipitation is the primary route for converting dissolved plutonium into solid form in nuclear fuel cycle facilities, yet the millisecond kinetics governing nucleation and early crystal growth under different conditions are challenging to observe directly. We have designed and constructed a rapid mixing flow cell for time-resolved small- and wide-angle X-ray scattering (SWAXS) at the Advanced Photon Source with the goal of achieving millisecond time resolution, compatibility with strongly acidic solutions, and two layers of containment for actinide experiments. The high flux at beamline 12-ID-B of the Advanced Photon Source enables X-ray scattering experiments with good counting statistics at a data collection frequency of up to 40 hz. Using this apparatus, we studied the precipitation of *f*-element oxalates to resolve nucleation induction times, initial particle size, and growth kinetics for each system. This work demonstrates how purpose-built sample environments coupled with modern synchrotron sources can open previously inaccessible windows into rapid chemical processes relevant to the nuclear fuel cycle.

NUCL 4535612

Influence of NO_x on formation of UO_3 during calcination of studtite

***Daniel E. Felton**[1], danielfelton@msn.com, Matt Vick[2], Chase Cobble[2], Tyler L. Spano[1], Andrew Miskowiec[1]. (1) Nuclear Nonproliferation Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States(2) Nuclear Energy and Fuel Cycle Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Studtite (uranyl peroxide, $UO_2O_2(H_2O)_4$) is present as an intermediate in front-end nuclear fuel cycle processes. Studtite is typically synthesized via precipitation from the addition of hydrogen peroxide to uranyl nitrate solutions. Industrially, samples of studtite can contain excess nitrate from sorbed nitric acid or unreacted uranyl nitrate. When excess nitrate is present in a studtite sample, NO_x gas forms and changes the decomposition reaction pathway. This work explores the effect excess nitrates have on the mechanism of UO_3 formation during calcination of studtite. Typically, studtite begins to decompose to amorphous uranium oxide at temperatures greater than 180 °C and at ~500 °C forms alpha-UO_3. However, multiple crystalline forms of uranium oxides were found to form in the presence of NO_x gas. Calcination products were examined using powder X-ray diffraction, Raman spectroscopy, and scanning electron microscopy with

energy dispersive X-ray spectroscopy to examine the influence of NO_x gas on mechanisms and products of studtite decomposition.

NUCL 4536606

Spatially resolved uranium isotope measurements by triple quadrupole time of flight mass spectrometry

***Michael Romero**, michaelfromero@gmail.com, Joeseph Brennan, Jon M. Schwantes. Nuclear Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States*

The Penn State REACTR lab has acquired a Nu Vitesse inductively-coupled-plasma time-of-flight mass spectrometer (ICP-TOF-MS) with a triple quadrupole addition. The system is coupled to an ImageGeo 193 (ESL) laser ablation (LA) system to perform spatially resolved isotopic and chemical analyses of uranium bearing materials. The time-of-flight mass spectrometer allows for correlating elemental composition with uranium isotopic information as a function of ablation spot size, assuming the spatial extent of elemental and uranium isotopic compositional features within the material are larger than the area being ablated.
When the spatial extent of the characteristics being measured are close in size or smaller than the ablated area, false correlations between measurements are possible. To avoid this, the ablation spot size can be varied, allowing for the spatial extent of changes in the measured compositions to be quantified and then correlated with each other. This outcome led us to create a generic framework for quantifying measured heterogeneities within materials that consider both the spatial extent of the feature being measured and the resolution of the technique being used to measure that feature.
With spatial analysis there is an inherent tradeoff between resolution and signal. With LA higher resolution measurements produce less signal. This presents a problem with measuring small features, as ablation volume stays just above the limit of detection. Because MS is a destructive technique samples cannot be analyzed twice. This can be alleviated by using computer simulations to get an estimate of what settings are necessary.
Computer simulations of spatially resolved elemental and isotopic analyses were compared to measurements collected at various spatial scales to test the viability and usefulness of a generic framework for quantifying material heterogeneity. This was primarily used to evaluate the ability of LA-ICP-TOF-MS to characterize elemental and isotopic heterogeneities at various spatial scales. This generic framework, combined with machine learning algorithms, is also being investigated as an approach for effectively and efficiently correlating a wide range of spatially resolved measurements (e.g., optical spectroscopies, scanning and transmission electron microscopies, atom probe tomography, secondary ion mass spectrometry) in an attempt to quantify and exploit material heterogeneity as an identifying feature in bulk materials.

NUCL 4536931

Olation and oxolation pathways in the early-stage nucleation of tetravalent actinides species

***George Donkor-Gyami**, george-donkor-gyami@uiowa.edu, Pere Miro. The University of Iowa, Iowa City, Iowa, United States*

Actinide molecular metal oxides are a class of clusters composed of tetravalent actinide centers connected through oxo and hydroxo bridges and are relevant to nuclear waste reprocessing and environmental remediation. Despite their importance, the aqueous speciation of actinide ions and the nucleation pathways leading to higher-nuclearity clusters remain poorly understood compared to those of transition metals. In this work, a computational investigation of the speciation and early-stage nucleation of tetravalent actinide ions (Th–Pu) in aqueous solution in the presence of formate and zwitterionic glycine ligands is presented. In both ligand environments, substitution of aquo ligands by carboxylate-containing ligands is thermodynamically favorable and reduces the number of available An–H_2O moieties, thereby moderating hydrolysis and cluster growth. Distinct condensation pathways are observed across the actinide series: thorium preferentially forms olation products containing two μ_2-hydroxide bridges, whereas the stability of oxolation products increases toward the heavier actinides, becoming dominant for plutonium. These results highlight the strong influence of ligand environment and actinide identity on the nature of nucleation intermediates and provide insight into the mechanisms governing actinide cluster formation in aqueous media.

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NUCL 4537191

Chromium and MiL based metal organic frameworks for aqueous uranium ion adsorption

***Amanda Anderson**, aanderson0205@gmail.com, Daniel Kissel. Chemistry, Lewis University, Romeoville, Illinois, United States*

Nuclear energy is responsible for providing approximately 20% of power nationwide. The fission reactions that take place inside fuel rods are capable of outperforming traditional fuels like coal or oil by over two million times. It also produces zero CO_2 emissions, making nuclear power the cleanest and most environmentally sustainable energy producer. The key component in nuclear fuel is uranium-235, an isotope with less than 1% natural abundance. With such a low natural supply, uranium harvesting methods must be optimized to continue steady nuclear energy production. While uranium is typically mined from terrestrial reserves, most of the world's supply is found in low concentrations in seawater. This study analyzes the efficiency and optimization conditions for capturing this aqueous uranium using metal organic frameworks (MOFs) as adsorbents. MOFs are porous polymeric crystalline materials with high surface areas and low densities, making them ideal candidates for guest-host interactions. The MIL based frameworks with chromium metal centers feature increased coordination and exceptionally high surface areas, potentially reaching over 4000 m^2/g. Synthesis of MIL, however, can influence the rigidity and breathability of the polymer, thereby altering its guest-host capabilities. For a dynamic uranium capture, a continuous column-based system was engineered using a surrogate uranyl acetate solution and various chromium-based MIL MOFs. The uptake of uranium was tracked spectrophotochemically by monitoring the disappearance of uranyl acetate from solution over various periods of time. Initial experimental results showed that over 50% of uranium was adsorbed from solution when pH, timing, and concentrations were optimized.

NUCL 4537191

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***Amanda Anderson**, aanderson0205@gmail.com, Daniel Kissel. Chemistry, Lewis University, Romeoville, Illinois, United States*

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NUCL 4537849

Spectroscopic study of the extraction of nitric acid and Fe(III) nitrate from aqueous solution using tri-butyl phosphate

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Extraction and concentration of fission and activation products is a key step in nuclear forensic analysis. Post detonation debris and samples from urban environments contain high amounts of first row transition metals, especially iron, cobalt and chromium. How these first row elements interact with tri-n-butyl phosphate (TBP) is not completely understood under trace conditions.
This study specifically investigates the distribution of nitric acid between aqueous and TBP organic phases and evaluates how varying acid concentrations affect metal extraction behavior. Through utilizing acid-base and complexometric titrations the distribution coefficients for Fe(III) Nitrate could be determined. NMR spectroscopy was used to probe changes in the chemical environment of TBP and study the interactions between TBP, nitric acid, and Fe(III). Results indicate that increasing nitric acid concentration significantly impacts TBP complexation behavior and alters the distribution of acid into the organic phase. Furthermore, increasing concentration of nitric acid increases Fe(III) extraction demonstrating how high concentrations of acid

affect metal extractions. The extracted species structure was also probed via x-ray absorption spectroscopy and NMR. This work provides insight into the role of nitric acid and metal speciation in TBP-based extraction systems and offers a framework for predicting extraction performance for other transition metal systems.

NUCL 4537938

Removal of radon progeny from delicate surfaces

*Dmitry Chernyak[1,2], Andreas Piepke[1], **Parker Back**[1], PBBack@crimson.ua.edu. (1) Physics and Astronomy, The University of Alabama System, Tuscaloosa, Alabama, United States(2) Tohoku Daigaku, Sendai, Miyagi Prefecture, Japan*

Radon progeny deposited on material surfaces present an important radiochemical challenge for rare-event searches because the radon decay chain can produce neutron backgrounds through Po-210-driven (α,n) reactions. This work, performed at the University of Alabama department of Physics and Astronomy, evaluates a simple, minimally invasive cleaning approach for delicate copper and silicon surfaces using α-spectroscopic measurements collected before and after acetone wiping. An initial cleaning step is shown to remove approximately half of the surface Po-210 activity from both materials. For copper, time-dependent analysis further shows that Pb-210 is removed with comparable efficiency, indicating that the treatment reduces not only the immediate α-emitting daughter activity but also its long-lived radiochemical source. Additional wiping is largely ineffective for copper, while silicon shows larger uncertainties and only a small additional improvement after repeated cleaning. These results demonstrate that a straightforward solvent-wipe procedure can substantially reduce radon-progeny contamination without harsh surface treatment. For low-background experiments, this provides a practical contamination-control strategy with direct benefits for allowable air exposure during assembly, construction timelines, and cost.

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NUCL 4537954

Heterometallic acetylacetonate capped cerium-oxo clusters

***Sabrina A. Jackson**, Sjgreen8@verizon.net, Jeffery Bertke, Karah E. Knope. Georgetown University, Washington, District of Columbia, United States*

Metal-oxo clusters are relevant to areas spanning biomedicine, energy conversion and storage, defense technologies, and spent nuclear fuel management. Cerium-oxo clusters are of particular interest because they adopt the same core as CeO_2 and in this way, may serve as atomically precise models for understanding the chemical behavior of bulk ceria. These clusters also exhibit structural similarities with actinide-oxo clusters and thereby serve as a starting point for pursuing related transuranium work. With these considerations in mind, our group has been examining the synthesis, structural chemistry, and properties of Ce-oxo clusters across a range of conditions. As an example, our group previously reported the synthesis of chloride decorated $\{Ce_{38}\}$ and $\{Ce_{52}\}$-oxo clusters isolated from aqueous halide media, as well as acetylacetonate-capped $\{Ce_{10}\}$ and $\{Ce_{12}\}$ clusters from methanol. Structural analysis as well as X-ray Photoelectron Spectroscopy and X-ray Absorption Spectroscopy showed that the clusters contained both Ce^{3+} and Ce^{4+}, with Ce^{3+} located at the peripheral positions of the cluster cores. Building on this work, we recently sought to understand how the incorporation of other trivalent lanthanide affects the structure and properties of these clusters. Interestingly, we found that incorporation of trivalent lanthanides can push the formation of novel cluster topologies, that incorporate both Ln^{3+} and Ce^{4+}. The synthesis, structural analysis, and spectroscopic characterization of these mixed-metal oxo clusters will be discussed.

NUCL 4538171

Production and separation of Pt-197 through novel solid harvesting at the Facility for Rare Isotope Beams (FRIB)

***Deepika Davuluri**[1,2], davulur8@msu.edu, Daniel G. Racz[4], Evan J. Williams[4], Kala Perry[4], Emilia Majka[2], Ivis Chaple[4], Katharina Domnanich[1,3]. (1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Facility for Rare Isotope*

Beams, Michigan State University, East Lansing, Michigan, United States(4) Nuclear engineering, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States

Platinum radionuclides exhibit decay properties suitable for cancer therapeutics and diagnosis. ^{197}Pt (t1/2 = 19.9 h) is an isotope that decays by simultaneously emitting β^- and Auger electrons, which are suitable for cancer therapy. It also emits a 77 keV γ ray (I_γ = 17%) that can be used for single photon emission computed tomography (SPECT) imaging. Despite these competitive characteristics there was no reported literature relating to the ^{197}Pt production.

A novel solid harvesting procedure has been developed at the Facility for Rare Isotope Beams (FRIB) for generating ^{197}Pt. The isotope is harvested within a stack of tantalum and aluminum foils arranged and clasped in a cassette to capture beam particles. Two experiments, a test and main experiment for a duration of 13.55 h and 24.15 h respectively were performed. In the test experiment, a total of 437.59±40 μCi and during main experiment 494.09±48 μCi of ^{197}Pt was produced.

The separation chemistry was initially established with stable analogues using extraction chromatography with TK 200 resin, achieving the elution of 99.1±2% of Pt in a single fraction. However, decreased ^{197}Pt recovery yields were observed during the radiochemical processing, possibly due to the reduction of ^{197}Pt ions during embedding into the Al foil matrix. The pretreatment with aqua regia and hydrogen peroxide was presumed to oxidize ^{197}Pt to the +4-oxidation state, the species for which the separation was optimized, thereby improving the elution yield. Reconstitution with aquaregia helped in attaining a ^{197}Pt recovery of 82.3±7%, while the incubation with hydrogen peroxide [DK2] resulted in recovering 87.4±9% of ^{197}Pt.

Overall, the study demonstrated a novel method to generate ^{197}Pt isotope together with a radiochemical separation method tailored for the obtained samples. In future studies The obtained ^{197}Pt activity is envisioned to be used for synthesis of radiocisplatin or alternatively, in combination with suitable chelators for application in cancer therapy.

Keywords: ^{197}Pt, Radiochemical separation, Cancer Theranostic, Radiocisplatin, Solid isotope harvesting.

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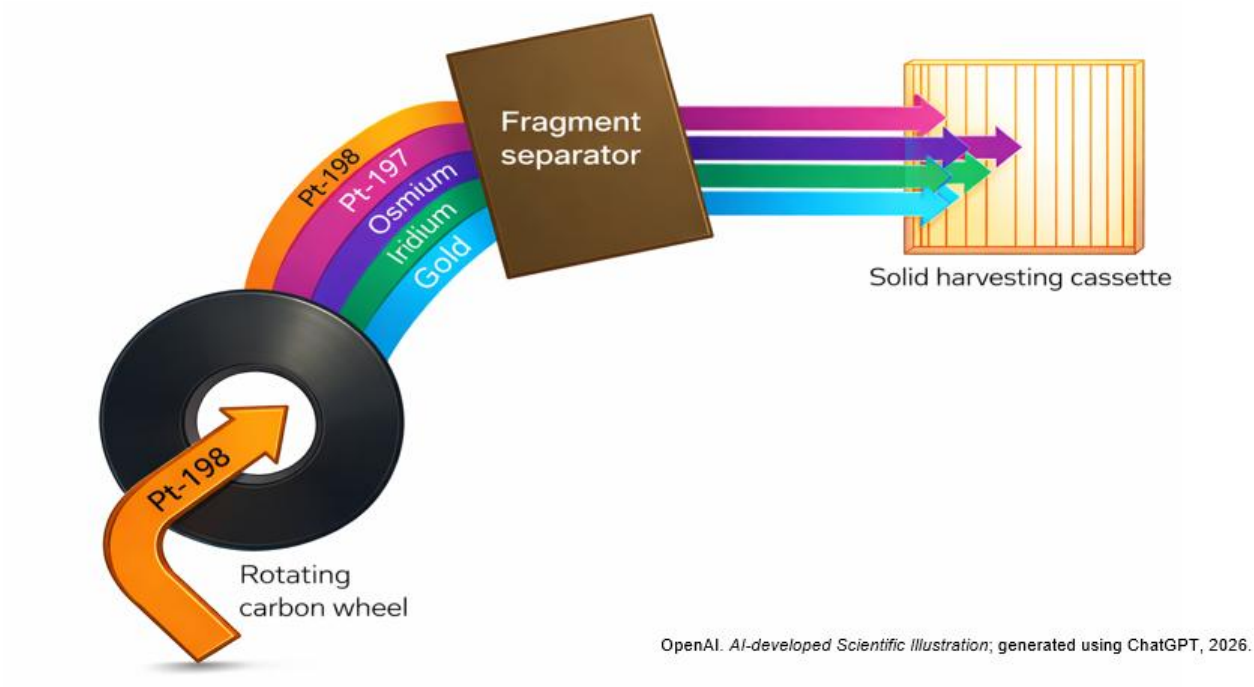

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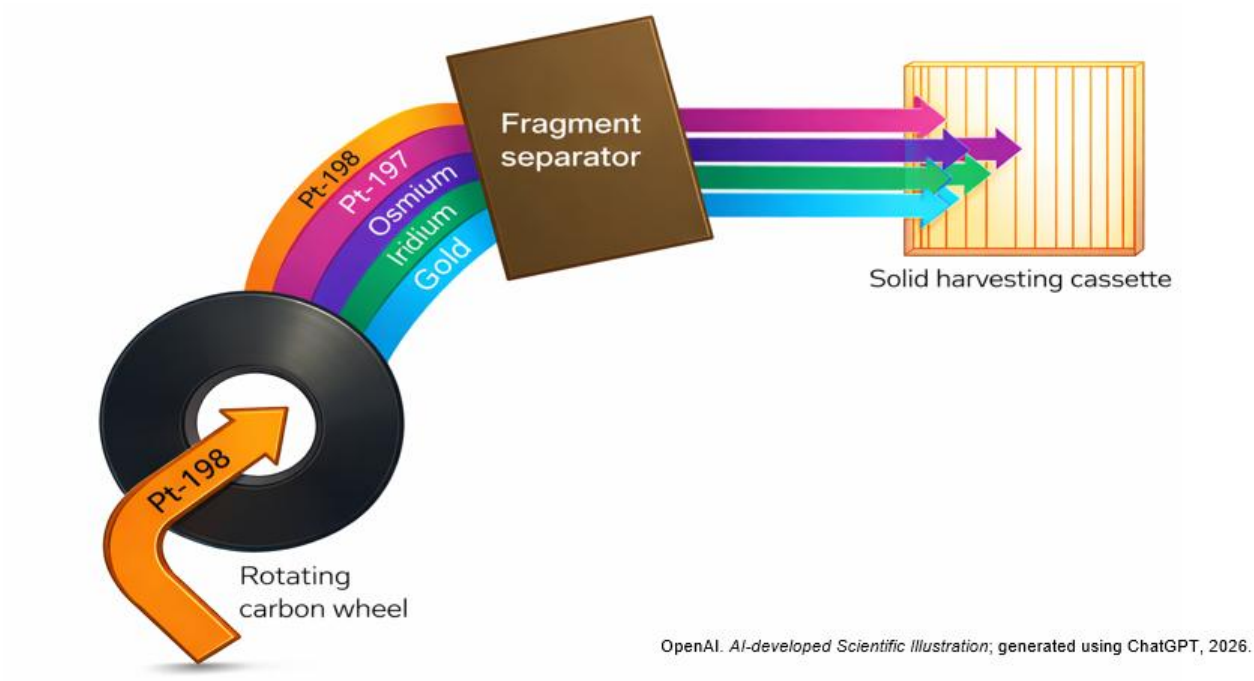

NUCL 4538212

Measurement of heat conduction to improve astatine-211 yield

Yahirnitza Torres Cruz[1]*, yahi.torres.05@gmail.com, Robert Bartsch*[2]*, Sherry Yennello*[2]*. (1) Chemistry, Texas A&M University System, College Station, Texas, United States(2) Texas A&M University System, Pittsburgh, Pennsylvania, United States*

Astatine-211 (At-211) is a short-lived alpha emitter with promising use in targeted alpha therapy for the treatment of cancer. We are seeking to improve the yield of At-211 made at the Texas A&M University Cyclotron Institute, one of the few facilities in the world capable of producing it. The basis of our work will be to build an instrument, based on an existing instrument at Los Alamos National Laboratory, to measure thermal conductivity, since the limiting factor for our yield is the intensity of beams that can be impinged at the bismuth targets. Thus, with the instrument we want to test the targets ahead of our intended irradiations without having to waste valuable beamtime and test the targets quality with the overarching purpose of measuring how much heat can be deposited in the bismuth without it melting.

NUCL 4538250

Designing a flowsheet for the recycling of Np from used nuclear fuel using centrifugal contactors

Gabriel A. Flores*, gflorese@hotmail.com, David J. Bettinardi, Laura E. Maggos, Candido Pereira, Peter Tkac. Argonne National Laboratory, Lemont, Illinois, United States*

The Co-Decontamination (CoDCon) process is based on a modified Plutonium Uranium Reduction Extraction (PUREX) process that uses tributyl phosphate (TBP) to co-extract uranium (U), plutonium (Pu), and neptunium (Np) from used nuclear fuel (UNF) dissolved in nitric acid (HNO_3). One major challenge is controlling the redox chemistry of Np so that Np(V) is oxidized to Np(VI) which is more readily extractable by TBP. Nitrous acid (HNO_2) is a radiolytic byproduct of HNO_3 and plays a complex role in the process as it can catalyze both oxidation and reduction pathways as it is continuously generated and consumed. Designing a flowsheet requires understanding how Np, HNO_3, and HNO_2 interact to affect redox kinetics under relevant reprocessing conditions.
In this work, batch studies were done in which >99% of Np was extracted from simulated reprocessing-relevant aqueous solutions. The concentration of HNO_3 was increased from that of typical processing conditions while HNO_2 was kept at relevant concentration to promote the oxidation of Np(V) to Np(VI). Once optimal conditions for Np extraction were found, an 8-stage 1.25-cm centrifugal contactor was used to run a process flowsheet. >99% of the U and 96.5% of the Np present were extracted from dissolved UNF simulant using 30% TBP in n-dodecane.

NUCL 4538707

Spectroscopic signatures of Co(II)–TODGA binding: Insights into structure and selectivity

Carl Vincent D. Arizala[1,2]*, carizala@gradcenter.cuny.edu, Brittany Stieferman*[5]*, Rachel F. Wood*[3]*, Penafrancia Monte*[4,2]*, Lynn C. Francesconi*[4,2]*, Deborah A. Penchoff*[5]*, Nathalie A. Wall*[3]*, Benjamin P. Burton-Pye*[1,2]*. (1) Department of Chemistry, Lehman College, New York, New York, United States(2) Department of Chemistry, CUNY Graduate Center, New York, New York, United States(3) Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, United States(4) Department of Chemistry and Biochemistry, Hunter College, New York, New York, United States(5) Department of Chemistry, University of Central Florida, Orlando, Florida, United States*

N,N,N′,N′-tetraoctyl diglycolamide (TODGA) is widely used for the extraction of lanthanides and minor actinides in nuclear fuel reprocessing. We are exploring the extraction of Co(II) under acidic conditions which can impact the extraction efficiency of critical isotopes in forensic analyses. This study aims to elucidate the molecular-level interaction between Co(II) and TODGA and identify factors governing coordination and selectivity. TODGA was synthesized via a solvent-free approach and analyzed using ^{1}H and ^{13}C NMR. Solution structure under extraction conditions was probed using ^{1}H NMR and NMR relaxometry over a range of HCl concentrations (6 – 9 M) and the paramagnetic influence of Co(II) within the system is presented. Spectroscopic changes shed light on the key interaction sites of the TODGA ligand and the extracted Co(II) species. NMR results are compared with X-ray absorption spectra and computational analyses.

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NUCL 4538940

Solid harvesting of ^{62}Zn for in vivo ^{62}Zn/^{62}Cu radionuclide generators

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Solid isotope harvesting at the Facility for Rare Isotope Beams (FRIB) is a unique production route that extracts valuable radionuclides which are produced via heavy ion fragmentation and implanted into a solid matrix. As part of the development of solid harvesting methodology at FRIB, a preliminary experiment was performed demonstrating the production of the medically-relevant zinc-62 ($t_{1/2}$=9.2 h) via this technique. As the radioactive parent of the short-lived copper-62 ($t_{1/2}$ = 9.7 m), an attractive imaging agent for positron emission tomography (PET), ^{62}Zn has been utilized in column-based radionuclide generators and has more recently been proposed as a novel in vivo generator system. In this work, ^{62}Zn was produced via the fragmentation of a stable ^{64}Zn primary beam and deposited into a series of copper collection foils. Analysis of the collection foils showed near-quantitative (94 ± 3%) implantation of the produced ^{62}Zn into three copper foils with a corresponding total thickness of 75 μm. Anion exchange chromatography was then used to isolate the ^{62}Zn from the bulk foil material and trace co-produced radionuclides and to concentrate the purified ^{62}Zn product, resulting in an overall yield of 63 ± 3% of ^{62}Zn in 1 mL of dilute hydrochloric acid with no detectable radionuclidic contamination. Subsequent radiolabeling studies used the ^{62}Zn produced via this solid harvesting to investigate the DOTA and NOTA ligands as potential chelators for application in a ^{62}Zn/^{62}Cu in vivo generator. This approach would enable PET imaging over extended time periods compared to the use of ^{62}Cu alone owing to ^{62}Zn's longer half-life. Initial results showed a higher degree of ^{62}Zn complexation with the NOTA ligand compared to DOTA, indicating that NOTA may have increased chelation affinity for zinc and thus provide greater stability for ^{62}Zn/^{62}Cu in vivo generators.

NUCL 4539075

Deep eutectic solvents for the efficient separation of lithium isotopes via electromigration

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^{6}Li, as a strategic resource, is used in controlled thermonuclear fusion reactors to produce fuel tritium. To ensure the continuity of the fusion fuel cycle, the ^{6}Li abundance must exceed 30%. However, the natural abundance of ^{6}Li in the environment is only about 7.5%. Therefore, ^{6}Li enrichment technology is crucial for the development of the nuclear fusion industry. The use of electromigration technology to enrich ^{6}Li in molten salt systems offers an environmentally sustainable alternative to the COLEX process. However, the high-temperature molten salt and room-temperature ionic liquid-based systems reported face challenges related to implementation difficulties and high costs, respectively. Therefore, there is a need for a more economical, environmentally friendly molten salt suitable for lithium isotope separation at room temperature. Deep eutectic solvents possess properties similar to ionic liquids, and offer the advantages of low cost, environmental friendliness, and high design flexibility. As a result, deep eutectic solvents hold significant potential. In this study, the composition of the deep eutectic solvent was designed, and it was found that choline chloride, a hydrogen-bond acceptor, and hydroxyl-based hydrogen-bond donors are highly suitable for lithium isotope separation. Further optimization of the hydrogen-bond donors led to the selection of ethylene glycol. Subsequently, in the choline chloride–ethylene glycol–lithium chloride system, key parameters such as composition ratio, temperature, voltage, LiCl concentration, and time were optimized. The results showed that the lithium isotope separation coefficient reached a maximum of 1.087 under under optimal conditions. At the same time, the long-term impact of electrode byproducts on the separation efficiency was investigated. Through a combined analysis of CV curves, FTIR, and gas chromatography–mass spectrometry, the anode and cathode products were identified as Cl_2 and $C_2H_4O_2$, respectively. Quantum chemical calculations indicate that $C_2H_4O_2$ does not impair lithium isotope separation. This study demonstrated the feasibility of using deep eutectic solvents as electromigration solvents for lithium isotope separation and provided concrete guidance for the design of deep eutectic solvent compositions.

NUCL 4539133 - Withdrawn

NUCL 4539133 - Withdrawn

NUCL 4539167

Studies of the coprecipitation of plutonium and cerium with gibbsite and magnetite: An approach to nuclear waste management

***Peter Oyeleke**, oyelekepetertunde@yahoo.com, Brian A. Powell. Clemson University, Clemson, South Carolina, United States*

Mechanistic understanding of the interactions between radionuclides and nuclear waste minerals is crucial to developing appropriate treatment technologies. Aluminum and iron (oxyhydr)oxide are two of many solids present in the sludge of legacy nuclear weapons waste processing tanks. This study investigated the coprecipitation of plutonium (Pu) and cerium (Ce) with gibbsite (α-$Al(OH)_3$ and magnetite (Fe_3O_4) as surrogate minerals

under waste tank-relevant conditions. These minerals were synthesized at room temperature, under high ionic strength, and at pH >12. The as-synthesized materials were characterized by X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). Aqueous concentrations of Ce and Pu measured using inductively coupled plasma mass spectrometry (ICP-MS) indicated that almost all the Pu and Ce fractions were associated with the solid precipitates. The XRD analysis for Ce-gibbsite system showed characteristic patterns for gibbsite and CeO_2, indicating no clear evidence of Ce incorporation into the gibbsite structure consistent with the difference in ion size between Al(III) and Ce(III). Furthermore, the clusters of Ce around gibbsite were confirmed by SEM imaging of microtomed samples. It appears that Ce is primarily associated with Ce-oxide phases or possibly surface complexes on gibbsite, rather than incorporating into gibbsite.

In contrast, Ce/Pu incorporation into the magnetite structure is suspected, with the noteworthy observation that Ce and Pu are both readily removed from solution upon precipitation of magnetite. However, in the presence of 0.08 mol/L initial Ce and a Ce/Fe ratio of 0.2, both goethite and magnetite are observed rather than pure magnetite in the absence of Ce. SEM-EDX revealed the crystal morphology and elemental composition of magnetite showed typical rhombohedral particles in the absence of Ce but ‘rod-like’ structures for Ce-magnetite that were consistent with formation of goethite. Thus, incorporation of Ce into the iron oxide phases induces the formation of a different crystal structure. Pu concentrations in similar samples were too low to observe differences on XRD or SEM but removal of Ce and Pu from solutions upon precipitation were comparable. These findings show that Pu and Ce have a strong affinity for gibbsite and magnetite phases but potentially via different attenuation mechanisms.

NUCL 4540030

Sulfonamide extractants for direct Uranium dissolution without acid pretreatment

***Nabarupa Bhattacharjee**, bhattacharjn@ornl.gov, Marcy Lamb, Jeffrey D. Einkauf, Santa Jansone-Popova. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Reprocessing of used nuclear fuel (UNF) is fundamentally constrained by the need to dissolve the fuel matrix in hot nitric acid, followed by recovering the useful components using complex solvent extraction systems. While tri-*n*-butyl phosphate (TBP) remains the standard extracting agent, limitations in combustibility and secondary waste drive the development of viable alternatives. Neutral amide-based direct extractants such as *N*,*N*-di(2-ethylhexyl)isobutyramide (DEHiBA) show promise; however, challenges remain in achieving high selectivity, and the required acidic pretreatment generates unwanted NO_x species leading to reduced extraction efficiency and gas evolution. Herein, we report a new class of sulfonamide-based direct extractants designed to enhance performance through increased lipophilicity and improved phase behavior while eliminating the need for acidic pretreatment. The ligand’s alkyl chain length and branching were systematically modified to establish structure-property relationships

governing aggregation, viscosity, and phase stability. Direct dissolution of uranium was evaluated in *n*-dodecane without any pretreatment with nitric acid. Branched derivatives exhibited improved extraction behavior relative to straight chain ligands and demonstrated improved phase behavior compared to monoamides. These initial results establish key molecular design principles for next-generation novel sulfonamide-based extractants and provide necessary fundamental knowledge toward a simplified, more robust separation strategy for nuclear fuel reprocessing.

NUCL 4540207

Soft and hard X-ray spectroscopy studies of actinyl tris(benzoate) complexes using STXM

Haisley Windsor[1,2]*, haisley_windsor@berkeley.edu, Olivia Gunther*[2]*, Cambell Conour*[1,2]*, Nic Cicchetti*[2]*, Gabe Herrera*[1]*, David K. Shuh*[2]*, Polly L. Arnold*[1,2]*. (1) Chemistry, University of California Berkeley, Berkeley, California, United States(2) Chemical Sciences, E O Lawrence Berkeley National Laboratory, Berkeley, California, United States*

As the use of actinide materials increases in industrial processes such as catalysis, energy products, medicine, magnets, and national security, a deeper understanding of their electronic structure is needed. Electronic properties of actinides directly affect reactivity and mobility, strongly impacting their applications. There are still many unanswered questions about the interactions between actinides and their ligands, particularly how the 5f and 6d orbitals contribute to bonding. A deeper understanding of actinide electronic structures impacts our knowledge of actinide covalency. To address these questions, actinyl tris(benzoate) complexes with a range of donating substituents were synthesized and studied using the soft x-ray scanning transmission x-ray microscope (STXM) and time dependent density functional theory (TDDFT). Lighter actinides such as Uranium are used due to their ability to readily form linear dioxo cations with the Np and Pu complexes to follow. Oxygen K-edge and metal L3-edge spectra enable differentiation of oxygen and equatorial oxygens bound to the metal center, which gives insight into oxygen-actinide bonding. The probing of the 5f, 6d, and 7p orbitals and their interactions allowed us to observe unique spectroscopic signatures dependent on ligands of the complex. This work advances fundamental science and will help to refine current theoretical models of actinide bonding and observe how subtle ligand and coordination environment differences strongly influence separation and redox behavior.

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NUCL 4540444

Complex electronic structure of molybdenum chalcogenide clusters as supports for low-valent actinides

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The metallation, bonding, and electronic structure of redox active incomplete-cubane $Mo_3(\mu_3\text{-}X)(\mu_2\text{-}X)_3$ chalcogenide clusters with early actinides were studied using density functional theory and multireference methodologies. We confirmed that the incorporation of low-valent U(III) leads to its oxidation to U(IV) due to an intramolecular redox reaction with the molybdenum sulfide core. On the contrary, open questions remain with respect to the oxidation state of low-valent transuranic elements upon their coordination to the molybdenum sulfide core. Density functional theory calculations indicate that the transuranic center remains An(III), while complete active space calculations suggest an actinide oxidation analogous to the one observed in the uranium species. The predominantly electrostatic bonding between the actinides and the molybdenum sulfide cluster was assigned using the quantum theory of atoms in

molecules. Our results on clusters with harder and softer chalcogenides are in agreement with a preferential soft–soft interaction between the actinide and its support. The electronic structure and redox profile of other f-element species based on molecular metal oxides and bis-di(silylamido)silane ligands will also be presented.

NUCL 4540546

Feasibility of ^{129}I measurement by total evaporation negative thermal ionization mass spectrometry

Sunanta Juijongrak[1], *namnoey46@gmail.com, Zahra Zandvakili*[1], *Asuka Tanaka*[2], *Katsuhiko Suzuki*[1,2], *Yoshitaka Takagai*[1]. *(1) Fukushima University Faculty of symbiotic systems science, Fukushima, Japan(2) Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan*

Precise measurement of the long-lived fission radionuclide iodine-129 (^{129}I, half-life 1.57 × 10^7 y) is important because it is produced during nuclear fuel reprocessing and nuclear accidents and can be migrated globally (e.g., following the Fukushima accident in Japan). Therefore, accurate determination of ^{129}I is required to trace nuclear releases and to evaluate the long-term safety of radioactive waste repositories. Conventional analytical techniques for ^{129}I measurement include accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS). AMS provides extremely high sensitivity but requires large and expensive accelerator facilities. ICP-MS is more accessible and modern ICP-MS/MS systems can suppress xenon interferences using reaction gases; however, ultra-trace isotope ratio measurements remain challenging due to memory effects and residual xenon background. In this study, Negative Thermal Ionization Mass Spectrometry (NTIMS) combined with a Total Evaporation (TE) technique was used for the stable and precise measurement of iodine isotope ratios at ultra-trace levels. The TE approach addresses mass fractionation during ion emission by enabling integration of the entire evaporation signal, thereby improving the accuracy of the ^{129}I/^{127}I ratio determination. Iodine ion beams were successfully generated and detected using NTIMS, where $^{127}I^-$ was collected with the L1 Faraday cup and $^{129}I^-$ was detected using a secondary electron multiplier (SEM) positioned at the center detector with the Retarding Potential Quadrupole (RPQ) enabled. $^{127}I^-$ was measured at m/z 126.95, while $^{129}I^-$ was monitored at m/z 128.87 to avoid potential molecular interferences near m/z 129. The two signals were clearly separated at their expected mass positions. Optimized TE conditions produced stable evaporation profiles for both isotopes and allowed integration of the full ion signal, providing reproducible measurement of the $^{129}I^-/^{127}I^-$ isotope ratio using TE-NTIMS. Based on the measured ^{129}I/^{127}I ratios and known amounts of ^{127}I, this approach also demonstrates the potential for quantitative determination of ^{129}I at ultra-trace levels. These results highlight TE-NTIMS as a promising alternative analytical method for precise and quantitative iodine isotope analysis.

This research was implemented under the Decommissioning, Contaminated Water and Treated Water Management Program supported by the Ministry of Economy, Trade and Industry (METI), Japan.

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NUCL 4540581

Synchrotron based spectroscopy and chemical imaging of actinides: Spectroscopy and HERFD imaging for nuclear forensic applications

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Microscale synchrotron radiation-based x-ray fluorescence (SR-XRF) chemical analyses can provide a unique capability for chemical signature recognition and classification capabilities for actinide micro-particle analysis. SR-XRF is well suited to the analyses of small particles because it is rapid, non-destructive, highly sensitive, has good spatial resolution, and can provide chemical information on the elements that are present when combined with x-ray absorption spectroscopy (XAS). The combination of spatially resolved distribution and chemical information, often known as chemical imaging, effectively provides a “chemical morphology” of the sample of interest and can show how chemical states are distributed within and among a series of particles. Chemical speciation is a critical component for the understanding of actinide reactions and transport in natural systems. This type of measurement can also be combined with other forms of traditional microscopies, such as FTIR or Raman microscopy, to enhance multi-modal information from these systems.

However, the conventional XAS capability in the near edge region as commonly implemented is often inadequate for systems that require high sensitivity or require a higher detail of spectroscopic information. The limitations from the x-ray point of view are often due to the length core-hole lifetime which broadens XAS measurements and makes interpretation and fingerprinting of species difficult. This can be overcome with the combination of traditional micro-SR-XRF and XAS, integrated with a high energy resolution fluorescence detector (HERFD) crystal analyzer. This has been recently implemented at BL 6-2b at SSRL and applied in the determination of the micron-scale oxidation state of uranium in particles and soil matrixes. A discussion of the image and data processing techniques that can be applied using spatially resolved HERFD to obtain chemical and structural information, as well as the integration of micro-HERFD data and microscopies to determine the distribution of phases across different particles at the micro-scale, will be presented.

NUCL 4541214

Tailorable oxygen donor scorpionate ligands for *f*-element separations

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The *f*-elements are widely used in a variety of applications, such as in energy production, electronics, and medical treatments. However, separating the lanthanide series and trans-plutonium elements is extremely challenging due to their similar ionic radii and preferred trivalent oxidation state. To improve current separation technologies, tailorable oxygen-donor scorpionate ligand systems can be employed. Scorpionate ligands are named after their tridentate coordinate modes, with two metal to ligand

bonds of the same length and one longer bond. Such systems are easily synthetically modifiable, allowing curated separations between adjacent *f*-elements. Current investigations utilize an oxygen-donor scorpionate ligand that is novel to the *f*-elements. Initial studies demonstrate a break in absolute structure between gadolinium and terbium. Early lanthanides demonstrate a three to one ligand to metal complex, while the later lanthanides show a two to one ligand to metal structure. These differences in coordination allow for significantly different chemistries between complexes that can be used for effective separations. Additionally, the luminescent properties of these complexes are of interest, as they show unique luminescent behavior. Through the use of tailorable scorpionate ligand systems, subtle differences between *f*-elements can be exploited for effective separations.

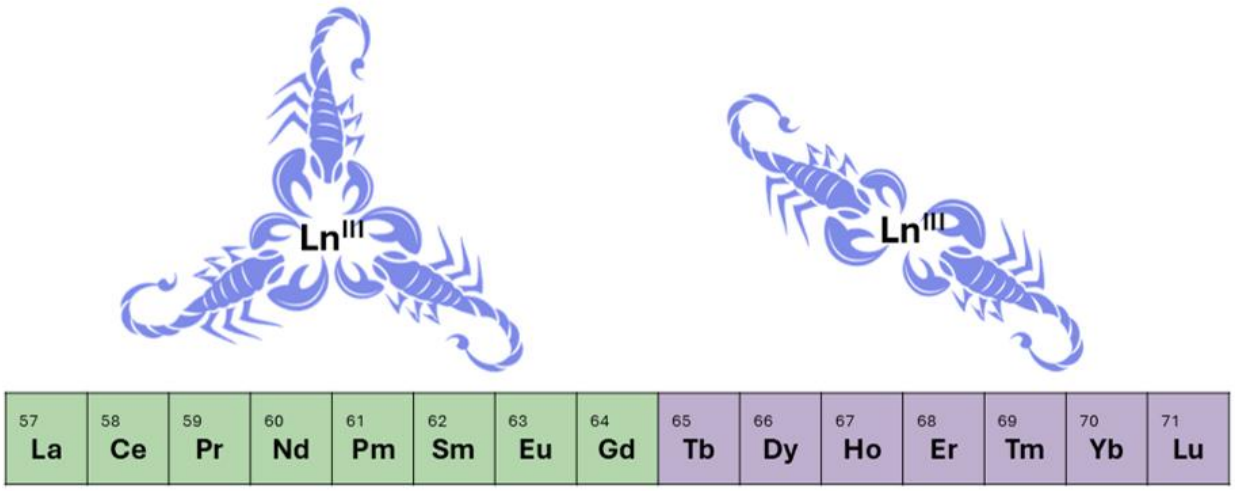

Figure 1. Illustration showing differences in coordination across the lanthanide series using a scorpionate ligand.

NUCL 4541214

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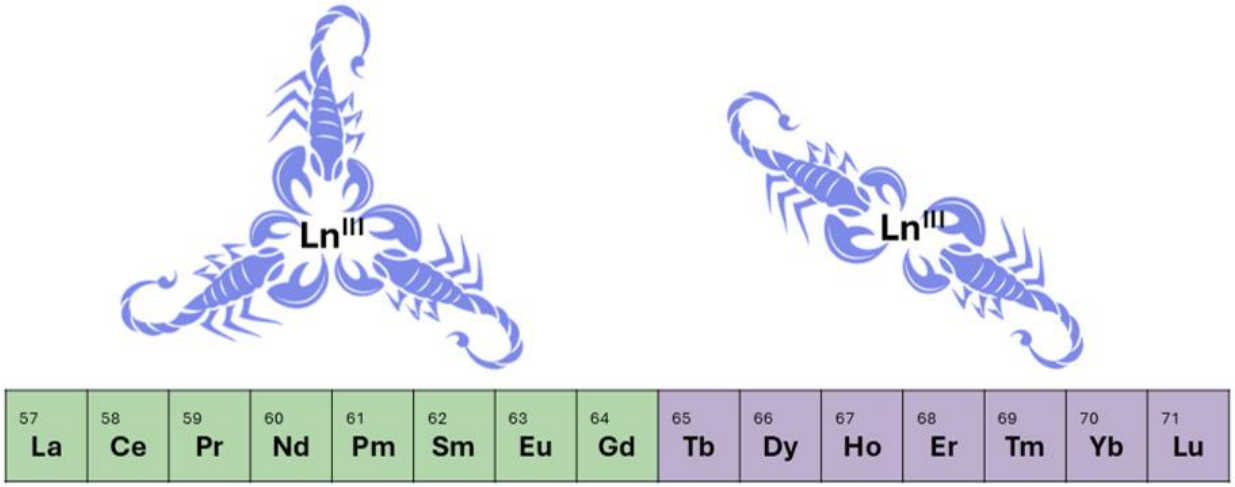

Figure 1. Illustration showing differences in coordination across the lanthanide series using a scorpionate ligand.

NUCL 4541391

Exploring ring substitution of tris pyrazolyl borate derivatives for *f*-element coordination with a homoleptic nitrogen donor

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Tris pyrazolyl borate (Tp) was first synthesized by Trofimenko in 1966 and was established as a monoanionic, tridentate ligand characterized largely with transition metals until Apostolidis et al. published a trivalent lanthanide (Ln) Tp series (excluding promethium) and uranium, neptunium and plutonium Tp structures. The $LnTp_3$ series follows the lanthanide contraction trend with the lanthanide-nitrogen bond lengths decreasing steadily across the series with three Tp molecules fully bound to the Ln ions until there is a coordination break in the series at dysprosium. This work expands on the trend established by Apostolidis by exploring how substituting an electron-withdrawing bromo group on the Tp rings extend the coordination break within the lanthanide series to erbium as well as completing the Ln series with the **first reported promethium Tp structure** (Figure 1). This structural investigation reveals the possibility of Tp modification through electron-donating or electron-withdrawing groups to effectively select where the divergence in the series occurs for potential adjacent lanthanide separations. Ring substitution also increases the solubility of the complexes, opening up more potential synthetic routes that are optimal for radioactive element syntheses. Unsubstituted *f*-element Tp complexes are highly insoluble with crystals obtained after extraction over several weeks or sublimation. Substitution with a bromo group allows for crystals to be grown overnight down to the 0.1 mg metal scale. This work involves synthesis optimization for direct lanthanide and actinide comparison with a homoleptic, pure nitrogen donor ligand.

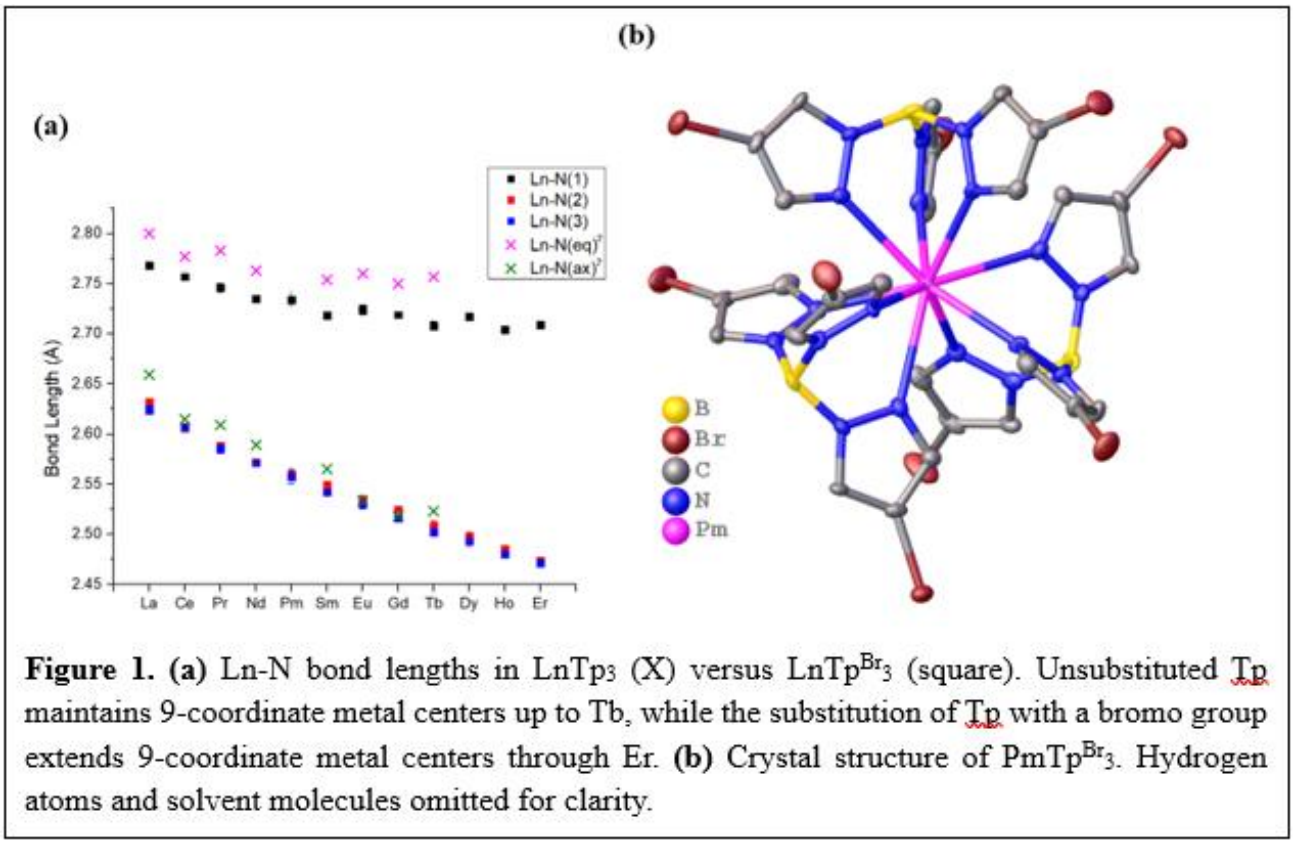

Figure 1. (a) Ln-N bond lengths in $LnTp_3$ (X) versus $LnTp^{Br}_3$ (square). Unsubstituted Tp maintains 9-coordinate metal centers up to Tb, while the substitution of Tp with a bromo group extends 9-coordinate metal centers through Er. **(b)** Crystal structure of $PmTp^{Br}_3$. Hydrogen atoms and solvent molecules omitted for clarity.

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NUCL 4541559

Structure and thermal decomposition of thorium peroxynitrate: insights from neutron scattering and *In-Situ* Raman spectroscopy

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Thorium peroxide materials are relevant to multiple stages of the nuclear fuel cycle, including fuel production, reprocessing, and the long-term storage of used nuclear fuel, where peroxide species form through the radiolysis of water. Despite their identification decades ago, the structural and thermal properties of many thorium peroxide compounds remain poorly understood due to their tendency to precipitate as fine, poorly crystalline powders. In particular, the structure of thorium peroxynitrate has remained unresolved, and prior studies of similar materials suggest that the acidity of the mother liquor may influence the structure of the resulting phase. In this work, thorium

peroxynitrate was synthesized from nitric acid solutions of varying concentration to evaluate the influence of solution conditions on structure and thermal behavior. Structural characterization was carried out using powder X-ray diffraction, Raman spectroscopy, and total neutron scattering measurements collected on the Nanoscale Ordered Materials Diffractometer (NOMAD) at the Spallation Neutron Source, enabling improved sensitivity to peroxide and nitrate coordination environments without the need for a single crystal. Thermal stability and decomposition pathways were investigated using simultaneous thermal analysis with off-gas mass spectrometry and in situ heated Raman spectroscopy to identify intermediate species and reaction mechanisms. These results provide new insight into peroxide coordination in tetravalent actinide systems and establish structure–property relationships relevant to actinide peroxide chemistry in nuclear fuel cycle environments.

NUCL 4541771

Advances in aqueous and solid phase isotope harvesting at the facility for Rare Isotope Beams

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At the Facility for Rare Isotope Beams (FRIB), exotic secondary beams are created via fragmentation of a high-power primary beam. Only a small fraction of the beam products are selected for dedicated scientific user experiments. At the same time, co-produced fragments are intercepted by accelerator components, and the unreacted primary beam will be stopped in a water-traversed beam dump. The accumulated radionuclides in all these components represent a valuable resource that can be recovered through targeted isotope harvesting efforts from the aqueous, solid, and gaseous phases [1].
This contribution will provide an overview of isotope harvesting at FRIB, first focusing on aqueous harvesting. In particular, the collection of ^{62}Zn from a stopped ^{78}Kr beam will be highlighted. The ^{62}Zn is relevant for nuclear medicine as part of a ^{62}Zn/^{62}Cu radionuclide generator system, as well as a radioactive tracer in plant science [2]. Results from an online isotope harvesting experiment and subsequent radiochemical purification will be presented, along with recent optimizations aimed at improving collection and separation.
In addition, isotope collection from the solid phase is another possible approach to isotope harvesting. Recently, we have begun investigating the collection of radioisotopes such as ^{197}Pt, ^{47}Ca, and ^{62}Zn, all of which are relevant for diagnostic or therapeutic applications in nuclear medicine. This presentation will provide an overview of initial developments in solid-phase harvesting, with particular emphasis on ^{47}Ca, which serves as a precursor to the therapeutically valuable ^{47}Sc.

NUCL 4542001

Surface-mediated plutonium redox transformations on metal (hydr)oxide minerals under high ionic strength conditions

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Plutonium remains one of the most chemically complex and environmentally persistent elements in the nuclear waste tanks. It's ability to exist in multiple oxidation states allows dynamic redox transformations that influence solubility, sorption, and complexation behavior. Predicting these transformations is particularly urgent for high-ionic strength environments such as the Waste Isolation Pilot Plant (WIPP), where brine chemistry and surface interactions control long-term radionuclide fate or the Hanford Reservation Waste tanks where high NaNO3 levels influence Pu partitioning between sludge and salt solution phases. Yet, despite decades of study, the mechanisms that drive plutonium's redox cycling at mineral–water interfaces remain poorly constrained. This study investigates the coupled sorption–redox behavior of plutonium on goethite across NaCl and NaNO3 media ranging from 0.1 to 3 M ionic strength. Batch experiments demonstrate extensive sorption of Pu(VI) at circumneutral pH, revealing strong dependence on oxidation state, and pH. Raman spectroscopy shows the progressive loss of the Pu(VI) plutonyl symmetric stretch, while XPS reveals reduction to Pu(IV) and the unexpected appearance of transient Pu(III) species. PuO2 nanoparticles were not observed in TEM imaging, suggesting that reduced plutonium remains as monomeric or oligomeric surface complexes. A thermodynamically based surface complexation model based on parameters determined from the 0.1 M NaCl system were unable to predict the data in 1 and 3 M NaCl, providing insight into electrostatic compression and competitive effects in brines.
Following the detection of transient Pu(III) on goethite, complementary experiments were conducted using Pu(III) as the initial oxidation state to determine whether surface-mediated oxidation occurs on different minerals which are hematite, goethite, gibbsite, and quartz. These experiments probe the stability of sorbed Pu(III) and clarify whether oxidizing versus redox-inert surfaces promote oxidation of Pu(III) to Pu(IV). Together, these studies provide a mechanistic, spectroscopically validated, and quantitatively modeled framework for predicting plutonium behavior in high-ionic strength nuclear waste repositories.

NUCL 4542070

Support loading effects on the performance of a polymer microcapsule-based extraction chromatographic material: Toward improved separation of trivalent lanthanides

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The effect of varying levels of support loading on the elution behavior of lanthanide ions on an extraction chromatographic (EXC) sorbent comprising polysulfone (PS) microcapsules impregnated with various quantities of the extractant *bis*(2-ethylhexyl)phosphoric acid (HDEHP) has been determined. Elution data for Eu^{3+} indicate that at a level of loading well below that corresponding to complete filling of the pores of the support, peak asymmetry and tailing reach a minimum, while column efficiency and metal ion uptake capacity reach a maximum. The improved chromatographic behavior resulting from such under-loading of the support is exploited in the separation of pairs of trivalent lanthanides of interest in nuclear medicine, including Eu^{3+} and Gd^{3+}, for which (in contrast to their poor separation on commercially available EXC resins) near-baseline resolution can be achieved.

NUCL 4542080

MetalMiner: High-throughput mining of metal coordination environments for data-driven actinide chemistry

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Advances in artificial intelligence and high-performance computing are increasing the use of data-driven methods in coordination chemistry, but progress in nuclear and actinide systems is limited by the lack of accessible, well-structured datasets. Crystallographic databases such as the Cambridge Structural Database (CSD) contain valuable coordination information, but inconsistent data quality, missing bonding information, and structural disorder make large-scale analysis difficult.
Here, we present MetalMiner, a high-throughput workflow that converts crystallographic data into site-specific coordination datasets suitable for data science and modeling. The workflow combines data filtering, cluster extraction, and disorder handling to isolate chemically meaningful metal-centered environments. Ligands are processed to assign hydrogens, bonding, and approximate charges, and key features such as coordination number, donor atoms, and metal–ligand distances are extracted. Oxidation states are estimated using both text information and structure-based methods, with uncertainty retained when needed. MetalMiner enables scalable dataset generation for modeling and prediction, particularly in data-limited areas such as actinide chemistry.

NUCL 4542139

Investigation into the rapid isolation of uranium(IV) using polyoxometalates

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Lacunary polyoxometalates (POMs) are inorganic metal-oxo clusters containing early transition metals (i.e., tungsten) and oxygen. Lacunary POMs have high binding affinity for f-block elements in the +3 and +4 oxidation states, as basic oxygen atoms at the defective site bind strongly to hard ions. Our previous studies showed that lacunary Wells-Dawson POM selectively extracted radio lanthanides (Lu-177 and Sm-153) due to differences in charge-to-size ratios between Lu(III) and Sm(III).
Our study aims to expand nuclear forensic capability for the rapid separation of targeted actinide ions from aqueous solutions to facilitate analysis. Leveraging the knowledge of POM binding affinities toward high-charge-to-size f-ions, the study focuses on separating the low-valent uranium (IV) ion from a mixture of f-ions containing europium and uranium under isolated conditions. Since U(IV) has a higher charge-to-size ratio than Eu(III), we demonstrate that POM preferably binds to U(IV) over Eu(III) in a mixture of ions. The POM-U(IV) complex is selectively isolated by precipitation with Cs ion. Unbound Ln(III) remains in the aqueous solution.

NUCL 4542217

Effect of fluorinated solvents and anion complexing agents on the balance of pathways in the extraction of metal ions by a crown ether into room-temperature ionic liquids

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The extraction of alkali and alkaline earth cations from nitric acid by a crown ether into room-temperature ionic liquids (RTILs) has been shown to occur *via* a combination of the partitioning of a neutral metal nitrato-crown ether complex or ion-pair (as seen with conventional organic solvents) (NC/IPE) and two distinct ion-exchange (IX) pathways. Because both forms of IX have been found to result in the degradation of the RTIL through loss of its cationic component to the aqueous phase, there has been considerable interest in the identification of means by which they can be suppressed. Previous studies have demonstrated that the balance among the three paths is affected by a variety of system properties, among them the Lewis acidity of the metal ion, the aqueous acidity, and the hydrophobicity of the ionic liquid, but the identification of conditions leading to the complete elimination of ion exchange remains a significant challenge.

In this study, the effect of the addition of nitrate anion-selective complexing agents and/or fluorinated alcohols to the RTIL phase was evaluated as a means of enhancing co-extraction of nitrate with the metal ions of interest (*e.g.*, Cs-137, Ba-133), thus favoring the NC/IPE pathway. The addition of fully fluorinated alcohols (*e.g.*, 2,2,3,3,4,4,5,5-octofluoro-1-pentanol) and, to a lesser extent, partially fluorinated alcohols (*e.g.*, 4,4,5,5,5-pentafluoro-1-pentanol) was found to increase the transfer of nitrate ion into the ionic liquid, likely due to increased hydrogen bond formation with the nitrate. Similarly, the addition of an appropriate anion complexing agent also increased

nitrate transfer, but neither approach significantly altered the balance of pathways. Some improvement was noted when both the fluorinated solvent and the anion complexing agent were added to the RTIL phase, but again, complete elimination of the IX mechanism was not achieved.

NUCL 4542343

Aqueous isotope harvesting of Ni radioisotopes from the FRIB beam blocker

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Nickel isotopes are applicable in many areas of research, this includes use as isotope sources in nuclear batteries (^{63}Ni), targets for cross-section studies in astrophysics (^{56}Ni, ^{59}Ni, and ^{63}Ni), and imaging probes in nuclear medicine (^{57}Ni). The Facility for Rare Isotope Beams (FRIB) at Michigan State University presents an especially unique opportunity to supply such rare and underproduced isotopes. In the production of exotic secondary beams for scientific user experiments, 90% of the primary beam remains unreacted and will be redirected to an aqueous beam blocker, resulting in the production of copious radionuclides. To take advantage of this production, radioisotopes of interest must be collected or ‘harvested’ from the beam blocker through selective separation from co-produced species. The goal of this work is the separation of Ni at near massless quantities from a list of other elements representative of those that will be present as co-produced radioisotopes, those being: Ca, Co, Cu, Fe, Mn, Na, and Sc. Current work focuses on the development of a combined ion exchange and solvent extraction (CIESE) separation scheme using stable isotopes and quantification via inductively-coupled plasma optical emission spectroscopy (ICP-OES). Using cation exchange resin, the initial separation of Ni from other transition metals has been successful with 95% of Ni recovered in 5 mL of eluate. Having replicated the initial separation results using ^{56}Ni supplied by the National Isotope Development Center, subsequent purification of Ni from remaining Na, Ca, and Sc has been pursued via anion exchange resin. Further, a small-scale system has been developed to model aqueous harvesting at FRIB.

NUCL 4542942

Radiometric aging of eastern Bering Sea snow crabs

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Bering Sea snow crabs (Chionoecetes opilio) constitute a majority of the commercial crab species that support high value fisheries in Alaska. However, the decreasing biomass trend of mature male snow crabs raises concern for commercial fisheries. Significant data gaps in snow crab growth, longevity, and mortality hinder the accuracy of assessment models. Aging of snow crabs can be performed through radiometric analysis of radium incorporated with calcium in the exoskeleton. While traditional aging methods are challenged by the crab's molting processes, the decay of radium through the crab's shell creates a chronometric clock that can be used to determine the age of the crab at the time of terminal molt. Radiometric measurement using gamma spectroscopy will improve the speed of analysis by decreasing sample preparation time as compared to previously used techniques such as alpha spectroscopy. This work aims to validate the use of gamma spectroscopy for radiometric age dating of Bering Sea snow crabs using 228Th/ 228Ra decay. Spectroscopy will be performed using a high purity germanium detector (HPGe) to measure gamma rays emitted by short lived decay products, 228Th and 228Ra. The work will determine crab ages at the time of terminal molt to close the data gap regarding the maximum age and natural mortality estimates in snow crab stock assessments.

NUCL 4542942

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NUCL 4543053

Underloaded and stagnant pore-blocked supports for improved extraction chromatography

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Despite ongoing improvements in the sensitivity and selectivity of many methods of analysis, separation and preconcentration frequently remain important first steps in analyte determination in a variety of matrices. In the determination of metal ions, one of the most important methods for accomplishing this is extraction chromatography (EXC), a specialized form of liquid chromatography in which the stationary phase comprises an extractant or a solution of an extractant in an organic solvent supported on a porous polymeric or inorganic substrate. Although widely employed in radioanalytical chemistry, EXC materials suffer from important limitations, most notably modest column efficiency, excessive peak tailing, and limited metal ion uptake capacity. Recent work in this laboratory suggests that poor column efficiency and excessive peak tailing arise from the presence of extractant in small, relatively inaccessible ("stagnant") pores present throughout the support. In this presentation, it is shown that if the extractant is prevented from occupying such pores, thus confining it to more accessible regions of the support, improved column performance (in particular, higher efficiency and less pronounced peak tailing) will result. Improvements in column performance can also be achieved simply by adjustment of the level of support loading, even when the stagnant pores of the support are not blocked. Both of these approaches are shown to be particularly effective when applied to supports based on polymer microcapsules. The practical significance of these observations for sorbents based on *bis*(2-ethylhexyl) phosphoric acid (HDEHP) is illustrated through the separation of several trivalent lanthanide ions.

NUCL 4543189

Selective reduction and removal of Sm from Pm with SREX inspired extractants

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Promethium-147 (E_β = 224.1 keV, $t_{1/2}$ = 2.62 y) decays to stable samarium-147 and has practical applications in beta-voltaic batteries used by NASA in satellites and space probes. The lanthanides elements have a stable trivalent oxidation state and minor deviations in ionic radii across the period. These nearly identical chemical and physical properties make the separation of adjacent lanthanides by common methods, ex. size exclusion and ion-exchange, extremely difficult. Modern approaches to the separation of

adjacent lanthanides exploit a minor difference in a chemical or physical property. One such physical property that can be exploited is the reduction potential (E° (Ln^{3+} à Ln^{2+})) of Pm and Sm. Sm has an easily accessible E° of -1.6 V; whereas, Pm has a relatively inaccessible E° of -2.6 V. 18-crown-6 derivatives have been shown to selectively chelate Sr^{2+} in the presence of trivalent lanthanides and actinides. Following reduction from the trivalent to the divalent state, Sm^{2+} has a nearly identical 8-coordinate ionic radius to Sr^{2+}. This work investigates the selective reduction and removal of Sm from Pm using 18-crown-6 derivatives. This is performed using liquid-liquid extraction and column chromatography with non-radioactive analogs. The adjacent lanthanide neodymium (Nd) is an ideal nonradioactive analog for promethium in this project as Nd has a nearly identical 8-coordinate ionic radium (1.109 Å for Nd and 1.093 Å for Pm) and an identical reduction potential of -2.6 V. Although Sm has stable isotopes, the separation scheme will be refined without electrochemical manipulation using Sr as the surrogate in initial studies due to their nearly identical ionic radii and Sr's natural divalent oxidation state.

NUCL 4543202

Design and synthesis of chelators for radium separation and treatment of malignant cells

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This research aims to better understand the preferred chelation of radium through functional group preference and coordination environment for radiopharmaceutical treatments or the removal of radium from environmental sources such as groundwater. This will be accomplished through stability/complexation studies, and first optimized with non-radioactive analogs of radium. Radium has prior effective use for bone metastasized cancer treatments due to bones being the natural biological accumulation point for radium, and the multiple quick high energy alpha decays of the medicinal isotope ^{223}Ra. These alpha decays offer sizeable advantages to current radiopharmaceutical medicines which rely primarily on beta particles. Alpha decays have a high linear energy transfer resulting in more reliable tumor cell death with less off target damage.
To achieve the goal of selectively chelating radium, a variety of chelator designs were selected. One of which resembles a tweezer using crown ethers moieties to satisfy the expected large coordination environment of radium. This chelator is designed to be easily modifiable with differing crown ether sizes, rigid versus flexible backbones, and the ability to modify the hardness/softness of the donating groups. Barium serves as a stable analog for radium, enabling process optimization prior to combination with radium. Studies with radium will include kinetic binding studies via radio-thin layer chromatography, single crystal x-ray diffraction, and ultraviolent-visible spectroscopy.

NUCL 4543269

Design and synthesis of radium chelators for the treatment of cancer

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Radium-223 chloride (Xofigo) is currently used to treat castration-resistant prostate cancer that has metastasized to bones. In the ALSYMPCA trial, $^{223}RaCl_2$ improved median overall survival of patients by 3.6 months compared to a placebo. This statistic is especially significant considering for patients to qualify for treatment using $^{223}RaCl_2$ they must have stage 4 cancer that is recalcitrant to chemotherapeutics. At this stage of cancer, a 3.6 month extension of life represents a very effective therapeutic.

Due to the similarities between radium and calcium, radium naturally accumulates in human bones. Current use of $^{223}RaCl_2$ is limited to cancers that have metastasized to bones, largely due to a lack of in-vivo efficacious ligands that can bind ^{223}Ra and controllably target tumors in other areas of the body. The ^{223}Ra decay chain results in the emission of alpha particles. Alpha particles are ideal for radiation-based cancer treatment due to several key features. Compared to beta particles, alpha particles have a far higher linear transfer energy, meaning that an alpha particle does more damage to a tumor and this damage is more likely to result in double-strand breaks, which will kill the tumor. Alpha particles also travel far less distances than beta particles, which helps limit potential off target irradiation.

This work seeks to synthesize novel ligands specifically for ^{223}Ra, so that Ra-based cancer medicines can target tumors outside of bones. These ligands need to be stable at pH 7.4 and robust enough to prevent degradation of the ligands until ^{223}Ra has had time to target the cancer. This class of porphyrin-based chelators will satisfy a high coordinate radium metal center and feature charge balancing moieties.

NUCL 4543269

Design and synthesis of radium chelators for the treatment of cancer

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NUCL 4543456

Trends of the Periodic Table: Insights from superheavy element homologue studies

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The Periodic Table of Elements is well-established framework for studying the chemical behavior of the elements. However, the periodic trend seems to break apart in the heaviest members (Z >103) of the table, the superheavy elements (SHE), due to the onset of relativistic effects. This results in new and unexpected chemistry at the edge of nuclear stability. A novel experimental method utilizing the FIONA mass spectrometer at Lawrence Berkeley National Laboratory (LBNL) enables the chemical studies of these elusive elements. Before probing the fundamental properties of the SHE, analogous studies of their lighter group homologues need to be performed first. In this work, we report the results of experiments involving the gas-phase fluoride formation of three lighter elements (ytterbium, hafnium and tantalum) produced in nuclear fusion evaporation reactions. The relative production rate of MF_n^+ indicates the availability of electrons needed to reach a certain oxidation state, which is a characteristic of the group the element belongs to. The results agree with the findings of similar studies performed on stable isotopes of the same elements. This sets the stage for a future experiment involving SHE, aimed at understanding their chemical behavior and the trends that they are expected to break due to an energetic reorganization of the valence orbitals.

NUCL 4543641 - Withdrawn

NUCL 4544664

Gold nanoparticles for separation and drug delivery of 211At

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Astatine-211 is a radionuclide with a 7.2 hour half-life that shows a high potential for use in targeted alpha therapy (TAT). Its production is limited to a small number of facilities equipped with cyclotrons capable of delivering the required energy range, such as the Texas A&M Cyclotron Institute, and is achieved via the Bi-209(α,2n)At-211 reaction. Following irradiation, the target is dissolved with nitric acid creating a matrix of bismuth and astatine. Separation of the astatine-211 from the acidic bismuth matrix is required prior to radiolabeling. Gold nanoparticles (AuNPs) offer a promising approach for isolating astatine-211 and attaching a targeting agent in one-step. By facilitating the selective binding of astatine to the nanoparticle surface, AuNPs enable its separation from the bulk matrix. Once isolated, the complexes can be easily functionalized with targeting agents for therapeutic application. This approach will enable a versatile platform for TAT with astatine.

NUCL 4544878

AI-driven precision modeling of electronic properties and stability for nuclear materials

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The evolution of high-performance computing (HPC) is redefining the boundaries of nuclear and radiochemistry, providing transformative pathways for the design of specialized shielding and fuel materials. To meet the technical demands of the nuclear sector, there is an urgent need for deep learning (DL) architectures capable of being effectively trained on sparse, high-quality experimental datasets rather than relying solely on traditional density functional theory (DFT). By streamlining the identification of radiation-resistant functional materials, this framework supports the responsible deployment of AI/ML, reducing the energy and material intensity typically associated with computation-heavy research.
In this work, I introduce an AI-based approach that achieves exceptional predictive accuracy for experimental formation enthalpies and band gaps in complex heavy-metal compounds, delivering results that match or exceed the fidelity of high-level hybrid functional calculations. By utilizing a crystal structure representation based on the orbital field matrix (OFM), this methodology incorporates valence electron configurations and fundamental elemental properties to capture the intricate bonding relationships within actinide and lanthanide systems. Such tools are essential for optimizing the material life cycles and chemical transformation pathways that underpin the resilience and efficiency of advanced nuclear systems.

Beyond its predictive performance, this model identifies robust physical trends while maintaining the scalability necessary for large-scale applications in spectroscopy and isotope detection. This capacity to bridge the gap between theoretical models and experimental outcomes is a critical step toward more precise morphology analysis of nuclear fuels and the design of next-generation containment materials. Ultimately, this methodology provides a sophisticated pathway for engineering specialized molecular systems while simultaneously enhancing the sustainability of chemical solutions for national and global nuclear interests.

NUCL 4545253

In-situ observation of uranium trioxide calcination using synchrotron X-ray scattering

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The calcination of UO_3 to U_3O_8 is an important step in the front-end of the nuclear fuel cycle. Though several studies have been undertaken to understand this transition, they have typically used either ex-situ measurements which can only provide a snapshot of the calcination process and may undergo transitions during cooling, thermogravimetric analysis that requires assumptions on the composition of gaseous byproducts, or high-temperature x-ray diffraction (HT-XRD) that requires significant time at a given temperature to collect a well-resolved diffraction pattern. In this work, we used small- and wide-angle X-ray scattering (SWAXS) at the Advanced Photon Source to collect density and diffraction data in-situ while transiting from room temperature to 800 °C. With this technique, we demonstrated the ability to rapidly characterize solid samples in-situ, observed several crystallographic transitions, and paved the way for future studies on nuclear materials at this beamline.

NUCL 4547893

Gallium-68 radiolabeling of monobodies using a THP chelator to preserve protein stability

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Next-generation PET radiopharmaceuticals require efficient labeling strategies that preserve protein structure while producing stable, high-purity imaging agents.

Monobodies are attractive molecular imaging scaffolds because of their small size, modularity, and high binding affinity, but conventional gallium-68 labeling methods often require elevated temperatures and acidic conditions that can compromise protein integrity. In this work, we developed a site-specific radiolabeling strategy for monobodies using a maleimide-THP chelator to enable rapid gallium-68 complexation under mild conditions. Monobody constructs were functionalized via thiol-mediated conjugation to form mal-THP derivatives and subsequently labeled with [68Ga]GaCl3 at room temperature and near-neutral pH. This approach allowed efficient radiometal incorporation within minutes without the need for heating, providing a workflow that is better suited for thermally sensitive protein-based ligands. Radiochemical evaluation showed quantitative labeling efficiency by instant thin-layer chromatography and high final product purity by size-exclusion radio-HPLC. The labeled monobody retained its structural integrity under these mild conditions, supporting the compatibility of THP-based chemistry with delicate protein scaffolds. In contrast to DOTA-based labeling, which often requires harsh reaction conditions and can lead to reduced yield or protein destabilization, the THP platform offered a simpler, faster, and more radiopharmacy-friendly alternative. The method also aligns well with kit-based production strategies, which are attractive for routine preparation of PET tracers at the point of care. These findings demonstrate that THP-based gallium-68 labeling can preserve monobody function while producing stable radiotracers with excellent radiochemical quality and support the development of next-generation protein-based PET imaging agents for molecular imaging and theranostic applications.

NUCL 4547898

From ^{212}Pb production to tumor delivery: Optimization of a ^{212}Pb-labeled LDLR-targeted peptide for cancer therapy

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Background: Advancing radioligand therapy for pancreatic ductal adenocarcinoma (PDAC) requires chelator-based conjugates that can be labeled efficiently with 212Pb, remain stable in vivo, and sustain tumor delivery. Low-density lipoprotein receptors (LDLR), overexpressed in PDAC and other solid tumors, represent a promising target for this strategy. Here, we report the generator-based production/purification of 212Pb and the structural optimization of the LDLR-targeted peptide, RMX-VH-PKM, with improved PK properties.
Methods: A novel RAHA 224Ra/212Pb generator (10-20 mCi, RadioMedix) was used to provide a high-purity isotope suitable for radiolabeling. RMX-VH-PKM was labeled with 212Pb at pH 6.0 and 80 °C in the presence of scavengers. SPECT/CT imaging (Bioemtech, Greece) and biodistribution studies of 212Pb-RMX-VH-PIB were performed in PDAC xenografts at serial time points up to 72 h post-injection. Pilot single-dose

efficacy and survival studies of the agent were also conducted in PDAC xenograft models.
Results: Radiolabeling of RMX-VH-PKM achieved 80-95% radiochemical yield, with stability maintained for up to 24 h, supporting robust isotope coordination. Biodistribution studies of radiopharmaceutical done in PDAC xenografts showed high and sustained tumor uptake, reaching 17.4 %ID/g at 1 h and remaining elevated at 24 h. Bone marrow uptake remained low, consistent with in vivo stability of the complex. The liver and kidneys showed the highest normal-organ uptake. In pilot therapy studies, the untreated control cohort had a median survival of 39 days. The strongest antitumor activity was observed at a 50 μCi dose, producing complete tumor regression in 25% of animals and durable tumor control in the remaining 75% ($p < 0.04$ vs control). Median survival was 54.4 days and 60 days in the 20 μCi and 30 μCi groups, respectively, while the 50 μCi cohort remained alive and under observation beyond 130 days. Only mild, transient body weight loss was observed at higher doses.
Conclusions: Generator-based production provides a practical source of 212Pb. The radiochemical and biodistribution data identify 212Pb-RMX-VH-PKM as a promising LDLR-targeted scaffold for targeted alpha radioligand therapy.

NUCL 4548544

Investigation of heavy element chemistry with novel self-assembled monolayer-coated silicon detectors

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Chemically characterizing transactinide elements is difficult, due to low production cross-sections and short half-lives. Isothermal gas chromatography can characterize atom-at-a-time interactions on detector surfaces. Traditionally, SiO_2 or Au surfaces are used when studying these interactions, however we propose using self-assembled monolayers (SAMs). SAMs are thin films with interchangeable terminal groups, which can be easily exchanged to alter the chemical surfaces available on which to perform adsorption studies. Monte Carlo simulations can be performed to determine the limits of ΔH_{ads} on the surface, providing information about chemical trends among the elements studied.
At Texas A&M University, three fusion evaporation experiments were performed to produce ^{152}Er, ^{196}Po (homolog to Lv), and ^{198}At (homolog to Ts). The products were separated using the AGGIE gas-filled separator prior to the desired products being thermalized utilizing a combination of a rotating degrader and a simple recoil transfer chamber to the SAMs Polonium Isotope Detector ARray (SPIDAR) – an isothermal gas chromatography setup. Isothermal chromatograms in SPIDAR for Po, Er and At were measured on three surfaces: bare Si, bare Au, and 12-mercaptododecanoic acid

(MDDA), which is a SAM. These results were matched with Monte Carlo simulations to estimate the limits of ΔH_{ads} for each element on each surface. This poster will discuss our results and future plans.

JOINT 4505918

Development and application of americium forensics for an aged historical ^{243}Am source

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Americium is a widely proliferated nuclear material yet receives little attention in the field of nuclear forensics. Both major isotopes, $^{241, 243}$Am, exhibit favorable characteristics for use in radioactive dispersive devices (“dirty bombs”) and modeling has suggested feasibility as fuels in improvised nuclear devices. Am is produced from Pu decay, and this unique relationship can allow Am sources to contain similar contaminants as Pu sources, allowing for indirect measurement of Pu forensic vectors. For these reasons, Am is an intriguing element worth developing targeted forensic methods for.
Previous work created a library-based forensic method for reactor-type discrimination of purified Pu based on purification-resistant intra-elemental isotope ratios of actinides and fission products, including $^{239\text{-}242}$Pu, ^{133,134,137}Cs, ^{153,154}Eu, and ^{149,150,152}Sm. Measured ratios are compared to values from simulations of various reactor types to identify a most likely combination of reactor-type, time since irradiation, and burnup. Isotope ratios are measured through a combination of decay-radiation spectrometry where viable and ICP-MS for stable nuclides. This requires chemical separation of isobar lanthanide isotopes and has previously been achieved with α-HIB column chromatography.
Am sources may contain the same fission product ratios as Pu sources, but Am sources require special considerations. An LN-resin-based separation scheme has been developed that is capable of separately and sequentially eluting Cs, Am, Ce-Gd without the need for α-HIB. The early elution of Am minimizes handling time and increases safety, and its removal from the Ln fission products allows for long count times to assay trace amounts of these radionuclides.
A ^{243}Am historical source has been analyzed. Prior to the reactor-type discrimination method, small aliquots were taken for traditional α- and γ-spectrometry measurements, which quantified sufficient ^{242m}Am that a ^{242m}Am-^{238}Pu radiochronometric pair could be established through α-spectrometry. ^{241}Am interferes with ^{238}Pu, so two different column separations schemes to quantitatively separation Am/Pu have been explored. A modification of the LN resin scheme to selectively elute Pu after all other elements has been tested, as well as an alternative pre-separation on TEVA resin. This talk will cover the work done to adapt this methodology to Am samples and the latest results of its application to a historical ^{243}Am source.

JOINT 4515349

Pu 5f population: the case for n = 5.0

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The quantitative determination of the 5f population in α-Pu and δ-Pu is considered in detail. Trends across the 5f series are discussed, including atomic sizes, 5f populations and computational modeling. A detailed spectroscopic analysis of the original Pu N4,5 and O4,5 x-ray absorption spectroscopy has been performed, including the correction of a fatal flaw in the Electron Energy Loss Spectroscopy (EELS) measurements. Thus, the determination of the 5 f occupation (n) in elemental Pu has been re-evaluated with the result that n = 5.0 ± 0.1 for αPu and n = 4.9 ± 0.2 for δPu. These values are significantly lower than the value of ~ 51/2 that was propagated earlier.

JOINT 4515959

Creating new chemical process monitoring for Pu processing

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Lawrence Livermore National Laboratory's (LLNL) plutonium (Pu) facility has successfully demonstrated the full lifecycle of Pu processing and is now leveraging ongoing operations to achieve two primary objectives: 1) develop robust chemical models for each Pu processing step in both aqueous and pyrochemical operations, and 2) train a capable workforce to meet future production needs. To support these goals, LLNL's Pu processing facility is implementing expanded analytical capabilities to generate high quality process data for model development and validation. This data will enable accurate simulation of key unit operations, including dissolution, anion exchange, precipitation, direct oxide reduction, and electrorefining. Data science approaches, including machine learning, will be applied to accelerate model development and improve predictive capability across the flowsheet. Close collaboration between theoretical and experimental teams is establishing a strong, traceable knowledge base in Pu processing for the current workforce. In parallel, Jupyter notebooks are being used to capture both newly generated and historical data within a structured Learning Tracks program, providing a scalable and efficient mechanism to onboard and train future Pu recovery personnel. This presentation will provide an overview of the ongoing efforts to integrate modeling, experimentation, and workforce development within LLNL's Pu facility. Key challenges, lessons learned, and the planned path forward for advancing Pu processing capability and institutional knowledge will be discussed.

JOINT 4522042

Novel, high-performance sorbents for chlorine capture

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Chlorine gas (Cl2) and volatile metal chlorides are produced during molten chloride pyrochemical processes as part of the molten chloride reactor (MCR) fuel cycle. These are valuable, toxic, and/or radioactive species which must be recovered and can be recycled back into the MCR processes. As such, effective recycling of metal chlorides and chlorine from MCR fuel cycle is highly critical to further advance nuclear energy research. However, there are no reusable commercial technologies that can selectively capture, store, and release metal chlorides and chlorine. This illustrates a critical need to develop nuclear waste reprocessing technologies that can efficiently capture and release chlorine and metal chlorides that are produced in the MCR fuel cycle.

Under a Department of Energy (DOE) sponsored program and collaboration with Argonne National Laboratory (ANL), Physical Sciences Inc. (PSI) developed a high performance, reusable, and remotely handled turnkey absorber system that can efficiently capture chlorine and volatile chloride salts produced during pyroprocessing operations (Chlorine/Chloride Capture and Recovery System or CCRS). PSI's innovative CCRS Technology is comprised of two units: (1) Chloride salt condensing unit and (2) Chlorine sorbent unit - this is the key innovation and is based on PSI's spherical mesoporous silica sorbent with high surface area >400 m2/g and pore diameter of 20 nm. The baseline silica sorbents were engineered with highly active surface functionalities which enables selective chlorine capture, storage, and release. This approach results in an overall reusable system with enhanced capabilities, reduced operational cost, and enhanced safety compared to that of single-use technologies.

This presentation will discuss the following technical results: (a) Novel sorbents with high Cl2 capture capacity (>0.18 g/g), robust storage (7 days), fast desorption kinetics (< 1 hr.), and reusability, (b) Scale-up production of sorbents on kg-scale, (c) Detailed models of the CCRS system including process flow diagrams, piping and instrumentation diagrams, and CAD models, and (d) Techno-economic analysis of reusable sorbent and CCRS system. This presentation will also provide plans for sorbent and CCRS technology validation studies at PSI and at Argonne National Laboratory.

JOINT 4523209

Expanding radium structural characterization

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Interest in radium has been renewed because of its applications in the production of Ac-225 and as a radionuclide for cancer treatments. However, the high radioactivity and scarcity of this element present challenges in obtaining structural studies. Due to these difficulties, many studies use Ba as a surrogate for Ra. However, recent advances highlighted bonding and reactivity deviations between these elements, therefore further studies are necessary to elucidate key deviations among the alkaline earth metals. Several approaches to advance the coordination chemistry of Ra will be presented, including employing macrocycles, using large bulky counter ions to facilitate crystallizations, performing hydrothermal syntheses and comparative bonding analyses to Sr and Ba analogues.

JOINT 4523298 - Withdrawn

JOINT 4523316

Uranium chloride production by halide exchange with uranium fluoride

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Molten chloride salt reactors (MCSR) require a reliable and scalable source of uranium chloride fuel. Current synthesis methods for uranium(III) chloride (UCl_3) depend on uranium metal or oxide feedstocks, but enriched sources of these are derived from uranium fluorides. A direct conversion pathway from uranium fluoride to uranium chloride via anion exchange would therefore provide an economical and scalable route to MCSR fuel from an abundant feedstock.

A systematic thermodynamic survey identified magnesium(II) chloride ($MgCl_2$) as a suitable exchange reagent for conversion of uranium(IV) fluoride (UF_4) to uranium tetrachloride (UCl_4). The reaction, $2MgCl_2 + UF_2 \rightarrow UCl_2 + 2MgF_2$, is thermodynamically favorable across all practical synthesis temperatures, and UCl_4 is readily separated from the non-volatile MgF_2 byproduct by distillation. Anhydrous $MgCl_2$ is commercially available, relatively inexpensive, and manufactured by metal hydrochlorination, which lends itself to production with enriched ^{37}Cl — an important requirement in fast reactor fuels.

Scoping experiments conducted within an inert-atmosphere glovebox confirmed UCl_4 formation from a mixture of UF_4 and $MgCl_2$, with phase identification by powder X-ray diffraction (XRD). No unreacted UF_4 was detected, indicating high conversion consistent with thermodynamic predictions. Subsequent distillation of the reacted mixture yielded substantially pure UCl_4, which fractionally separated along a thermal gradient from the $MgCl_2/MgF_2$ residue. These results establish direct anion exchange of UF_4 with $MgCl_2$ as a technically feasible, practically advantageous pathway to UCl_4 — a direct precursor

to UCl_3 by established reduction methods — and lay the groundwork for development of a scalable MCSR fuel production process.

JOINT 4523628

Importance of actinide chemistry in molten salt reactor redox control

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For about 20 years, we have revived the idea of using molten salts as coolants and fuel carriers for nuclear reactors because of their advantages of high temperature and low-pressure operation, flexible fueling, and limited potential for radionuclide release under adverse conditions. Molten salts prove to be excellent solvents, allowing dissolution of actinide fuel and capture of fission and activation products. However, the changes in salt composition during burnup means that understanding the chemical aspects of MSR operation are crucial to maintaining performance over the long term. This talk will provide an overview of salt chemistry, and the importance of redox control imposed by coupled actinide salts. Safe operation is established within a redox window, with fluorine or chlorine potential on one axis and temperature on the other. Thermodynamics based on redox state will determine the corrosivity of the salt, radionuclide release, and the formation of precipitates in the salt. However, the system is dynamic and compositional changes accrue over time, which necessitates the use of kinetic models for radionuclide decay and transport. These models can be validated from data collected from direct measurement of actinide and radionuclide behavior.

JOINT 4523872

Toward an integrated measurement platform for molten salt reactor monitoring

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Accurate in situ monitoring of molten salt reactors (MSR) demands more than measurement of a single variable, because salt composition, uranium redox chemistry, and impurity buildup evolve simultaneously and influence each another. Here, we outline a measurement platform for MSR monitoring that expands our previously validated cooling-curve thermometry method into a broader diagnostic framework. In this platform, a high-throughput cooling-cup sensor will generate rapid phase-transition data using minimal salt volumes and controlled cooling conditions, creating large datasets for rigorous interpretation. These thermal signatures will be anchored to a thermophysical database constructed from high-throughput measurements, literature curation, and CALPHAD-based modeling of key chloride salt systems. In parallel, electrochemical diagnostics will be developed to estimate U(III)/U(IV) ratios in concentrated uranium salts, and plasma-based spectroscopy will provide qualitative

identification of major impurities and salt components that can bias thermal or electrochemical responses. Combined, these measurements feed machine-learning models that refine predictions of salt composition and redox condition even when individual signals are noisy, incomplete, or affected by impurity interference. The overall goal is to establish a path toward autonomous MSR diagnostics that supports reactor operation, sensor optimization, thermodynamic database refinement, and safeguards-relevant monitoring in complex molten salt environments.

JOINT 4526317

Evaluating effect of Np concentration on redox chemistry

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The synthetic transuranic element Np possesses a rich redox chemistry and is capable of adopting multiple oxidation states. Of all its oxidation states, Np(V) is dominant in dilute acidic conditions without adding redox reagents or complexing ligands. However, the effect of Np concentration on its redox chemistry is not well-studied due to its strategic availability, which typically limits experiments with Np to the millimolar concentration scale. To address this knowledge gap, we leveraged Oak Ridge National Laboratory's unique access to radioisotopes to prepare and study the redox chemistry of samples with molar concentrations of Np via ultraviolet–visible–near-infrared spectroscopy. Spectroscopic data revealed that at molar Np concentrations in dilute HNO_3 and HCl, both Np(V) and Np(VI) are present, which deviates from typical redox behavior at lower Np concentrations. In situ spectra of chemical and electrochemical manipulations of Np oxidation state ratios explained the difficulty in stabilizing pure Np(V) at molar concentrations in dilute acidic media. In this presentation, spectroscopic data will be presented, and hypotheses for this unusual redox behavior will be discussed.

JOINT 4526610

Structural investigations of early lanthanides and late actinides

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The separation of early lanthanides (La–Eu) from late actinides (Am–Es) remains a persistent challenge in nuclear science with significant implications for waste management, medical isotope production, and advanced fuel cycles. Systems such as Am/Cm/Eu and the recently highlighted Pm/Cm pair represent particularly difficult separations, with the latter being critical for recovering ^{147}Pm from fission waste streams. To elucidate the fundamental factors governing these separations, we examine isostructural early lanthanide and late actinide complexes featuring ligands

containing functional groups relevant to *f*-element separation chemistry. Comparative structural analysis reveals subtle yet consequential differences in metal-ligand bonding across lanthanide/actinide systems. Understanding these distinctions provides insight into the chemical origins of selectivity and informs strategies for improving challenging separations.

JOINT 4527042

Plutonium Chloride speciation as a function of pH, temperature, and ionic strength

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Plutonium (Pu) is present in the environment as a direct consequence of nuclear energy production and weapons development. Although underground nuclear weapons testing has ceased, long-term safety assessments and remediation planning remain essential due to the continued storage and disposal of transuranic waste and the potential for accidental release. In the United States, the Waste Isolation Pilot Plant (WIPP) – the only operating deep geologic repository for transuranic waste – is hosted in the Salado Formation of southern New Mexico, a salt bed system where Pu has also been introduced through legacy nuclear activities. Predictive modeling of Pu transport and retention in such environments depends critically on accurate descriptions of Pu(VI) aqueous speciation under variable pH, temperature, and salinity conditions.
This work will describe Pu(VI) speciation in NaCl and $MgCl_2$ solutions (0.1–10m) as a function of pH (2–11) and temperature (25–95 °C) using Ultraviolet–Visible–Near Infrared (UV–Vis–NIR) absorption spectroscopy. Experiments were conducted under oxic conditions to allow hydrolysis and potential carbonate uptake, reflecting realistic environmental and repository scenarios. Spectral evolution was used to assess transitions from the uncomplexed plutonyl ion (PuO_2^{2+}) to chloride coordinated species and identify the formation of other mixed chloro–hydxo and chloro–carbonato complexes.
Comparisons between NaCl and $MgCl_2$ systems provide insight into how background electrolyte composition and ionic strength influence ligand competition and Pu(VI) coordination geometry. The resulting spectroscopic results will be interpreted in the context of established actinide ligand-affinity trends and prior studies of Pu(VI) hydrolysis and stability in saline systems.
This study aims to generate useful thermodynamic data relevant to the aqueous speciation of Pu(VI) under coupled pH, temperature, and salinity conditions, strengthening the mechanistic basis for predicting plutonium behavior in salt-based nuclear waste disposal environments.

JOINT 4527808

Bonding of soft-donor ligands with americium, curium, and trivalent lanthanides

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The goal of this work is to exploit the selectivity of soft-donor ligands as a means to improve challenging but critical actinide (An) separations, especially Am/Cm and lanthanide (Ln)/An separations. This research benefits the US Department of Energy (DOE) Isotope Program and Office of Nuclear Energy by enhancing our understanding of the trivalent actinides—namely, Am and Cm. Currently, O-bearing analogues are employed across the DOE complex for Am/Cm separations and Am/Ln(III) separations. Studying coordination by identical structural motifs with O or S substitutions allows for a direct comparison of bonding efficiencies, which will ultimately inform separation studies. Solid-state crystallographic and computational analyses will probe the coordination behavior and electronic structure of these compounds; crystallographic techniques provide quantitative bond distances and coordination geometries that can help inform overall separation sciences. This work seeks to test a one-to-one comparison of O-donor ligand systems with directly analogous S-donor ligands. Goals include identifying commercially available soft-donor ligands to probe the coordination and complexation of these ligands with f-block elements and performing computational studies to relate solid-state structures to electronic covalency behaviors. In the context of this work, soft-donor ligands are considered to be any ligand softer (i.e., more polarizable) than O—commonly, S, N, and P. These goals will be achieved through quantifying the ability of each ligand to chelate Am, Cm, and Ln(III) by studying the structural and electronic bonding properties before scaling toward developing new separation schemes. This work will also augment the literature data for sparse Am and Cm crystallographic structural datasets that have been published.

JOINT 4528086

Dynamic covalency in molten actinide salts

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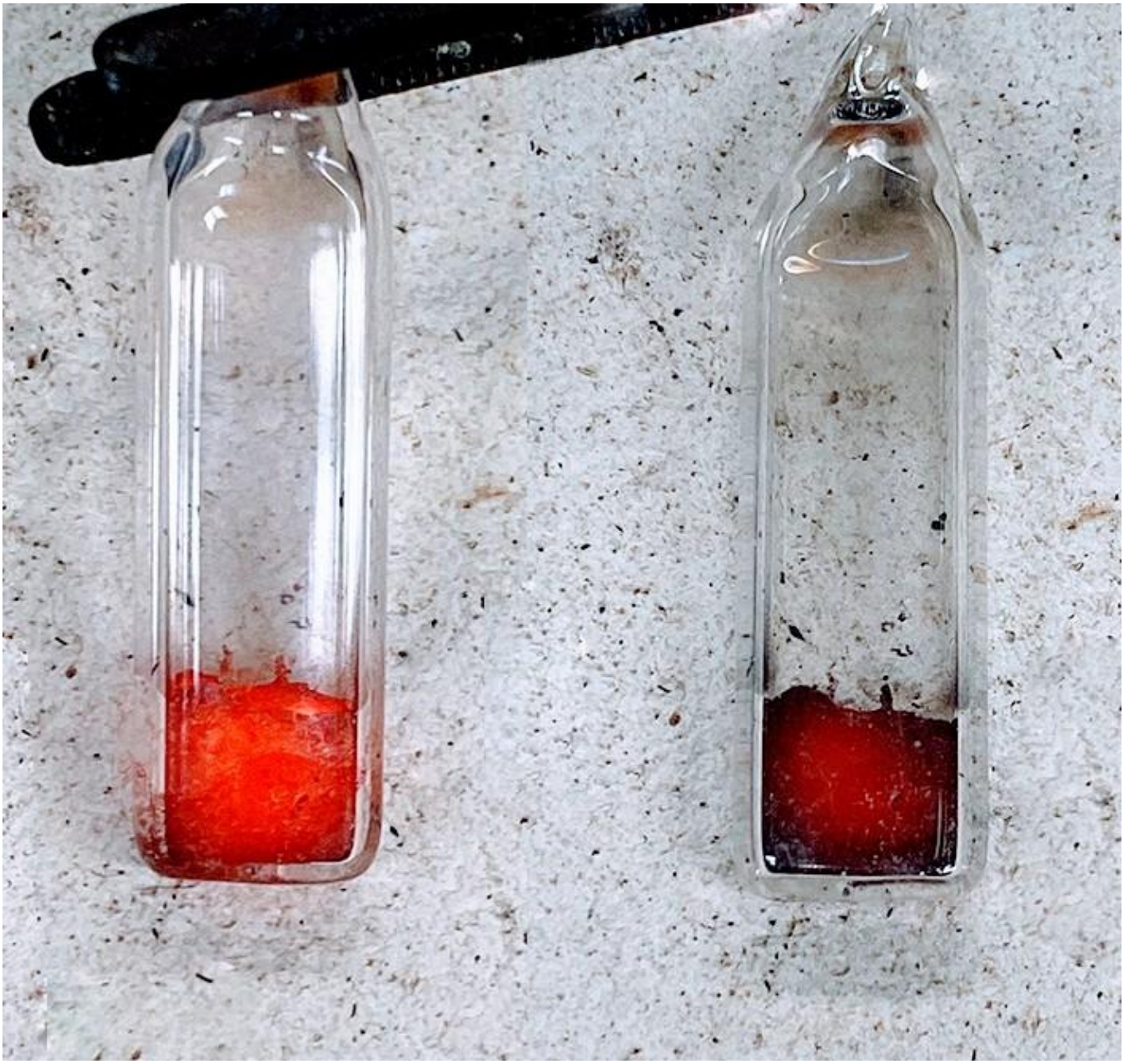
Understanding the coordination chemistry and bonding of actinides in molten salts is critical for predicting the behavior of nuclear fuel materials and developing next-generation reactor technologies. In this talk, I will discuss recent experimental and computational investigations into the structure and bonding of molten uranium(III) chloride under high-temperature conditions. Using neutron scattering measurements combined with ab initio molecular dynamics simulations, we examine how the local coordination environment around U(III) evolves upon melting. The results reveal a contraction of the average U–Cl bond distance in the molten phase, arising from a heterogeneous first coordination shell composed of short and long U–Cl interactions. Electronic structure analyses indicate that the shorter contacts exhibit enhanced participation of uranium 5f orbitals, leading to transient covalent character, while longer interactions remain largely ionic. Time-correlation analyses further suggest that these

short U–Cl bonds are highly dynamic, forming and breaking on sub-picosecond timescales. Simulated vibrational spectra indicate that these transient interactions may be spectroscopically observable. Together, these findings highlight how extreme temperatures can fundamentally alter actinide bonding in molten environments and provide new insight into the dynamic coordination chemistry of actinides in nuclear-relevant molten salts.



JOINT 4528303

Effects of redox conditions and temperature on diffusion of 99Tc and 237Np

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Understanding the transport of radionuclides through clay buffer materials is key to risk assessment for the burial of spent nuclear fuel in deep geologic repositories (DGRs). In such a scenario, tight packing of the clay buffer is expected to limit advective flow such that diffusion is the main mass transport mechanism. Transport behavior will also be affected by retardation mechanisms such as sorption and precipitation which are in turn influenced by the oxidation state of the radionuclide. For redox sensitive radionuclides such as Tc, Np, and Pu, redox states can have a profound impact on diffusion rates. For example, under oxidizing conditions 99Tc(VII) will exist as the aqueous pertechnetate oxyanion which is expected to diffuse quickly due to low affinity for mineral surfaces while under reducing conditions at environmentally relevant pH values, formation of sparsely soluble and strongly sorbing Tc(IV) can limit Tc mobility. However, the impacts of temperature on Tc(IV) sorption and solubility are unknown.
We have investigated the diffusion behavior of 99Tc and 237Np through Na-montmorillonite at 25, 50, and 75 C under both atmospheric and reducing (2% H2 / 98% N2 anaerobic chamber) conditions. Stainless steel diffusion cells were set up with dry clay packed between 10 µm pore size stainless steel filters and saturated from the bottom up with 0.01 M NaCl in ultrapure DI H2O. Temperatures were set using resistive heating coils fitted around the stainless steel clay housing cylinder. Diffusion experiments were performed by circulating a 10-7 M 99Tc/237Np solution through one of the porous filters while circulating a second, initially radionuclide-free solution through the opposite filter. Aliquots were periodically taken from the reservoirs to assess the extent of diffusion over time. At the end of the experiment, the clay was sliced and digested to determine the spatial distribution of the nuclides. The diffusion results show significant differences in the diffusion behavior for both 99Tc and 237Np between the benchtop and the anaerobic chamber, suggesting that Na-montmorillonite is facilitating reduction in the anaerobic chamber at elevated temperatures.

JOINT 4529651

Redox-non-innocent catecholate shifts the oxidation state break in the actinides

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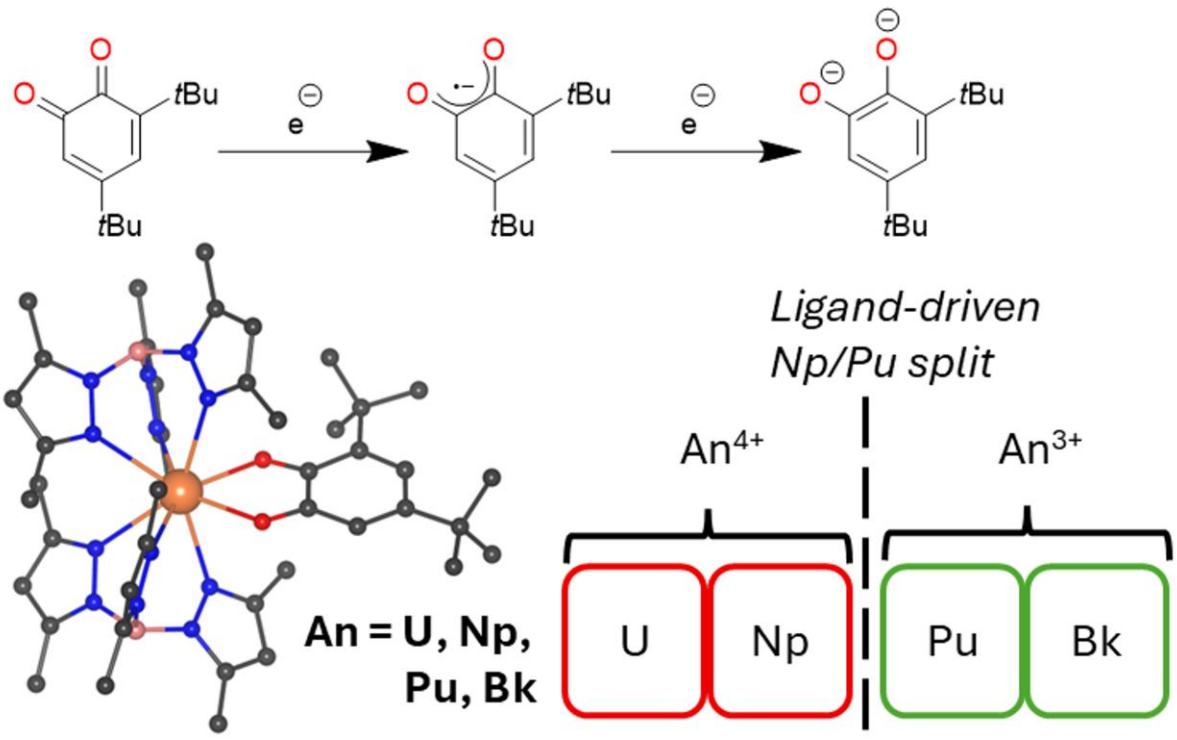
A further understanding of the fundamental electronic structure and bonding of the actinide (An) elements is critical for future nuclear stewardship and further development of applications of the electronically and magnetically unique 5*f* series. A theory-led study of $(Tp^*)_2An(dtbsq)$ complexes (An = U, Np, Pu, Bk; Tp* = tris(3,5-dimethyl-1-

pyrazolyl)borate [$HB(C_3N_2Me_2H)_3]^-$; dtbsq = 3,5-di-*tert*-butyl-*o*-semiquinone [$C_6O_2{}^tBu_2H_2]^-$) uncovers a change in oxidation-state preference along the series from 4+ to 3+ between the chemically similar Np and Pu, the first time found to be driven by differential oxidation state stabilization by an organic radical. Experimental structural and spectroscopic data are consistent with this trend, as exemplified by the experimentally isolated complexes **1-U^{exp}** ([(Tp*)(Bp*)U^{IV}_2(dtbc)$_3$], Bp* = dihydrobis(3,5-dimethylpyrazolyl)borate [$H_2B(C_3N_2Me_2H)_2]^-$; dtbc = 3,5-di-*tert*-butyl-catecholate) and **1-Pu^{exp}** [(Tp*)$_2Pu^{III}$(dtbsq)], where the radical ligand is consistently reduced to a catecholate only in the presence of U^{III} in contrast to Pu^{III}. Electronic-structure calculations for (Tp*)$_2$An(dtbsq) (An = U, Np, Pu, Bk) reveal tunable $An^{III/IV}$ oxidation states—supported by highly multiconfigurational ground states—and oxidation-state-dependent covalency. Comparison with analogous lanthanide (Ln) complexes (Tp*)$_2$Ln(dtbsq) (Ln = La-Gd except Pm) demonstrates the significant impact of redox-non-innocent organic ligands on the fundamental electronic structure and bonding of the *f* block, for which the subtle yet critical bonding differentiation through the 4*f* series is significantly increased upon translation into the 5*f*. These data highlight the current predictive power of theoretical electronic structure modeling methods as well as a potential direction for future refined An/An separations schemes, highlighting how redox-active ligands can be employed to differentiate neighboring actinides by oxidation state.



JOINT 4530176

Interfacial mechanisms in molten salt electrodeposition: From carbon formation to critical metal recovery

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Molten salt electrochemical systems offer a promising pathway for selective recovery and production of critical materials, yet significant gaps remain in understanding materials compatibility, interfacial reactivity, and governing mechanisms' influence on metal deposition. Here, we examined recycling of scrap metals/alloys and carbon deposition in molten Li–K salts at 715 °C on mild steel and graphite cathodes with an inert SnO_2 anode, with emphasis on how cathode chemistry governs interfacial growth and salt–solid interactions. Carbon deposition occurred on both cathode substrates under sufficiently cathodic conditions, but the growth behavior and resulting deposit architecture were strongly substrate dependent. Mild steel promoted faster initial deposition and more uniform electrolyte incorporation, whereas graphite supported slower early-stage growth and initially formed a salt-poor carbon layer adjacent to the cathode. In both cases, the deposit evolved into a conductive carbon framework that progressively displaced the original cathode/electrolyte interface during electrolysis, consistent with a transition from substrate-controlled nucleation to carbon-on-carbon growth.

These results show that electrode compatibility in molten salt electrolysis extends beyond corrosion resistance to direct control over interfacial growth, impurity incorporation, and recoverable carbon structure. Additionally, a framework is developed for recycling scrap alloys using molten salt electrochemical methods, spanning both single and multi-electron systems. This work seeks to resolve how electrolyte composition, electrode materials, and interfacial phenomena control selectivity and product stability, with relevance to critical materials processing in defense and other applications.

JOINT 4531115

Diamonds are an actinide's best friend: Electrochemical discrimination of U and Pu redox couples using boron-doped diamond

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The resurgence of molten salt technologies for advanced nuclear and energy systems has created a critical need for analytical tools capable of operating in high-temperature, corrosive environments. In particular, real-time monitoring of actinide redox chemistry is essential for reactor control, fuel cycle management, and safeguards for Molten Salt Reactors. Conventional electrode materials (metals, graphite) are limited by corrosion, narrow potential windows, and high background currents, restricting their effectiveness

for electrochemical analysis in molten salts.

Plutonium detection has traditionally focused on the Pu^{3+}/Pu^{0} couple; however, this reaction is poorly suited for analytical applications due to overlap with the U^{3+}/U^{0} couple and complications arising from coupled phase transitions. In contrast, the soluble Pu^{4+}/Pu^{3+} redox couple provides improved electrochemical distinction from uranium species and is a more promising target for selective detection, yet remains underexplored in molten salts due to insufficient electrode resolution. This work evaluates boron-doped diamond (BDD) as a designer electrode platform for high-resolution actinide electrochemistry. BDD exhibits wide potential windows, low background currents, rapid electron-transfer kinetics, and exceptional chemical inertness, enabling interrogation of soluble redox couples inaccessible with conventional electrodes.

A systematic investigation of uranium and plutonium redox chemistry across aqueous and molten salt environments is presented to benchmark performance and establish structure-property relationships governing electron transfer. Aqueous measurements of U and Pu provide diffusion, kinetic, and thermodynamic parameters to validate analytical methodologies. Molten chloride and fluoride studies of U^{4+}/U^{3+} demonstrate BDD stability and improved signal resolution under extreme conditions. Complementary aqueous Pu data establish proof-of-concept detection of the Pu^{4+}/Pu^{3+} couple, with ongoing work extending this approach to molten salts. These results demonstrate that BDD enables electrochemical discrimination of actinide species by shifting focus from metal deposition to soluble redox chemistry. This approach advances analytical capabilities for molten salt systems and supports improved monitoring and control of actinides in advanced energy technologies.

JOINT 4531230

Effects of ionizing radiation on actinides in caustic carbonate media

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Alkaline processing has been proposed as an alternative to traditional acidic solvent extraction methods for recovering uranium from used nuclear fuel. A particularly promising approach utilizes guanidinium carbonate for both the selective dissolution and subsequent precipitation of uranium. It is critical to understand the impacts of ionizing radiation on this caustic system relative to its yield and recyclability in order for its successful industrial-scale implementation, yet they are currently unknown. To address this knowledge gap, we conducted studies on the gamma irradiation of various carbonate-based systems (sodium and guanidinium carbonates) with actinides (uranium and neptunium) both in regard to their kinetics and thermodynamics. Kinetic studies were conducted using electron pulse radiolysis studies to explore transient species and

their lifetimes, giving reasoning to the mechanisms which dictate the long-term speciation of both the media and the actinide present for dose accumulation studies.

JOINT 4531884

Berkelium starting materials from aqueous solutions

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The actinide elements display an extensive range of redox chemistries, which allows for many accessible oxidation states. While early actinides can adopt a diverse range of oxidation states in aqueous solutions, elements heavier than plutonium predominantly exist in the +3 state, except for berkelium (Bk), which can readily oxidize from +3 to +4 in aqueous solutions. Although reports are relatively extensive for thorium (Th^{IV}), uranium (U^{IV}), neptunium (Np^{IV}), plutonium (Pu^{IV}), little is known about Bk^{IV} despite its relevance towards the element's generation and reprocessing. Even more, Bk is largely understudied due to its limited accessibility and high radioactivity compared to its actinide congeners. As a result, there is a lack of available starting materials for Bk, thereby limiting our capacity to predict and control its behavior in aqueous media. To fill this deficiency, our work seeks to develop complexes of berkelium from inorganic acids and bases to serve as easily accessible starting materials for Bk coordination compounds. Herein, the synthesis and characterization of Bk molecular compounds, along with a comparison to its lanthanide surrogate cerium, will be discussed in the context of future progress towards the fundamental understanding of this element in aqueous media. These complexes will be analyzed both in the solution and solid state to understand the coordination environment, oxidation state assignment, and stability of Bk^{IV}. Additionally, these compounds will be explored as starting materials for coordination complexes with several Lewis bases. Overall, Bk starting materials will be used to not only answer questions related to the element's electronic structure, but will also be used to generate a library of +3 and +4 Bk compounds to further reveal the role that *f*-electrons play in the heavy actinides.

JOINT 4532329

Atomistic simulations and experiments to complete the thermodynamic representation of NaCl – $MgCl_2$ intermediate compounds

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Our recent investigation of the NaCl – $MgCl_2$ phase diagram highlights the existence of multiple stable intermediate phases. These compounds are of immediate interest to the molten salt reactor community as the salt composition is seen as a coolant and/or fuel solvent. A full understanding of the thermodynamic properties of all phases in the system is important, yet, a complete experimental study of the properties is challenging due to the air-sensitivity of the intermediate compounds and the slow kinetics seen in their synthesis. The present study combines atomistic computational and experimental methods to gain a complete picture of these intermediate compounds so as to most efficiently gain the necessary understanding. Specifically, experimental results are utilized as reference points for selecting an appropriate density functional theory approach. That effort was followed by the development of a machine learning interatomic potential to fill information gaps that would be costly to do experimentally.

JOINT 4533439

Oxygen K-edge XAS and theoretical studies of $M_2AnO_2Cl_4$ (An = U, Np, Pu; M = Cs^+, Me_4N^+)

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The hexavalent actinyl ions AnO_2^{2+} (An = U, Np, Pu) form a unique series of linear dioxo cations that show a high degree of covalency and chemical inertness with respect to the axial An≡O bonds. We report O K-edge X-ray Absorption Spectroscopy (XAS) using a scanning transmission X-ray microscope (STXM) to study polarization dependence for the observed transitions from O 1s to An-O antibonding orbitals to evaluate axial An≡O covalent bonding interactions across the light actinide series of $M_2AnO_2Cl_4$crystals (An = U, Np, Pu; M = Cs^+, NMe_4^+). Relativistic DFT calculations performed for the ground- and excited-states of the molecules with and without spin-orbit coupling are used to validate and simulate results from the O K-edge XAS polarization data.
The experimental and computational results showed significant covalent mixing between O 2*p*- and An 5*f*- and 6*d*-orbitals ($5f_{\pi^*}$, $5f_{\sigma^*}$, and $6d_{\pi^*}$). Traversing the series from U, to Np, and Pu shows an increasing 5*f* and O 2*p* orbital mixing, while actinide 6*d* and O 2*p*-mixing decreases. We find no An-O bonding contribution from the $6d_{\sigma}$, and that inclusion of $7p_{\sigma/\pi}$ orbitals are essential in TDDFT and experimental data analysis. Spin-orbit coupling redistributes O 2*p* character from the $5f_{\pi^*}$ orbital into nonbonding $5f_{\delta}$ and $5f_{\varphi}$ orbitals. The O 2*p* mixing into the $5f_{\delta}$ and $5f_{\varphi}$ orbitals is both observed and calculated to be small for U and Np but increases significantly for Pu. This ‘intensity stealing’ mechanism was noted by Denning and coworkers but not observable in their U data. In our high-resolution STXM data, these pre-edge features are clearly observable for U, Np and Pu, and considerations of spin-orbit coupling are essential for correct

interpretation of spectra. The implications of these observations on advancing understanding of actinide covalency will be presented.

JOINT 4533448

Synthesis and qualification of high-concentration molten chloride fuel salts

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Synthesis and qualification of molten salt reactor (MSR) fuel salts will require robust and accurate monitoring tools that can operate in a broad range of salt compositions. To support the deployment of MSR concepts that may require salts with greater than 70 wt % uranium, we have developed coupled salt synthesis and monitoring approaches capable of being scaled to large scales. The synthesis methods make use of $ZnCl_2$ as a chlorinating agent, which results in a liquid metal Zn byproduct that can be distilled from the reaction vessel. This process has been demonstrated in molten LiCl-KCl-UCl_3 containing between 55 and 72.3 wt % UCl_3, followed by extension to the synthesis of NaCl-KCl-UCl_3 with UCl_3 concentrations between 15 and 75 wt % UCl_3. Inline electroanalytical approaches have been developed to enable accurate in-situ measurements of zinc chloride and uranium chloride concentrations in these highly loaded fuel salts in support of understanding reaction kinetics. Digital simulations are used in the measurements to overcome previous challenges in accounting for non-idealities, such as uncompensated resistance effects. The efficacy of the production of UCl_3 from uranium metal utilizing $ZnCl_2$ as a chlorinating agent is demonstrated using online voltammetry and offline inductively coupled plasma optical emission spectroscopy (ICP-OES) and differential scanning calorimetry (DSC). Ultimately, the accurate, near-real-time voltammetric monitoring of uranium concentrations will be a key technology for fuel salt qualification in the MSR fuel cycle.

JOINT 4533502

Molten salt thermophysical property developments at ORNL

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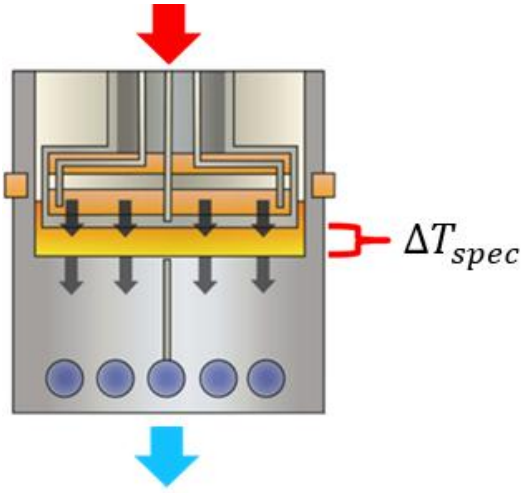
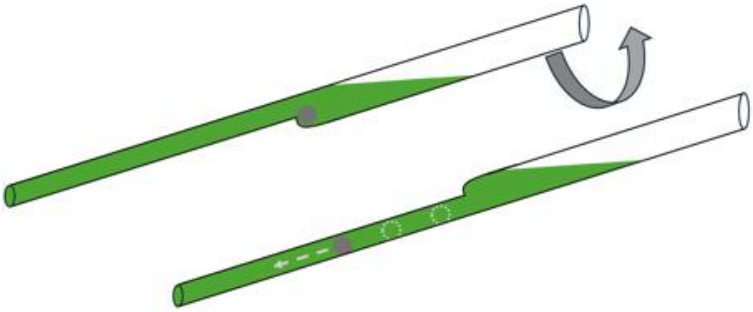
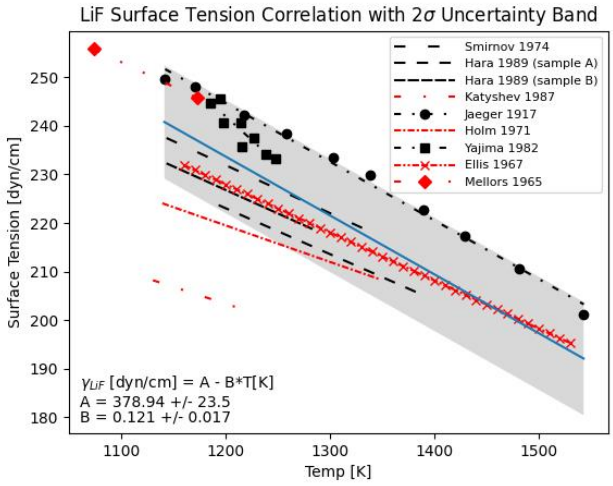
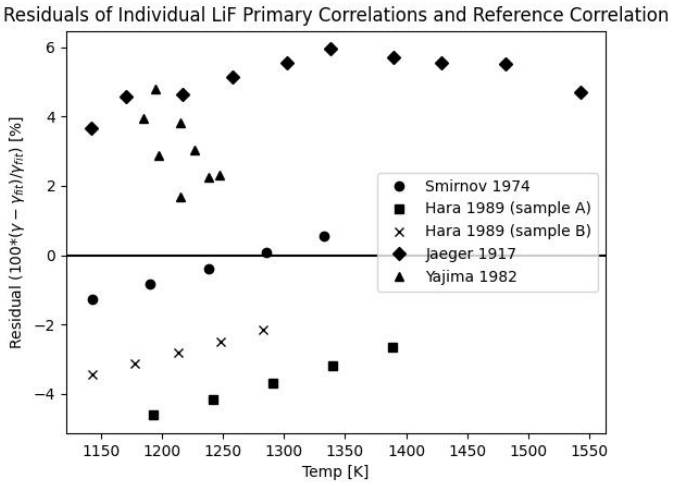
Well-characterized thermophysical properties (density, viscosity, thermal conductivity, surface tension) of molten halide salts are vital information for safely designing and operating molten salt-cooled and salt-fueled energy systems. Researchers at Oak Ridge National Laboratory (ORNL) continue to evolve these efforts to include both chloride and fluoride species and actinide-bearing systems as well as to reduce experimental uncertainty. Recently, viscosity and thermal conductivity experiments have concluded studying the effect of surrogate fission products on the beginning and end-of-life behavior of an operating molten chloride salt reactor. These results indicate a small

but statistically significant increase in viscosity while no statistically significant difference was observed in thermal conductivity. Additionally, multiple beginning-of-life actinide fluoride mixtures underwent similar testing. These results, along with similar studies published around the world, are available through the thermophysical arm of the molten salt database (MSD-TP) managed by ORNL. This database includes several storage format options to facilitate code integrations. Recently, MSD-TP was used to develop surface tension reference correlations for several pure component halide salts.









JOINT 4533540

Evaluation of modified amidophenolate ligands for redox reactivity at thorium centers

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The redox restriction of thorium greatly limits its reactivity particularly when compared to uranium. In order for thorium to access the rich redox chemistry seen in other actinides, electrons must be provided from sources other than the metal center. One way this can be achieved is by storing electrons in redox active ligands around the metal. Electrons can then be accessed from the ligands to achieve redox reactivity at the metal. The 4,6-di-tert-butyl-N-(2,6-di-isopropylphenyl)-o-iminobenzoquinone (^{dipp}iq) ligand and particularly its doubly reduced amidophenolate form (^{dipp}ap^{2-}) have previously been used to provide the necessary electrons for the activation of dioxygen in dry air by thorium, forming a rare terminal thorium oxo species. Through this work and characterization of the thorium oxo complex, two challenges have become clear. First, the bulky di-isopropyl moieties provide steric protection to the oxo ligand, stabilizing it, but also inhibiting further functionalization. Second, the oxidation of the ligands reduces the ligand charge which in turn leads to weaker binding following the activation of dioxygen. In particular, full oxidation to the neutral iminoquinone ligands is accompanied by ligand dissociation in many cases. This presentation will discuss a ligand modification approach to addressing these steric issues including the impacts on structure, electronic properties, and reactivity that result from modifications to the ligand system.

JOINT 4533869

Exploring the redox behavior of U, Np, and Pu with a Tetrapicolinic acid chelate

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The minor actinides (Np, Am, Cm) are major contributors to the long term radiotoxicity of High Level Liquid Waste (HLLW). Isolating and transmuting these isotopes into short lived radionuclides offers a viable strategy to help close the nuclear fuel cycle. Among the minor actinides, Np poses a particular challenge as it has the potential to access a wide range of oxidation states (III - VII) with varying chemical and physical properties. Consequently, it remains challenging to partition and often tracks with other actinide (U, Pu, Am, Cm) elements throughout the nuclear fuel cycle. Picolinic acids have been established as effective holdback agents that synergize with select extractants to enhance the selective separation of Am or Cm from lanthanide elements. Critically, the impact of ligand coordination on the redox behavior of Np remains poorly understood, limiting the design of the next generation nuclear waste remediation workflows that couple speciation control with redox tuning. Here, a combined electrochemical, and computational investigation is reported where key electron transfer parameters ($E_{1/2}$, k_{et})

are quantified for the $An^{4+/3+}$ redox couple of U, Np, and Pu coordination complexes derived from a high-denticity tetrapicolinic acid ligand. These results are then discussed in the context of solid-state and solution spectroscopic measurements to gain insight into the impact of the actinide contraction and electronic structure on the electron transfer reactivity of these complexes. By uncovering the fundamental electrochemical properties of the early actinides, these findings offer insight into the design principles for ligand frameworks that advance minor actinide separation technologies

JOINT 4534353

Processing of heavy actinides at Oak Ridge National Laboratory

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As the primary producer of transplutonium isotopes for the Western world, Oak Ridge National Laboratory (ORNL) plays a critical role in industrial applications and fundamental research. The lab's main transplutonium product, ^{252}Cf, is used as a neutron source in oil exploration, in initiation of nuclear reactors, in power generation, for detection devices, and in medical research. Historically, ORNL has been the sole source of ^{249}Bk, ^{254}Es, and ^{257}Fm which are in high demand for performing fundamental studies and discovering superheavy elements. Current purification methods rely heavily on established knowledge of these elements, whose chemistry—unlike that of earlier-series members—is predominantly governed by the trivalent oxidation state. This work highlights the importance of developing fundamental work on these elements for applied chemistry.

JOINT 4534402

Oxidation of f-block metals using gallium(III) chloride

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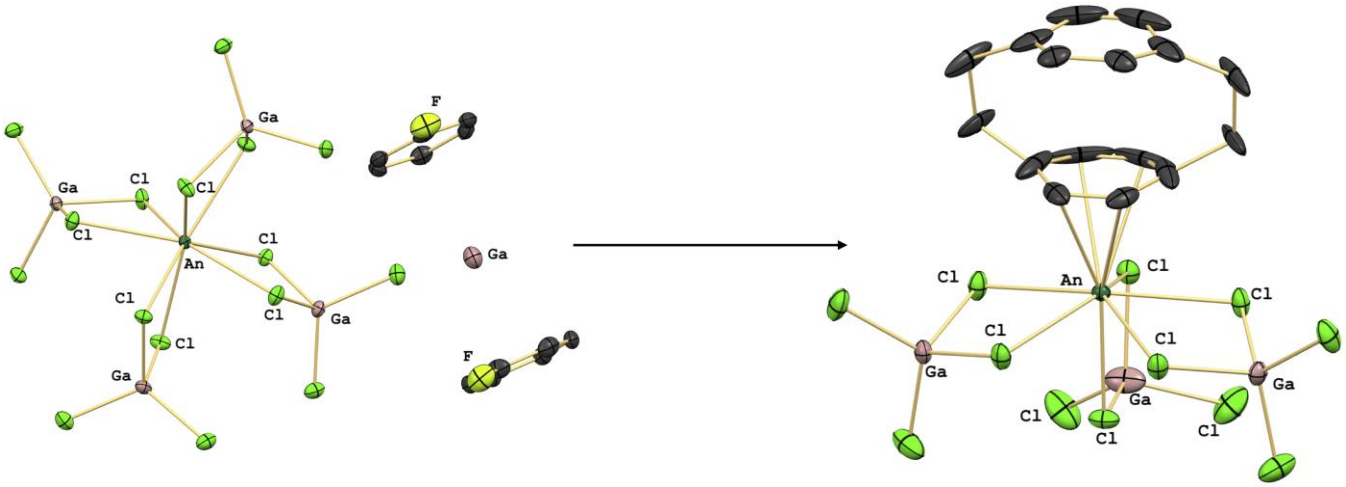
Gallium(III) chloride ($GaCl_3$) has proven effective for the oxidation of lanthanide (Ln) and actinide (An) metals, offering a mild, anhydrous metallurgical processing method. We have explored the reactivity between $GaCl_3$ and a range of *f*-block elements to explore applications such as element separations and generation of Ln(II/III) and An(III) chloride starting materials. Synthetic results arising from reactions in various carrier matrices, as well as comparisons between products from lanthanide and actinide reactivity, will be presented. Additional reactivity and derivatization—extending to organometallic complexes and multinuclear synthesis—of (Ln/An)-gallate products has been accomplished, and characterization of the products has been achieved. Observed differences in reactivity and product outcomes is ascribed to differences in physical

properties across the f-block series. These observations, along with characterization and prospective directions for this chemistry, will be discussed.



Inorganic species that arise from the dissolution of lanthanide and actinide metals using $GaCl_3$ generally adopt the rare coordination motif $[Ga][M(GaCl_4)_4]$. We have synthesized such species from an array of f-elements. Investigations into employing these species as starting points for additional synthetic transformations has been fruitful, and here the transformation arising from the addition of *para*-cyclophane to the uranium derivative $[Ga][U(GaCl_4)_4]$ is shown; loss of Ga_2Cl_4 has been confirmed.

JOINT 4534494

Spacer-salt effects on lanthanum networks and speciation in molten salts: Beyond intuition

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In recent years, there has been significant advancement in understanding the structure of molten salts involving multivalent cations. Among these salts, those containing lanthanum ions are particularly critical due to their implications as fission products in nuclear reactor applications. Extensive computational and high-resolution X-ray scattering studies have revealed that these ions exhibit a broad range of structural features, ranging from nearest-neighbor correlation and charge alternation to network formations. When molten lanthanum chloride is mixed with molten monovalent salts such as NaCl or KCl, the latter serves as a ‘spacer’ salt between the lanthanum networks. Temperature and the mol fractions of NaCl or KCl directly control the spacing

between these networks. In this presentation, we will discuss our recent efforts to elucidate these ‘spacer’ salt effects using MD simulations, X-ray scattering measurements and modeling, and free energy landscape analysis. We will show that, depending on the selection of spacer salt, in-network and cross-network structural correlations can be quite different and are non-intuitive. However, by analyzing the free energy landscapes of local coordination environments and aggregate distributions at different lanthanum concentrations, we can shed light on these effects.

JOINT 4534798

Aging gracefully, even when impure: Determining production ages of impure uranium materials

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Radiochronometry is a predictive tool used to estimate the “production age” of nuclear materials, specifically the time since the last chemical purification. Conventional model-age calculations assume (1) no progeny isotopes were present at the time of production and (2) the parent-progeny system has remained closed since that time. Many real-world uranium materials, however, retain impurities after purification, including measurable progeny present at production. This initial progeny, combined with spatially heterogeneous distributions of parent-to-daughter nuclides, can yield discordant ages among aliquots from the same bulk material, even for a single chronometer (e.g., $^{230}Th/^{234}U$).

To address this challenge, we apply an isochron-based model-age calculation to determine the production age of impure materials. This isochron approach addresses nonzero initial progeny by estimating its contribution and simultaneously yielding a corrected production age. Implementing this method requires: (1) quantifying magnitude and spatial scale of parent/daughter isotope ratio heterogeneity, (2) developing FIB-SEM subsampling strategies tailored to the observed heterogeneity, and (3) optimizing ion-exchange separations to enable high-precision MC-ICP-MS isotopic measurements of small sample sizes (e.g., individual particles to micrometer-to-millimeter scale fragments). In this talk, we summarize our workflow and key practical considerations for dating impure uranium materials using small-aliquot isochron methods.

JOINT 4534829

Towards the discovery of new elements

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Since the first artifical element was created at Berkeley Lab in 1937, 30 elements have been added to the periodic table - nearly one new element every three years! In the

early 2000s, significant progress was made with the discovery of elements Z=114-118 through reactions between ^{48}Ca beams and actinide targets, achieving production rates of atoms-per-day or more. Unfortunately, new element production has stalled and no new elements have been discovered since 2010. The pursuit of elements beyond Oganesson (Z=118) faces substantial challenges. The synthesis of elements with Z=119 or 120 using ^{48}Ca would necessitate targets of Es (Z=99) or Fm (Z=100), but these elements cannot be produced in sufficient quantities. This limitation necessitates exploring new reaction pathways.

Numerous theoretical studies have aimed at predicting production rates for new elements using actinide targets and heavier ion beams. While these models reliably reproduce excitation functions for SHE production with ^{48}Ca beams, predictions diverge significantly for reactions involving heavier beams. For instance, the predicted cross sections for reactions to produce Z=120 vary by more than three orders of magnitude and tens of MeV. These discrepancies hinder experimental efforts, as the low expected cross sections suggest the detection of only one event every few weeks or months under ideal conditions.

Berkeley Lab has been proactively addressing these challenges to push beyond E118. By testing theoretical predictions, we have begun the ^{50}Ti+^{244}Pu experiment to understand the impact of using ^{50}Ti instead of ^{48}Ca beams on cross sections. This presentation will highlight significant upgrades to our experimental facilities, including ion sources, target setups, detectors, and electronics, aimed at enhancing our capability to produce and detect elements beyond E118. We will also present the initial results from the ^{50}Ti+^{244}Pu experiment, showcasing our progress in this ambitious endeavor.

JOINT 4534886

Advancing solid-state actinide chemistry and physics at INL's Glenn T. Seaborg Institute: From chemical bonding to electronic correlations

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Actinide materials occupy a unique position at the intersection of condensed matter physics and solid-state chemistry due to the dual localized–itinerant nature of their 5*f* electrons. Among them, plutonium remains one of the most complex and fascinating elements in the periodic table. Its rich phase diagram, multiple allotropic forms, strong electronic correlations, and delicate balance between competing ground states make it an exceptional platform for exploring emergent quantum phenomena. From a chemical perspective, the spatially extended yet strongly interacting 5*f* orbitals give rise to unusual bonding characteristics, enhanced covalency, and strong spin–orbit coupling, placing actinides between localized 4*f* lanthanides and more itinerant *d*-electron systems. Recognizing the strategic importance of advancing actinide science, Idaho National Laboratory established the Glenn T. Seaborg Institute to integrate expertise in synthesis, advanced characterization, theory, and modeling. Within this framework, the

Solid-State Actinide Chemistry and Physics focus area seeks to understand how electronic correlations, spin–orbit coupling, and chemical bonding cooperate to generate novel electronic and magnetic states.
In this talk, I will provide an overview of this focus area and highlight recent advances in selected *f*-electron systems, including (i) investigations of the electronic structure and correlation effects in UO_2, a prototypical Mott insulator with strong 5*f*–ligand hybridization, and (ii) studies of magnetoelastic coupling in uranium single crystals, where the interplay among lattice, magnetic, and electronic degrees of freedom reveals the chemical sensitivity of 5*f* states to their local environment. These examples illustrate how integrating solid-state chemistry with modern experimental and theoretical approaches enables new insights into the fundamental behavior of actinide materials.

JOINT 4535568

Low-temperature conversion of actinide oxides to chlorides

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Actinide chlorides are useful for the fabrication of many materials in the nuclear industry including fuels and waste. Despite this prevalence, literature shows that their syntheses are reliable with several starting materials by refluxing in liquid organics like hexachloropropene with the exception of the dioxide, a commonly utilized oxide. While there are reported attempts of its chlorination, they claim unfavorable yields or the absence of a reaction. This work showcases results that are contrary to these claims under conditions both unalike and similar to what has been tried in the past. The synthetic atmosphere has been altered in several ways to investigate the limits of this reaction and under what seemingly unfavorable conditions it can proceed. Experimental influences of the oxide reagent, dryness of liquid reagents, atmosphere, and the temperature and duration of time in which the reaction took place will be discussed. Actinide chlorides and side products of these reactions have been identified or suggested by means of powder x-ray diffraction, UV-Visible light spectroscopy, nuclear magnetic resonance, and energy-dispersive x-ray spectroscopy.

JOINT 4535606

Accessing f-element multimeric complexes to explore metal-metal interactions

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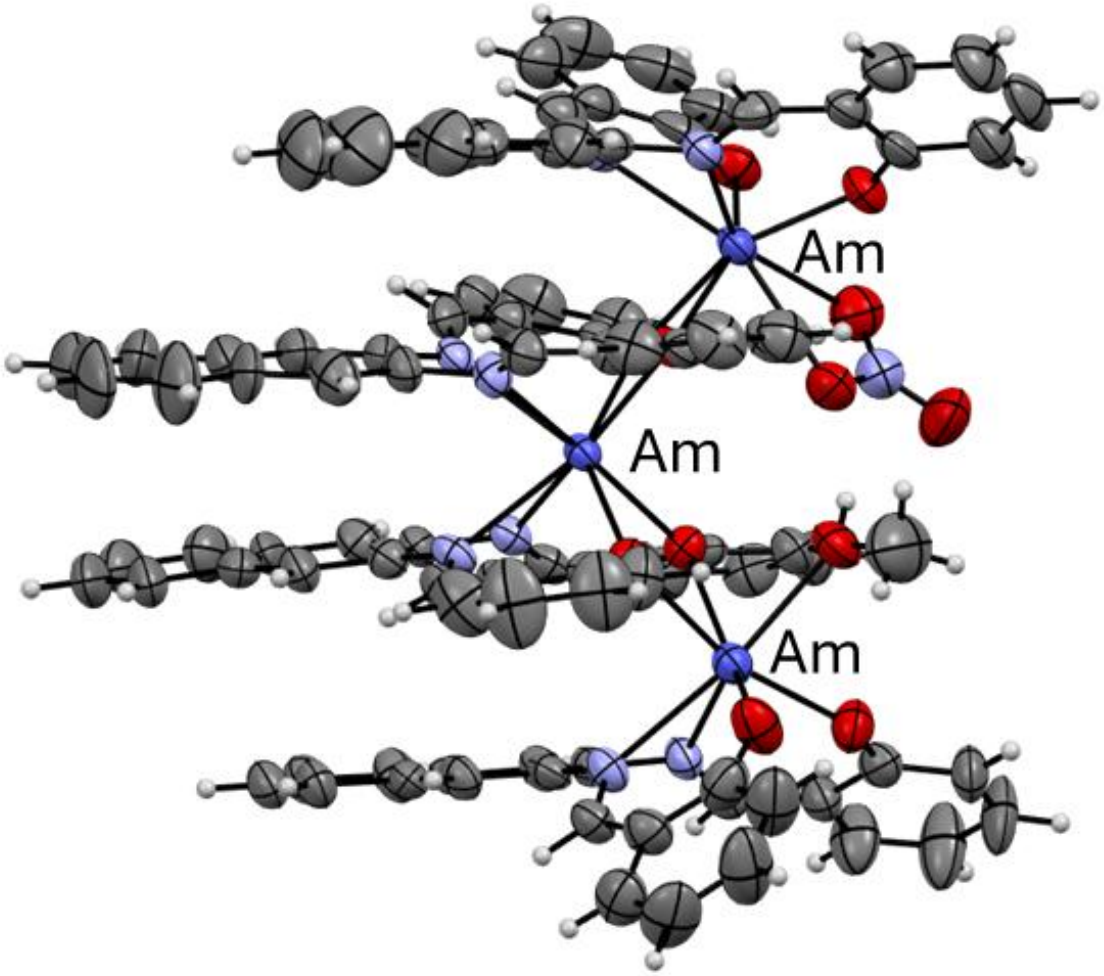
Lanthanide-lanthanide interactions are limited by the short radial extent of the 4f orbitals. These interactions are predicted to be greater for actinides which have more extended 5f orbitals. Thus, experimental efforts are needed to investigate the degree of interaction that can be achieved.

Due to the high radioactivity associated with actinides and more particularly trans-uranic ions, their coordination behavior is still being assessed. As such we propose a simple salen-derived ligand to be used as a platform for structural and magnetic studies to investigate speciation and metal-metal interactions.

The dimeric lanthanide systems were characterized through single-crystal X-ray diffraction and magnetic investigations. The synthetic pathway was then adapted to the requirements of working with radioactive materials. The first transuranic system was obtained with americium-243 and the extension to other trivalent actinides will yield critical information regarding the interactions between the metallic ions.



JOINT 4536790

Characterizing Pu(IV) uptake on LN series resins in chloride media

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Plutonium (Pu) separations support a broad range of scientific applications but are often complicated by Pu's variable aqueous speciation and propensity for hydrolysis. Extraction chromatography is widely used in modern radiochemical separations to achieve diverse separation outcomes. Among the most commonly used materials are Eichrom's LN and LN2 extraction chromatographic resins, which contain organophosphorus-derived extractants. Although these resins are typically applied to adjacent lanthanide separations, they also exhibit strong uptake of tetravalent (Pu, Th) and hexavalent (U) actinides. While LN-series resins are well characterized in nitric acid matrices, Pu uptake from hydrochloric acid (HCl) matrices has not been systematically investigated. Here, we evaluate Pu(IV) extraction on LN and LN2 resins from HCl using batch uptake measurements and column chromatography. Plutonium recovery via reduction of Pu(IV) to Pu(III) is examined using metal-free reductants, including hydroiodic acid, hydroxylamine hydrochloride, hydrazine, and acetaldoxime, to identify conditions that enable efficient elution and support method development across varied radiochemical workflows.

JOINT 4536823

Modelling the direct disposal of spent TRISO fuels: Methods to prepare SiC powders from bulk materials for accelerated corrosion testing

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The inherent stability of tristructural isotropic (TRISO) particles within the extreme conditions observed in the core of a nuclear reactor make them not only an ideal fuel form but a potential waste form as well. To assess the viability of the direct disposal of spent TRISO fuels into deep geological repositories (DGR), their corrosion mechanisms and rates in the ever-evolving conditions of a DGR (i.e., pore-fluid composition, temperature, radiation field, etc.) must be well understood; these data can then be used to model the release of radionuclides from the waste form as a function of the varying parameters of the system over periods of tens to hundreds of thousands of years. Much of the data reported to date regarding the corrosion of silicon carbide (SiC) (the primary

impermeable layer of a TRISO particle) were collected in extreme conditions (i.e., high temperature) relevant to the core of a nuclear reactor rather than that of a DGR. At these extreme conditions, several corrosion mechanisms that are not thermodynamically possible in DGR conditions are observed, making the extrapolation of data to lower temperature environments a questionable practice. The few accelerated corrosion studies that were conducted in conditions related to DGR used differing SiC types, sample preparation techniques, and experimental designs, such that the direct comparison of these data requires significant assumptions that may be ill-advised. It is imperative that the accelerated corrosion testing of SiC subject to conditions related to a DGR be conducted in a standardized and systematic manner. In this work, we increase the communities' access to clean high-purity SiC powder starting materials, necessary for the standardization of accelerated corrosion measurements, by developing a simple and robust method to crush and purify readily available high-purity SiC substrates. The resulting starting material is then used to assess how SiC purity, temperature, and leachate pH affect measured corrosion rates. This foundational work facilitates the consistent and standardized measurement of SiC corrosion rates in conditions related to a DGR.

JOINT 4537110

Obviating hydrofluoric acid in the synthesis of actinide fluorides

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The need for high-purity, anhydrous actinide fluoride materials is driven by increasing ramp-up of advanced nuclear reactor systems including Molten Salt Reactors (MSRs), which in parallel require the development of safeguards and nonproliferation strategies. Furthermore, these compounds are essential building blocks in fundamental chemistry. Synthetic routes towards isolated actinide fluorides are dominated by the use of hydrofluoric acid (HF) using pressure or flow reactors at high temperatures, with significant infrastructure investments required to mitigate hazards these conditions pose to workers and the environment. We demonstrate the capability to generate anhydrous actinide fluorides at low temperatures, with minimal investment, using easy-to-handle main group fluoride reagents in reaction with actinide chloride coordination compounds. New synthetic routes to ThF4, UF4, and UF3 materials bypassing the use of HF, with progress towards the synthesis of analogous Pu materials will be discussed.

JOINT 4537147

Calorimetric measurements of actinide-bearing molten salt systems

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The deployment of molten salt reactors (MSRs) is on the near horizon, but the complexity and diversity of fuel salts mean there is still many fundamental properties that are not well defined. Additionally, the challenges of studying high-temperature, corrosive, radioactive liquid salts make experimental methods especially challenging, particularly for sensitive measurements like what is performed using differential scanning calorimetry (DSC). DSC is a powerful technique that can provide valuable information about the stability and transitions (e.g., melt point) of different phases in addition to the enthalpy of such transitions (ΔH_{fus}) and liquid heat capacity (C_p) of each phase. However, the influence of instrument maintenance, calibrations, sample preparation, and analysis of both the data and corresponding error are not often well described in the literature, yet each have significant, far-reaching implications that may explain important discrepancies. This work presents recent measurements of uranium-containing chloride (e.g., UCl_3-NaCl-$MgCl_2$) and fluoride (e.g., UF_4-LiF-NaF-KF) salts at varying compositions with an emphasis on the many ways in which disagreements may arise in reported data. The results described will confirm some studies reported in the literature while disagreeing with others but explore the possible explanations for why such differences exist. Additionally, novel experimental data that has otherwise only been computationally determined will be shared and discussed in the context of the broader needs of the MSR community. These results can be used to inform the modeling and simulation capabilities needed for the safe, secure deployment of MSRs.

JOINT 4537237

First results on small-scale column data collection for model development

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Lawrence Livermore National Laboratory (LLNL)’s plutonium (Pu) facility has successfully produced the overall lifecycle of Pu processing. Due to its frequent use in production, the Nonproliferation Stewardship Program (NSP) has requested LLNL’s computer scientists and nuclear processing handlers to create and build a chemical process model. The Simulating Processing of Actinides and Developing Expertise (SPADE) project aims to leverage DOE Defense Program’s Pu recovery operation by analyzing the anion exchange process. In this initial step of the aqueous purification, Pu is separated from impurities. To study overall recovery efficiency, there is a need to understand how Pu behaves on the anion exchange resin at each step of column process. Small-scale column studies were performed by changing nitric acid volume, pump flow, and Pu concentration to generate column effluent concentration profiles during the loading, wash, push, and elution steps. Effluent concentration data were collected and measured using Ultraviolet-visible (UV-vis) spectroscopy. Preliminary results indicate a higher peak intensity for push and elution steps as opposed to the loading and wash steps. This presentation will provide an overview on how each step of the column process affects the Pu absorption spectrum as a function of nitric acid

concentration while achieving model development of LLNL's overall Pu processing recovery.

JOINT 4537365

Effects of rhenium ions on radiolysis reactions in molten salt matrices

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The molten salt reactor (MSR) is a strong candidate for Gen IV nuclear reactors. In an MSR, the nuclear fuel is dissolved in molten salt, which is also used as the coolant and heat transfer medium. Fission products can alter reactor performance and chemical reaction kinetics in the molten salt. Therefore, understanding their effects on reactions on high radiation environments is necessary for reliable reactor operation, and fission product separation is a challenge for successful MSR deployment. Technetium-99 (Tc) is a high-yield problematic fission product that has a 210,000-year half-life. Understanding Tc behavior in molten salts under conditions approaching MSR operations, such high temperatures and including radiation fields, is essential for sustainable nuclear fuel cycles, especially for advanced reactor technology. Radiation induces two primary molten salt radiolysis species, the solvated electron (e^-_s) and dichloride radical anion (Cl_2^-). Different salt matrices change the speciation of radiation-induced species, which influences their reaction kinetics. Here we report on the reaction kinetics for e^-_s and Cl_2^- in molten salts doped with rhenium ions. Rhenium (Re) is used as the third-row congener of Tc and is often considered a non-radioactive surrogate. K_2ReCl_4 and $ReCl_3$ were dissolved in different molten salts such as LiCl-KCl and $MgCl_2$-KCl for pulse radiolysis measurements. The reaction kinetics of e^-_s and Cl_2^- was observed with and without rhenium ion additives in molten salts together with their speciation. The pulse radiolysis experiments were performed at the Brookhaven National Laboratory Laser-Electron Accelerator Facility using a custom-designed high temperature sample holder.

JOINT 4537747

Foundations for technetium-99 reactive gas studies

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Management of fission products, particularly those with half-lives longer than 30 years, is vital to the safe disposal of used nuclear fuel. The fluoride volatility process to recover desirable isotopes from used nuclear fuel employs elevated temperatures that increase

the volume and therefore activity of off-gas streams due to (semi-)volatile fission products. Technetium-99 (^{99}Tc) is a relatively high-yield (~6%) fission product that is of particular concern due to its long (~2.13×10^5 y) half-life, specific activity on par with plutonium-239, and geochemically unmitigated environmental mobility. In this work, the traditional and non-traditional syntheses of TcF_6 are explored to compare the reactivity of metallic Tc and its lower fluoride compounds towards F_2 and UF_6. The reactivity of TcF_6 towards stainless steel and various trapping mediums is explored in the presence and absence of UF_6. Current work uses rhenium (Re) as a non-radioactive surrogate for ^{99}Tc to develop and optimize methods. The results of this work lay the foundation for comparative ^{99}Tc studies that are planned for the coming fiscal year. Ultimately this work will provide direct evidence for whether ReF_6 behaves in the same way as TcF_6 while filling knowledge gaps to improve the capture of ^{99}Tc in off-gas treatment systems for nuclear waste processing.

JOINT 4537915 - Withdrawn

JOINT 4538044

Next generation of transactinide chemistry at Berkeley Lab

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The Periodic Table is a cornerstone of chemistry, but its validity is challenged by the extreme properties of superheavy elements (SHEs, Z ≥ 104) and actinides (Z > 88). Relativistic effects, stemming from their large nuclear masses, significantly alter their chemical behaviors, potentially limiting the predictive power of the Periodic Table. Recent breakthroughs have provided insights into the chemistry of these elements, including the direct identification of molecular species formed by actinium (Ac, Z = 89) and nobelium (No, Z = 102) ions. Using a cutting-edge, atom-at-a-time technique at the 88-Inch Cyclotron Facility at Lawrence Berkeley National Laboratory, we have synthesized and characterized molecular species produced by these ions in reactions with H2O and N2. Our findings underscore the importance of direct identification in SHE chemistry experiments and offer new perspectives on the chemical properties of these enigmatic elements. This presentation will explore the current state of superheavy element chemistry research, highlighting recent advances and future directions for unraveling the mysteries of SHE chemistry. By pushing the boundaries of our understanding, we aim to shed light on the chemical behaviors of these extraordinary elements and challenge our current understanding of the Periodic Table.

JOINT 4538426

Thermodynamic modeling of the LiF-NaF-PuF_3 system for molten salt reactor applications

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Understanding the thermodynamic properties of molten salt systems as a function of temperature and composition is key to developing molten salt reactors (MSRs). The CALculation of PHAse Diagrams (CALPHAD) method is a viable tool for making reasonable predictions of thermodynamic properties in multicomponent systems when sufficient foundational representations for the constituent unary, binary, and ternary systems are provided. However, experimental data are often limited, and thus correlational methodologies and first-principles calculations based on density functional theory (DFT) are necessary to properly describe the thermodynamics of a system of interest. The present work will discuss the use of such an approach, with DFT calculations and CALPHAD modeling utilized in developing a thermochemical understanding of the highly relevant LiF-NaF-PuF_3 pseudo-ternary system.

JOINT 4538449

High energy resolution X-ray fluorescence detection and prediction of uranium M-Absorption edges

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Multivalent metal ions in molten salt reactor fuels can exhibit varied coordination states that distort EXAFS spectroscopy, especially in uranium complexes due to their varied valence states and complex halide phase equilibria. However, high-energy resolution fluorescence detection (HERFD) X-ray absorption near edge structure (XANES) spectroscopy may overcome these challenges. By probing uranium properties at the atomic level at reduced experimental spectral width below the natural core-hole lifetime broadening in the XANES region, HERFD can sharpen spectroscopic features almost an order of magnitude when compared to conventional XAS.
Initial measurements of HERFD-XANES spectra of the uranium M_4 edge of pure UCl_4 were taken at Stanford Synchrotron Radiation Lightsource (SSRL) Beam Line BL6-2b. Spectra were compared to U M_4 edges simulated with FDMNES (Finite Difference Method Near Edge Structure), a computational code used for ab initio simulations of X-ray absorption spectra. The simulations include broadening effects, which replicates the experiment, and examined the removal of broadening effects by the HERFD crystal

analyzer. When the experimental emission spectrum was measured in regular fluorescence mode, the measurement matches FDMNES prediction with broadening effects. Results qualitatively corroborated the modeling accuracy of our FDMNES predictions and suggested that the uranium M_4 edge can be detected by this instrument. FDMNES provides two approaches for calculating X-ray spectra: (1) A finite difference method using the full potential of a cluster built around the absorbing atom, and (2) Multiple scattering theory (Green's Function approach) by assuming a crystal potential that has spherical symmetry around the atoms and is constant in the remaining space (muffin-tin approximation). FDMNES calculations performed using a finite difference method produced good agreement with experimental data at the cost of high computational time. The Green's Function approach was able to recreate the double peak structure of the UCl_3 M_4 edge at a significantly reduced computational load, though it was unable to replicate the correct peak positions.

JOINT 4538465

Structure and thermal stability of Cs_3UCl_6(s) in the CsCl-UCl_3 system

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The CsCl–UCl_3 system is of considerable importance in thermochemical modeling of actinide-containing molten salt systems. Despite its importance, this system remains incompletely understood due to unresolved phase stability and the absence of crystallographic data for critical intermediate compounds. The Cs_3UCl_6(s) phase, in particular, is not well characterized with conflicting reports regarding its stability and no experimentally determined structure. In this work, we address this critical gap through the first synthesis and structural characterization of Cs_3UCl_6(s). The compound was prepared via solid-state reaction and analyzed by powder X-ray diffraction with Rietveld refinement, with phase purity confirmed by ICP-MS and oxygen analysis. High-temperature X-ray diffraction revealed evidence of a polymorphic transformation, providing new insights into its thermal stability. These results resolve a long-standing deficiency in the CsCl–UCl_3 system and establish a critical foundation for thermodynamic modeling and integration into the publicly available Molten Salt Database Thermochemical (MSD-TC).

JOINT 4538679

Development and use of the molten salt database – thermochemical (MSD-TC) for predicting chemical behavior in molten salt reactors

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The Molten Salt Database-Thermochemical (MSD-TC) is a compilation of internally consistent values and models for computing the equilibrium state of salt and related systems over a wide range of temperatures and composition. With the objective of supporting molten salt reactor (MSR) design, operation, and safety assessment, the current version contains 24 salt cations for both fluoride and chloride systems, together with key iodine-containing compositions, noble metal phase representations, and structural alloy models. The presentation will provide detail on elemental content, a brief description of the nature of the thermochemical models utilized, and examples of applications of equilibrium calculations such as predicting changing chemical potential and propensity for corrosion during burnup in proposed reactor systems. Utilization of the database with codes describing multiple phenomena in MSRs will be demonstrated. As of this writing, registrants for the GitLab site for downloading the thermochemical database together with its companion thermophysical properties database MSD-TP (https://msd.ornl.gov) have exceeded 470 individuals representing 10 countries.

JOINT 4538894

Synchrotron radiation spectromicroscopy of actinide materials

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The capability to conduct x-ray synchrotron radiation spectroscopy on actinide materials has led to marked improvement in the fundamental understanding of *f*-electron behavior and chemistry of *f*-electron materials. Specialized beamlines and endstations capable of utilizing the unique spatial resolution, energy resolution, and intensity provided by the advent of near and third generation synchrotron radiation x-ray beams from storage ring user facilities, coupled to new sample holding techniques, has provided unmatched opportunities to characterize the chemical and physical properties for a range of actinide materials.

This has been particularly evident in the soft x-ray region of synchrotron radiation where resonant inelastic x-ray scattering (RIXS) has been employed to garner information about actinide metal centers and the scanning transmission x-ray microscope (STXM) to determine electronic structure from the ligand perspective via ligand K-edge spectroscopy. Both have emerged as uniquely powerful tools to elucidate the electronic structure of actinide materials. Additionally, these approaches have utility in more targeted applications, such as in actinide environmental science and national security. Several recent examples of actinide RIXS and STXM studies will be presented.

Similar to the synchrotron radiation user facilities, the 88" Cyclotron at LBNL provides a unique capability to elucidate the chemistry of the late actinides. Two recent campaigns

that we participated in, albeit without Darleane Hoffman on the author list, have recently been published and remind of us of our connection to Darleane.

JOINT 4538944

Electrochemical methods for halobasicity determination in molten salts

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The breadth of applications of molten salts is made possible by the wide range of thermo-physical and chemical properties that can be obtained by tuning the salt composition. This wide range of variability can in part be attributed to acid-base equilibria, which can affect both solvent and solute behavior, as well as the chemical interactions with surrounding materials. In halide melts, acid-base equilibria are often described in terms of halobasicity, which measures the activity of free halide ions in the salt.

In the context of molten salt reactors (MSRs), the development of halobasicity measurement techniques is important to establish a comparison across candidate salts and establish online monitoring capabilities during reactor operation. Electrochemical techniques offer promise for this application, benefitting from their versatility, robustness, limited footprint, and non-destructive character.

This talk will present our group's approaches towards the development of electrochemical approaches to measure halobasicity in chloride salts, leveraging techniques such as Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and Open Circuit Potential (OCP). EIS measurements were performed on the NaCl-$AlCl_3$ system at various compositions and showed a correlation between halobasicity and electrical conductivity. EIS and CV measurements were performed on binary mixtures of LiCl, NaCl, KCl, $CaCl_2$, and $MgCl_2$, displaying a relationship between halobasicity and the potentials for major metal reduction and chlorine evolution. Temperature-dependent OCP measurements on the same set of salts (with added probe solutes) are ongoing to investigate the effects of halobasicity on the Nernst potentials. Overall, the suite of techniques discussed in this work can support the characterization of acid-base effect in molten salts, supporting the investigation of the connection between salt chemical structure and physicochemical properties.

JOINT 4538979

Synthesis, structure, spectroscopy and reactivity of terphenolate complexes of the rare-earth metals in the +2 oxidation state

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The bulky terphenylthiolate ligand, $(SAr^{iPr6})^{1-}$ = SC_6H_3-2,6-(2,4,6-C_6H_2-$^iPr_3$)$_2$], has been used to expand the chemistry of complexes of the rare-earth metals in the +2 oxidation state beyond first-row main group donor atoms, C, N, and O, to the second row donor, sulfur. These complexes, $Ln(SAr^{iPr6})_2$, benefit from interaction of the flanking arene rings of the terphenyl groups to form a metallocene like environment for the metal. To compare the chemistry of these $Ln(SAr^{iPr6})_2$ complexes with their first-row analogs, $Ln(OAr^{iPr6})_2$, the latter complexes have been synthesized and crystallographically characterized. The substantial structural differences between the thiolates and the phenolates will be discussed as well as the implications on the EPR spectroscopy and reactivity. Comparisons with the $Ln[NH(SAr^{iPr6})]_2$ complexes will also be presented in efforts to develop a global view of the chemistry of the rare-earth metals with $(EAr^{iPr6})^{1-}$ ligands (E = O, S, NH).

JOINT 4539167

Studies of the coprecipitation of plutonium and cerium with gibbsite and magnetite: An approach to nuclear waste management

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Mechanistic understanding of the interactions between radionuclides and nuclear waste minerals is crucial to developing appropriate treatment technologies. Aluminum and iron (oxyhydr)oxide are two of many solids present in the sludge of legacy nuclear weapons waste processing tanks. This study investigated the coprecipitation of plutonium (Pu) and cerium (Ce) with gibbsite (α-$Al(OH)_3$ and magnetite (Fe_3O_4) as surrogate minerals under waste tank-relevant conditions. These minerals were synthesized at room temperature, under high ionic strength, and at pH >12. The as-synthesized materials were characterized by X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). Aqueous concentrations of Ce and Pu measured using inductively coupled plasma mass spectrometry (ICP-MS) indicated that almost all the Pu and Ce fractions were associated with the solid precipitates. The XRD analysis for Ce-gibbsite system showed characteristic patterns for gibbsite and CeO_2, indicating no clear evidence of Ce incorporation into the gibbsite structure consistent with the difference in ion size between Al(III) and Ce(III). Furthermore, the clusters of Ce around gibbsite were confirmed by SEM imaging of microtomed samples. It appears that Ce is primarily associated with Ce-oxide phases or possibly surface complexes on gibbsite, rather than incorporating into gibbsite.

In contrast, Ce/Pu incorporation into the magnetite structure is suspected, with the noteworthy observation that Ce and Pu are both readily removed from solution upon precipitation of magnetite. However, in the presence of 0.08 mol/L initial Ce and a Ce/Fe ratio of 0.2, both goethite and magnetite are observed rather than pure magnetite

in the absence of Ce. SEM-EDX revealed the crystal morphology and elemental composition of magnetite showed typical rhombohedral particles in the absence of Ce but ‘rod-like’ structures for Ce-magnetite that were consistent with formation of goethite. Thus, incorporation of Ce into the iron oxide phases induces the formation of a different crystal structure. Pu concentrations in similar samples were too low to observe differences on XRD or SEM but removal of Ce and Pu from solutions upon precipitation were comparable. These findings show that Pu and Ce have a strong affinity for gibbsite and magnetite phases but potentially via different attenuation mechanisms.

JOINT 4539679

Vitrification of molten chloride salts

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Vitrification of molten chloride salts offers a promising route to preserve liquid-phase structures as amorphous solids, enabling detailed structural analysis at room temperature. However, vitrifying simple salts (e.g., LiCl, KCl) remains challenging due to their strong propensity for crystallization. In this work, we address this limitation by supercooling molten salt systems (e.g., KCl–MgCl2, KCl–ZnCl2, LiCl-KCl) using a range of rapid quenching techniques. Structural characterization reveals a substantial reduction in crystallinity while retaining key short-range motifs characteristic of the liquid state. Furthermore, 4D-STEM analysis confirms the amorphous nature of the quenched materials. These results demonstrate the effectiveness of rapid vitrification strategies in preserving the structural features of molten salts. This work represents a significant advance in molten salt vitrification and opens new avenues for room-temperature structural investigations, with implications for molten salt reactors and other high-temperature chemical systems.

JOINT 4539766

When ligands go radical: Bonding and redox control across the *f*-block

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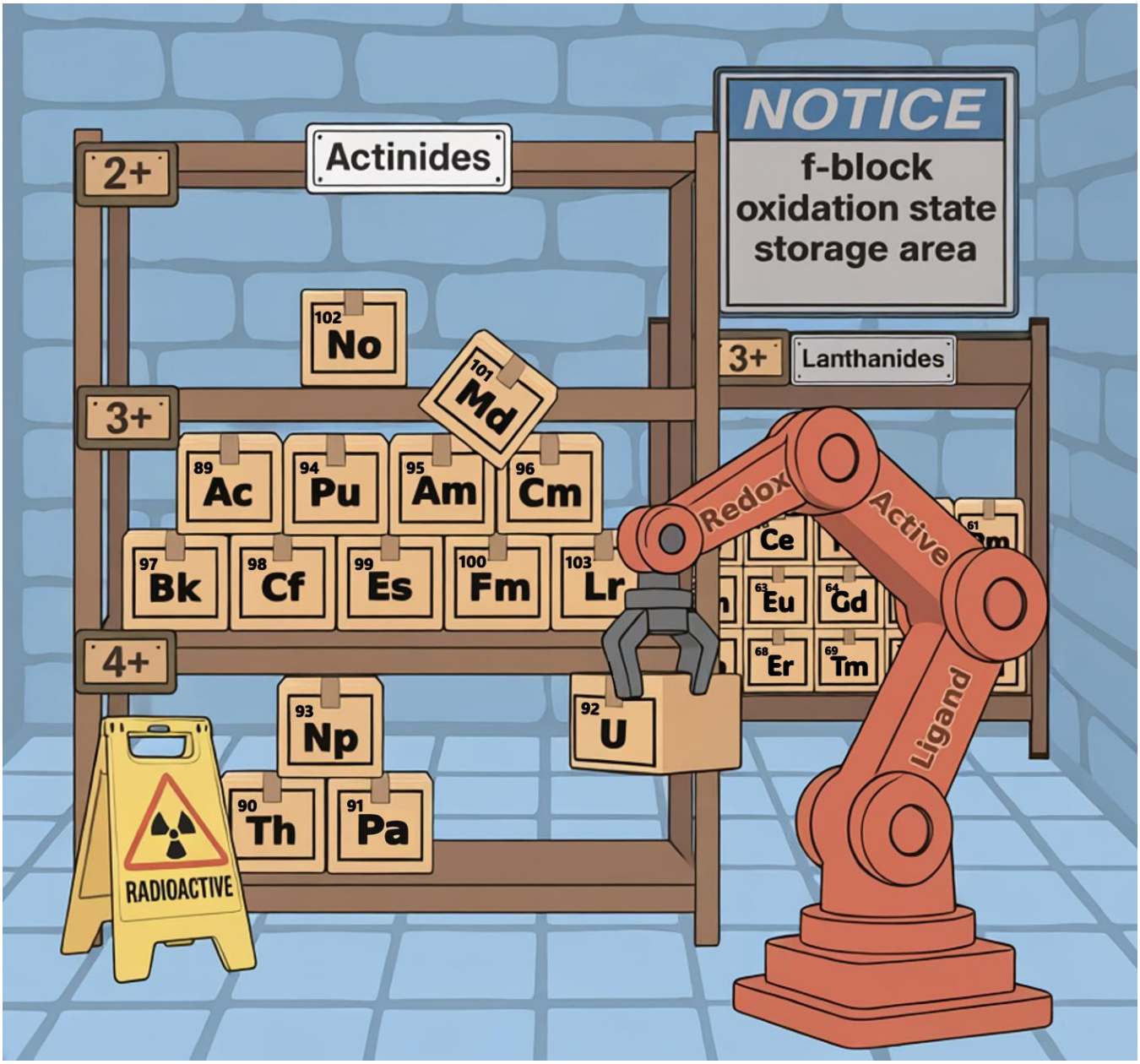
Unlocking the full potential of f-block chemistry requires an accurate understanding of metal-ligand bonding—an essential step toward advancing technologies such as quantum information science, single-molecule magnets, and chemical separations. A promising avenue lies in using redox-active ligands, such as radicals, which readily participate in electron transfer processes and provide dynamic control over the oxidation state and electronic structure of both lanthanides and actinides. Surprisingly, these interactions remain underexplored—particularly for actinides—where only a handful of molecular examples featuring radical ligands exist. This scarcity limits our fundamental understanding of oxidation state variability across the f-block and its impact on electronic structure and bonding. In this presentation, I will highlight our recent studies on this phenomenon by examining the coordination of soft- and hard-donor radical species across the actinide and lanthanide series. Using a combination of density functional theory (DFT) and multireference methods, we demonstrate that the coordination of radicals induces oxidation state shifts across the actinide series—discontinuities mostly absent in their lanthanide analogs—highlighting how redox-active ligands can enhance electronic differentiation among the f-block series within an identical molecular framework. The computational analysis also reveals that the observed oxidation state shifts are driven by a favorable alignment between metal and ligand frontier orbitals as well as the energetic stabilization of the resulting electronic configurations. Finally, our results underscore that oxidation state change do not inherently correlate with increased covalency. This study not only enriches our fundamental understanding of actinide bonding but also underscores oxidation state control as a powerful strategy to drive innovation across f-block chemistry.



JOINT 4540110

Conformational flexibility in chelator design: Applications in f-element separations and nuclear medicine

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Preorganization and rigidity within chelators have often been considered favorable properties that decrease the entropic penalties associated with metal ion coordination. Under some circumstances, however, conformational flexibility can confer advantages for different applications. Specifically, we have previously reported a class of chelating agents that undergo a dramatic conformational switch upon binding metal ions of different sizes. This property confers upon this class of chelators a dual-size selectivity, allowing it to bind equally effectively to both large and small ions while only weakly binding to intermediately sized ions. This class of chelators is discussed in this presentation. The applications of these chelators for unique rare earth element separations are presented, demonstrating that middle rare earths can be separated from light and heavy rare earth elements. In addition, the use of this class of chelators for nuclear medicine applications is also discussed. These chelators can be used to stably bind both large therapeutic radiometal ions, as well as smaller diagnostic radiometals. Lastly, fundamental coordination chemistry studies aimed at understanding how these chelators operate are presented.

JOINT 4540118

Unveiling hidden shake-up features in the actinyl M_4-edge spectra

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The $M_{4,5}$-edge high energy resolution X-ray absorption near-edge structure (HR-XANES) spectra of actinyls offer valuable insights into the electronic structure and bonding properties of heavy-element complexes. To conduct a comprehensive spectral analysis, it is essential to employ computational methods that accurately account for relativistic effects and electron correlation. In this work, we utilize variational relativistic multireference configurational interaction methods to compute and analyze the X-ray M_4-edge absorption spectrum of uranyl. By employing these advanced computational techniques, we achieve excellent agreement between the calculated spectral features and experimental observations. Moreover, the calculations unveil significant shake-up features, which arise from the intricate interplay between strongly correlated 3d core-electron and ligand excitations. This research provides important theoretical insights into the spectral characteristics of heavy-element complexes. Furthermore, it establishes the foundation for utilizing $M_{4,5}$-edge spectroscopy as a means to investigate the chemical activities of such complexes. By leveraging this technique, we can gain a deeper understanding of the bonding behavior and reactivity of heavy-element compounds.

JOINT 4540407

Development of a multilayer system for structural protection in molten salt reactors

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Molten salt reactors (MSR) are one of the options of the Gen IV reactor designs and exhibit inherent safety features. Common steels experience significant degradation in these harsh, corrosive environments due to formation of fluorides/chlorides. Historically, MSRs were studied in 1950s and 1960s; researchers at Oak Ridge National Laboratory developed Hastelloy B, N, and W, which are Ni-Mo alloys with low Cr content, as the material of choice for deployment in MSRs. However, these alloys are quite costly; here, we have taken inspiration from the earlier developments and designed a coating utilizing Ni, Mo, Cr with additional additives and alumina (Al_2O_3) as a base layer protection for a less expensive substrate steel. The multilayer coating is placed over SS316 via physical vapor deposition (PVD), primarily, while the Al_2O_3 layer has been prepared with atomic layer deposition (ALD). The coating has been subjected to ion radiation (1MeV Kr) at various intensities within the Intermediate Voltage Electron Microscope (IVEM) facility at Argonne. The coating has shown resilience against radiation at operating temperature (~650°C) and stability with LiF-NaF-KF (FLiNaK, a molten salt candidate) over 28 days. The post-irradiated sample has minimal cracks along its surface due to the additive metals and alumina acting as barriers/sacrificial components to prevent migration of Cr either from the substrate steel or within the layers. Additionally, the corrosion resistance to FLiNaK is confirmed from its cross-section STEM images as seen by minimal diffusion. Therefore, it has been demonstrated that this multilayer coating has the potential to be candidate barrier in FLiNaK or fluoride salt-based reactor designs.

JOINT 4541176

Designer scorpionate ligands for f-element separation and stabilization

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We investigate classes of scorpionate ligands composed of cyclic nitrogen-containing rings held together through a boron group. These scorpionates are highly customizable, tridentate ligands that have shown tremendous promise to directed adjacent f-element separations and exotic oxidation state stabilization. Here, substitutions are made on pyrazole rings that have allowed f-element crystallizations on the sub milligram metal scale, yielding the first homoleptic N-donor promethium crystal. In addition to the small-scale syntheses, the choice of substituent on the rings can direct where in the trivalent f-element series a break from a 9- to 8-coordinate metal center may occur, showing promise in future separation schemes. Particularly the promethium structure shows promise for its actinide size match, curium, and potential separation pathways from its longstanding challenging neighbor, americium.

JOINT 4541391

Exploring ring substitution of tris pyrazolyl borate derivatives for *f*-element coordination with a homoleptic nitrogen donor

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Tris pyrazolyl borate (Tp) was first synthesized by Trofimenko in 1966 and was established as a monoanionic, tridentate ligand characterized largely with transition metals until Apostolidis et al. published a trivalent lanthanide (Ln) Tp series (excluding promethium) and uranium, neptunium and plutonium Tp structures. The $LnTp_3$ series follows the lanthanide contraction trend with the lanthanide-nitrogen bond lengths decreasing steadily across the series with three Tp molecules fully bound to the Ln ions until there is a coordination break in the series at dysprosium. This work expands on the trend established by Apostolidis by exploring how substituting an electron-withdrawing bromo group on the Tp rings extend the coordination break within the lanthanide series to erbium as well as completing the Ln series with the **first reported promethium Tp structure** (Figure 1). This structural investigation reveals the possibility of Tp modification through electron-donating or electron-withdrawing groups to effectively select where the divergence in the series occurs for potential adjacent lanthanide separations. Ring substitution also increases the solubility of the complexes, opening up more potential synthetic routes that are optimal for radioactive element syntheses. Unsubstituted *f*-element Tp complexes are highly insoluble with crystals obtained after extraction over several weeks or sublimation. Substitution with a bromo group allows for crystals to be grown overnight down to the 0.1 mg metal scale. This work involves synthesis optimization for direct lanthanide and actinide comparison with a homoleptic, pure nitrogen donor ligand.

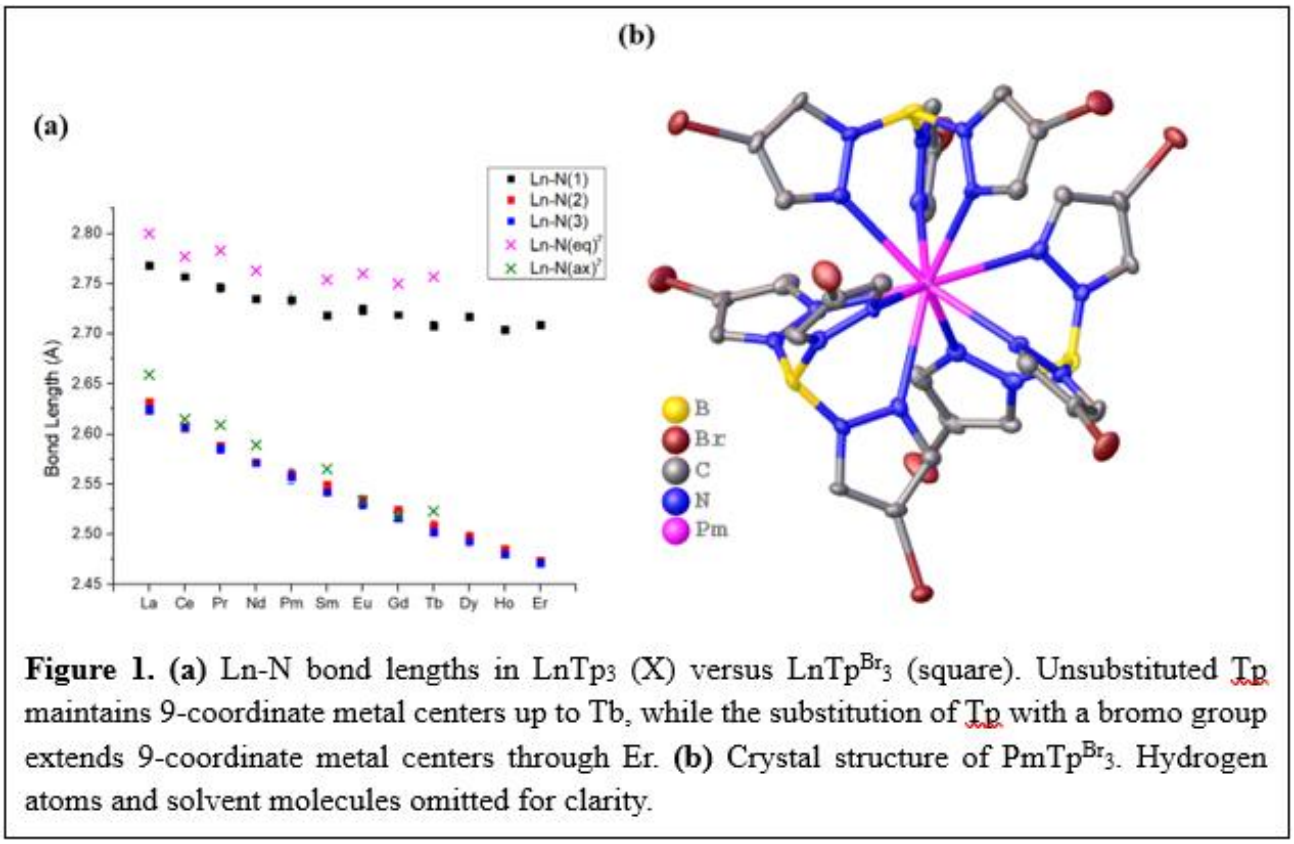

Figure 1. (a) Ln-N bond lengths in $LnTp_3$ (X) versus $LnTp^{Br}_3$ (square). Unsubstituted Tp maintains 9-coordinate metal centers up to Tb, while the substitution of Tp with a bromo group extends 9-coordinate metal centers through Er. **(b)** Crystal structure of $PmTp^{Br}_3$. Hydrogen atoms and solvent molecules omitted for clarity.

JOINT 4541531

Charged defects in actinide materials: Effect on surface chemistry

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Actinide compounds, particularly actinide oxides, play a central role throughout the nuclear fuel cycle. Their behavior under diverse chemical and environmental conditions influences processes ranging from fuel fabrication and crystal growth to the long-term storage and disposal of spent nuclear fuel. Many of these properties originate at material surfaces, where interactions with environmental species such as water, oxygen, or dissolved ligands can significantly alter chemical stability and reactivity. Surface-mediated catalytic reactions may contribute to corrosion or gas generation, potentially compromising storage safety. Similarly, the morphology of growing crystals is governed by the relative stabilization or destabilization of specific crystallographic planes by ligands present in solution, which ultimately determines particle shape and size.

Although computational studies have provided valuable insight into actinide materials, most focus on ideal, defect-free crystal structures. In reality, these systems contain intrinsic point defects that strongly influence electronic structure and chemical behavior. Defects frequently serve as reactive centers, where changes in local coordination and electronic structure can promote bond activation and surface chemistry. Our recent work investigates the energetics of point defect formation in actinide dioxides (AnO_2) and examines how these defects influence charge localization within the lattice. Because charge localization can enhance site-specific reactivity, understanding its relationship to defect structure is essential for predicting catalytic behavior and long-term material performance.
In this presentation, we describe computational methodologies for evaluating the formation energetics of charged defects, including strategies for treating finite-size effects and charge compensation. We present systematic results across a series of AnO_2 compounds, highlighting trends in defect stability and electronic structure. Finally, we discuss how differences in surface reactivity across crystallographic planes can be leveraged to rationally control growth morphology, enabling tunable structures from the nanoscale to bulk materials.

JOINT 4541792

Accelerating actinide molecular design with architector

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With the introduction of the Architector software in 2023 community members have leveraged its configurational search capabilities across the periodic table for uses spanning machine learned interatomic potential dataset generation, to targeted exploration of actinide chemistries. This talk will highlight recent updates to the Architector software (Architector 2.0) relevant to actinide chemists and chemistry including solvation shell sampling, a graphical user interface (GUI), and diverse ligand and symmetry handling. Recent efforts leveraging these capabilities for actinide-relevant redox chemistry and modeling choices will be highlighted.

JOINT 4541906

When counterions fall into place: counterion effects on F-element phosphomolybdate crystallization and speciation

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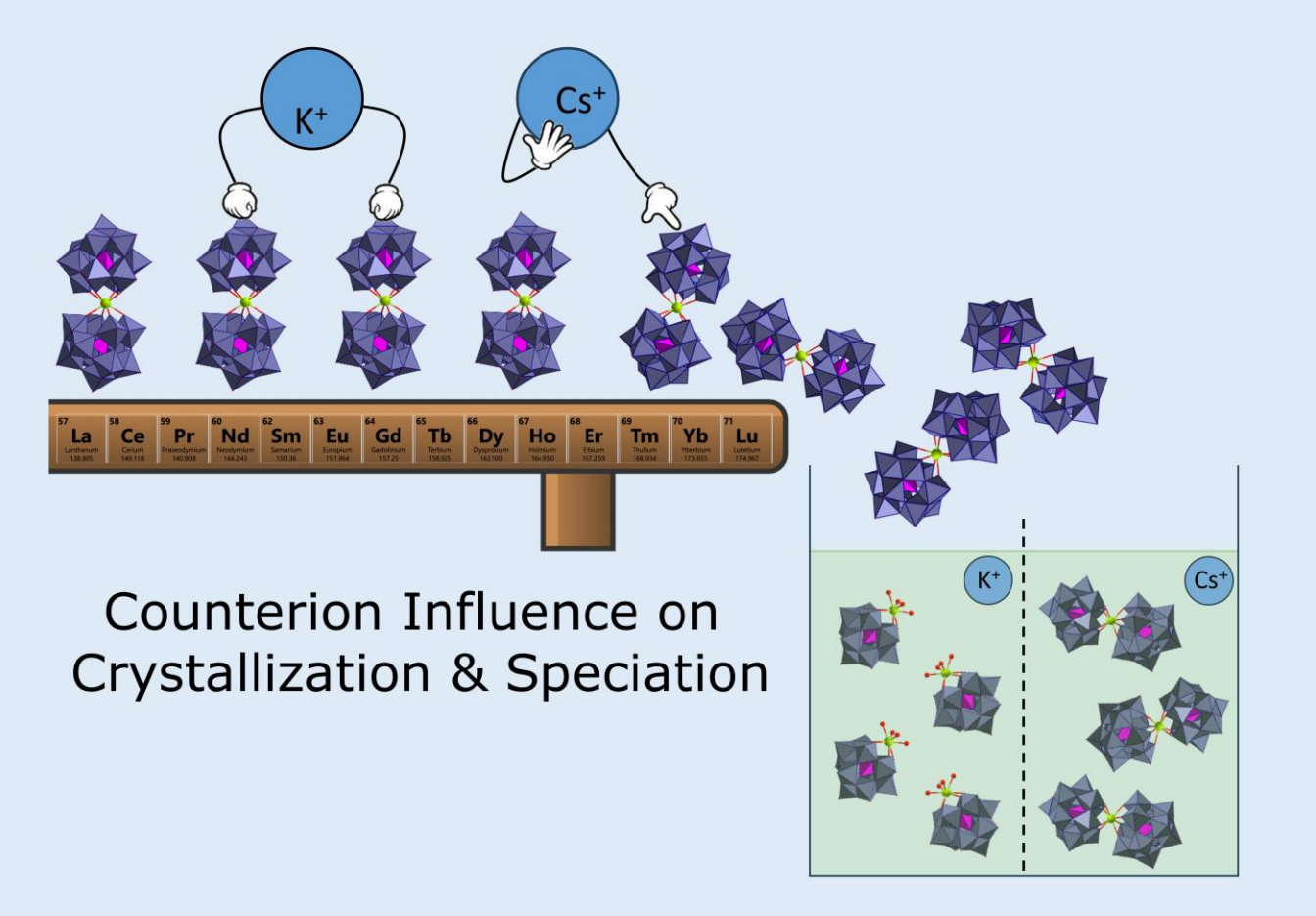
We are studying polyoxometalate-lanthanide (PMO-Ln) complexation and speciation as surrogates for transuranic An^{3+} complexes. Within these systems, countercations play a decisive role in shaping the structure and behavior of POM complexes including lanthanide-phosphomolybdate sandwiches. A series of $Ln(PMo_{11}O_{39})_2^{11-}$ complexes with charge-balancing K^+ and Cs^+ were synthesized across the lanthanide series and characterized by single crystal X-ray diffraction resulting in 16 total structures. Combined crystallographic and solution-phase studies enabled direct comparison of structural trends and countercation-dependent solution-state speciation. While potassium analogues exhibit consistent parallel arrangement of POMs in the crystalline lattice, cesium derivatives adopt distinct packing modes, including both parallel and perpendicular orientations. These structural differences are reflected in variations in lattice organization and inter-cluster interactions, highlighting the role of larger alkali cations in directing long-range assembly. Moreover, ^{31}P Nuclear Magnetic Resonance (NMR) spectroscopy and small-angle X-ray scattering (SAXS) reveal that the countercation (Li^+, Na^+, K^+, Rb^+ and Cs^+ studied) directly impact assembly and equilibrium between $PMo_{11}O_{39}^{7-}$, $Ln(PMo_{11}O_{39})^{4-}$ and $Ln(PMo_{11}O_{39})_2^{11-}$ in solution, prior to crystallization.



Alkali-directed POMo sandwich cluster synthesis, arrangement, and speciation.

JOINT 4541965

Tunable M···M distances in bimetallic f-element complexes using dispersion forces

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Non-covalent interactions (NCIs) are ubiquitous and play a key role in governing structure-function relationships by influencing the geometric and electronic properties of molecular systems. While interactions such as hydrogen bonding, dispersion, and π-cation effects are widely exploited in supramolecular and biological chemistry, their deliberate use in f-elements systems remains underdeveloped. In this work, we describe the use of London dispersion forces in bimetallic f-element metallocenes bridged by aryloxide or alkoxide moieties to modulate metal···metal distances. These structures are crystallographically characterized and suggest that their bimetallic structure is maintained in solution via DOSY NMR. A one-electron reduction of a

La(III)/La(III) analog shows the presence of a La(II) ion with no other La(II) speciation by EPR. Efforts to extend this approach to actinide analogs will also be discussed.

JOINT 4541985

Effect of radiation on metal organic frameworks

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As part of Molten Salt Reactor (MSR) Campaign, Pacific Northwest National Laboratory developed metal organic frameworks as a new class of materials for separation of xenon and krypton from MSR process off-gases at near room temperature. However very few studies were focused on effect of radiation on these class of materials and their perforamance before and after radiation. This presentation will provide impact of gamma radiation on noble gas adsorption.

JOINT 4542001

Surface-mediated plutonium redox transformations on metal (hydr)oxide minerals under high ionic strength conditions

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Plutonium remains one of the most chemically complex and environmentally persistent elements in the nuclear waste tanks. It's ability to exist in multiple oxidation states allows dynamic redox transformations that influence solubility, sorption, and complexation behavior. Predicting these transformations is particularly urgent for high-ionic strength environments such as the Waste Isolation Pilot Plant (WIPP), where brine chemistry and surface interactions control long-term radionuclide fate or the Hanford Reservation Waste tanks where high NaNO3 levels influence Pu partitioning between sludge and salt solution phases. Yet, despite decades of study, the mechanisms that drive plutonium's redox cycling at mineral–water interfaces remain poorly constrained. This study investigates the coupled sorption–redox behavior of plutonium on goethite across NaCl and NaNO3 media ranging from 0.1 to 3 M ionic strength. Batch experiments demonstrate extensive sorption of Pu(VI) at circumneutral pH, revealing strong dependence on oxidation state, and pH. Raman spectroscopy shows the progressive loss of the Pu(VI) plutonyl symmetric stretch, while XPS reveals reduction to Pu(IV) and the unexpected appearance of transient Pu(III) species. PuO2 nanoparticles were not observed in TEM imaging, suggesting that reduced plutonium remains as monomeric or oligomeric surface complexes. A thermodynamically based surface complexation model based on parameters determined from the 0.1 M NaCl system were unable to predict the data in 1 and 3 M NaCl, providing insight into

electrostatic compression and competitive effects in brines.
Following the detection of transient Pu(III) on goethite, complementary experiments were conducted using Pu(III) as the initial oxidation state to determine whether surface-mediated oxidation occurs on different minerals which are hematite, goethite, gibbsite, and quartz. These experiments probe the stability of sorbed Pu(III) and clarify whether oxidizing versus redox-inert surfaces promote oxidation of Pu(III) to Pu(IV). Together, these studies provide a mechanistic, spectroscopically validated, and quantitatively modeled framework for predicting plutonium behavior in high-ionic strength nuclear waste repositories.

JOINT 4542172

Tailoring metallic coatings through dynamic electrodeposition in molten salt systems

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This work presents an investigation into the dynamic electrodeposition of metallic coatings in molten salt systems. Molten salt electrodeposition is a highly effective technique for producing dense metallic deposits. However, persistent challenges such as dendritic growth, poor uniformity, and corrosion or contamination of both the salt and deposited coating remain. These limitations may be mitigated through controlled variation of electrochemical parameters during deposition. Dynamic electrodeposition, changing the electrochemical parameters over time, offers enhanced tunability over coating growth, morphology, and uniformity compared to steady-state approaches. This study examines how changing of electrochemical conditions, including current density and the incorporation of intermittent rest or oxidation steps, affects coating properties. Electrochemical techniques, including cyclic voltammetry, open circuit potential, and chronoamperometry, will be used to measure ion concentration and the deposition mechanisms. Post-deposition characterization will be conducted using scanning electron microscopy with energy-dispersive spectroscopy (SEM/EDS), X-ray computed tomography (XCT), X-ray diffraction (XRD), and profilometry to evaluate coating morphology, composition, and thickness and to enable comparison to steady-state methods. This work aims to establish fundamental relationships between dynamic electrodeposition and the quality of deposited metallic coatings.

JOINT 4542206 - Withdrawn

JOINT 4542245

Expansion of a reactor discrimination methodology to include high-assay low-enriched uranium (HALEU) fuel using γ-γ coincidence spectrometry

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Nuclear forensics is key in nonproliferation and anti-proliferation efforts as it can utilize radiochemical analysis techniques to determine a sample's history. For example, if special nuclear material is interdicted during a proliferation attempt, nuclear forensics can be used to investigate the type of reactor the sample originated from, as well as its burnup, and the time since its irradiation so a proper response to the proliferation may be initiated. A purification-resistant method for determining these attributes was previously developed through a collaboration between the Chemistry and Nuclear Engineering Departments of Texas A&M University. This method relies on intra-elemental isotopic ratios that are measured via γ spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) combined with chemical separations. The observed ratios are then compared to ratios simulated for spent fuel from a variety of reactors to determine the sample's most likely history.
The current work seeks to improve this method in a few major ways. First, the existing method focuses on intra-elemental isotopic ratios in reactor fuel below 5% initial ^{235}U enrichment, and higher enrichments are untested. However, with the world's attention turning to high-assay low-enriched uranium (HALEU) fuel for use in small modular reactors, we will expand the enrichments included in this method. This will be done by irradiating HALEU fuel between 5% and 19.75% ^{235}U and then analyzing the intra-elemental isotopic ratios using a simpler separation scheme before γ-γ spectrometry and ICP-MS quantification. The ratios will then be compared to an expanded database of simulated values. The increased sensitivity provided by the γ-γ coincidence technique will allow an investigation into the minimum sample size requirements of the reactor discrimination method and thus probe its application to a broader range of proliferation scenarios. This talk will discuss the most recent results and future plans.

JOINT 4542479

Molecular single source precursor for *f*-element materials

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Actinide oxides and chalcogenides represent a fundamental class of materials for probing the interactions between actinide ions and heteroatoms. The strong electron correlation of 5*f* electrons gives rise to exotic physical phenomena such as heavy fermion behavior and unique magnetism, while the chemical properties of these materials have broad implications for nuclear fuel cycle applications and nuclear forensics. Understanding the origins of their chemical and physical properties requires detailed investigation of electronic structure through spectroscopic and magnetic

measurements, which necessitates phase-pure and oxidation-state-pure materials. However, the synthesis of well-defined actinide materials remains a significant challenge due to the accessibility of multiple oxidation states in the early and mid-actinides (Th, U, Np, Pu), which frequently leads to mixed phase products. Single-source precursor (SSP) approach offers a powerful and complementary strategy to address these challenges. In contrast to conventional high-temperature methods such as flux growth and chemical vapor transport, SSPs contain pre-formed An–E (E = O, S) bonds in which the metal oxidation state is preserved during decomposition, circumventing unwanted redox reactivity. Another advantage of the SSP approach is that the volatility of the precursor can be tuned through its molecular design. Upon pyrolysis, the volatile component is cleanly eliminated at temperatures lower than those required by traditional synthetic routes, affording oxidation-state- and phase-pure target materials with minimal crystallographic defects and chemical inhomogeneity. Previous work on single source precursor approach to actinide oxides have demonstrated the utility of the approach in synthesizing oxidation state (4+) and phase pure products of U, Th, Np and Pu, in differnt morphoplogies of bulk, nanoparticles and thin films.The scope of this methodology has recently been extended to actinide chalcogenides, as shown in the reported synthesis of uranium disulfide (US_2).
This work further expands the SSP methodology to access actinide oxides and chalcogenides beyond the 4+ oxidation state and to encompass a broader range of chalcogenide compositions. Further development of this methodology facilitates the investigation of actinide electronic structures in various oxidation states and phase pure materials which are otherwise challenging to access.

JOINT 4542526

Assessment and predictions of fueled fluoride molten salt

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Molten fluoride salts such as FLUF play a central role in molten salt reactor concepts. While the thermophysical properties of the parent FLiBe system are relatively well established, the incorporation of uranium fluoride introduces significant structural and electronic complexity that alters transport behavior in ways not captured by simple extrapolation. Experimental data for FLUF remain sparse, limiting the development of reliable property models and complicating reactor design efforts. Ab initio molecular dynamics (AIMD) has become a standard approach for studying molten salts; however, its accuracy depends strongly on the choice of density functional, particularly for systems containing uranium.

In this work, we assess the performance of several density functionals in describing the structure and thermophysical properties of FLUF melts, with an emphasis on identifying reliable functionals for machine-learned interatomic potential (MLIP) development.

Benchmarking against available experimental insights is used to determine which approaches most accurately capture key structural features of the melt. Using the selected electronic structure framework, we construct an MLIP and employ it in molecular dynamics simulations to compute thermophysical properties across relevant conditions. Our results establish a physically grounded strategy for generating high-fidelity training data and demonstrate a pathway for developing accurate, transferable MLIPs for fueled molten salt systems.

JOINT 4542558 - Withdrawn

JOINT 4542589

Specific heat measurements of molten fluoride and chloride salts for molten salt reactor applications

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Reliable thermophysical property data for molten salts are essential for thermal-hydraulic and neutronics analyses in molten salt reactor (MSR) design. Specific heat capacity, in particular, remains challenging to measure with low uncertainty due to the hygroscopic and corrosive nature of relevant salt systems, coupled with instrumental limitations in conventional calorimetry. This work establishes a high-accuracy measurement protocol for air-sensitive molten salts using Calvet-type differential scanning calorimetry (DSC) with a small temperature step method. To maximize the sample-to-crucible mass ratio and minimize systematic error, custom laser-welded lightweight hermetic nickel crucibles were developed. Instrument reproducibility was benchmarked at 1.54% through triplicate measurements against NIST SRM 720 α-Al2O3 reference standard, confirming metrological traceability. Applying this methodology, heat capacities were determined for high-purity eutectic compositions relevant to both fluoride- and chloride-based MSR concepts: FLiNaK, NaCl-MgCl2, LiF-UF4, and NaCl-UCl3. These results provide much-needed thermophysical data for actinide-bearing chloride and fluoride eutectics and are incorporated into the Molten Salt Database - Thermochemical as validated reference values for MSR design and modeling.

JOINT 4542727

Structure of thorium chloride melts from neutron scattering

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Molten metal chloride salts containing actinides are of growing interest for advanced nuclear fuel cycles, pyrochemical reprocessing, and high-temperature separations due to their favorable thermophysical properties. Thorium based systems are particularly relevant to next generation molten salt reactors where understanding the short and intermediate range order is critical for predicting transport properties, redox behavior, and phase stability. Despite their importance, the local coordination environments of actinide ions and the evolution of structural motifs with composition and temperature remain incompletely characterized. In this work, total scattering experiments were performed using the Spallation Neutron Source Nanoscale-Order Materials Diffractometer to investigate the molten state structure of pure $ThCl_4$, NaCl-$ThCl_4$, $MgCl_2$-$ThCl_4$, and NaCl-$MgCl_2$-$ThCl_4$ compositions. Beyond the structural characterization, this study also details the synthesis and purification protocols required to obtain high-purity, anhydrous, metal chloride salts suitable for high-temperature experiments in sealed vessels. The reproducibility of sample preparation and considerations of material and sample environment compatibility are also discussed.

JOINT 4542803

Elucidating the electronic structure and topography of Sub-Monolayer F-element adsorbates using scanning probe microscopy

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The electronic and magnetic properties that are intrinsic to lanthanides and actinides make them attractive constituents in materials relevant to quantum information science. To this end, molecular compounds make for computationally and spectroscopically addressable surrogates that can be used to study complex phenomena observed in extended-solid materials. Among the many approaches to study molecular compounds, relatively few have focused on individual molecules adsorbed on surfaces. As such, molecule-surface orbital interactions remain elusive.

Herein, we present an experimental and computational effort to study the topography and electronic structure of a molecular europium complex adsorbed on Cu(111) and

Au(111) in sub-monolayer quantities using Scanning Tunneling Microscopy (STM), differential conductance (dI/dV) techniques, Molecular Dynamics simulations, and DFT calculations. Our calculations corroborated the experimentally observed topography of the adsorbed complex, which undergoes drastic structural ligand rearrangement when adsorbed on each substrate. Notably, our DFT calculations revealed a formal reduction of our complex from Eu(III) to Eu(II) when adsorbed on Cu(111), while retaining its trivalent state on Au(111). These differences in oxidation state manifested as differences in the calculated PDOS of the 4-f orbitals, which are reflected in our experimental dI/dV spectroscopy. Altogether, our findings reveal the potential our system has on understanding molecule-surface interactions and on the engineering of individual defects on 2D surfaces. Our methods also serve as a blueprint for future studies on actinide compounds to study structure-property relationships with atomic precision.

JOINT 4542983

Development of free energy methods to compute chemical and redox potentials in molten salts

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Quantitatively reliable condensed-phase free-energy simulations remain a longstanding challenge for chemically complex liquids such as molten salts, even when using modern machine learning interatomic potentials (MLIPs) trained on density functional theory (DFT). Here, we develop a methodology for computing free energies in molten salts that resolves thermodynamic inconsistencies through finite-size standard-state corrections and removes major numerical artifacts in thermodynamic integration through the use of soft-core repulsive potentials. We show that soft-core potentials are essential for preventing numerical instabilities and ensuring reliable error propagation at weak alchemical coupling. We further demonstrate how to construct thermodynamically consistent cycles by explicitly accounting for standard-state corrections in finite-size simulations, enabling direct comparison with tabulated thermodynamic data. We apply this framework to compute redox potentials of pure molten salts for LiCl, NaCl, and KCl, as well as the formal redox potentials of AgCl at infinite dilution in the same molten salts. We also demonstrate an efficient way to train MLIPs based on higher level quantum chemical methods using delta learning. The resulting protocol establishes a general framework for quantitatively reliable thermodynamic modeling of molten salts.

JOINT 4543014

Predictive modeling of solid and molten BeF_2 with density functional theory and machine learning potentials

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Beryllium fluoride (BeF_2) is an important component of molten fluoride salts mixtures used in next generation nuclear reactor technologies, since it strongly influences chemical speciation, transport properties, and overall thermophysical behavior. Nevertheless, predictive modeling of BeF_2 remains challenging across both solid and liquid phases. In the solid state, the relative stability of competing polymorphs depends sensitively on the level of electronic structure theory, while in the liquid state, the highly viscous, network forming melt exhibits slow structural relaxation that requires large length and time scales for reliable simulation predictions, beyond the reach of direct *ab initio* molecular dynamics. In this work, we combine density functional theory (DFT) and machine learning interatomic potentials (MLIPs) to achieve a consistent and quantitatively reliable description of BeF_2 across phases. We address the longstanding challenge of predicting the correct lowest enthalpy phase of BeF_2 at 0 K by incorporating dispersion interactions. To access the liquid state, we develop MLIPs based on two distinct architectures trained on DFT data, enabling tens-of-nanosecond long molecular dynamics simulations of molten BeF_2. These simulations provide fully converged predictions of equilibrium structure, density, self-diffusivity, ionic conductivity, and constant pressure heat capacity. Most importantly, we demonstrate that a quantitatively reliable description of BeF_2 requires going beyond standard semilocal DFT. We find that MLIPs trained at the hybrid PBE0-D3 level yield systematically improved agreement with available experimental data for both solid and molten BeF_2, providing a substantially more reliable basis for predicting liquid-state structural and thermophysical properties. Together, these results provide a foundation for parameterizing and benchmarking models of BeF_2-containing mixtures and for extending simulations into the largely unexplored BeF_2-rich composition space.

JOINT 4543130

First-principles insights into the structure of molten uranium chlorides

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Uranium trichloride (UCl_3) and uranium tetrachloride (UCl_4) are critical materials in the nuclear industry for molten chloride salt reactors (MSRs), but accurately resolving their liquid structure remains a significant computational challenge. Here, we use first-principles molecular dynamics simulations to investigate the atomic-scale structure of these uranium chloride melts. We evaluate the robustness of our predictions by

systematically varying the levels of theory, including an assessment of different basis set effects and the impact of different dispersion corrections and pseudopotentials. Through analysis of radial distribution functions, coordination behavior, and structure factors, we compare the local and intermediate-range ordering in UCl_3 and UCl_4.The results reveal clear structural differences between the two melts, demonstrating the effect of uranium oxidation state on coordination and cation–cation correlations, while also emphasizing the importance of computational methodology in modeling actinide chloride systems. Overall, this work provides atomistic understanding of the local and intermediate-range structure of molten uranium chlorides and offers guidance for future simulations of actinide-based molten salts.

JOINT 4543192 - Withdrawn

JOINT 4543416

Design and benchmark of the "Solubility and speciation of hydrogen in fluorides testing station" (SHIFT)

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Fusion reactors aiming for commercial viability rely on high-field superconductors to achieve stronger magnetic fields and improved efficiency.These conditions intensify magnetohydrodynamic (MHD) effects in conductive blanket materials, making their mitigation a key design requirement. Molten salts are attractive due to their lower electrical conductivity, which reduces MHD effects compared to liquid metals, but their deployment is limited by insufficient understanding of tritium (hydrogen) solubility.

A key knowledge gap involves the relationship between hydrogen solubility and speciation with salt redox potential. This work addresses this by developing an apparatus for in situ measurement of both properties in fluoride salts, including FLiNaK and FLiBe.

The Solubility and Speciation of Hydrogen in Fluorides Testing Station (*SHIFT*) was constructed at the ABC Lab. *SHIFT*consists of two chambers: a *Saturator*, where hydrogen is charged into the salt, and a *Stripper*, where dissolved hydrogen is removed using helium. The chambers are connected via an all-nickel transfer line. The resulting gas mixture is collected and subsequently analyzed using a gas chromatograph mass spectrometer, which can detect low ppm levels of hydrogen. A key feature distinguishing SHIFT from previous systems is the inclusion of access ports for electrochemical electrodes, enabling simultaneous solubility and speciation measurements.

Experiments will be conducted across a range of temperatures, charging pressures, and salt redox conditions to measure their influence on solubility and speciation. The

apparatus was successfully commissioned, pressure testing was completed, and benchmarking experiments at room temperature are in progress using the ionic liquid [C_4mim][NTf_2], selected for its safety and the availability of prior experimental data for validation. These experiments will assess the performance of SHIFT and establish an electrochemical workflow.

This talk will discuss instrument design, operational principles, benchmarking results, and planned activities towards preparing the system for high temperature measurements using breeding blanket candidate salts.

JOINT 4543456

Trends of the Periodic Table: Insights from superheavy element homologue studies

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The Periodic Table of Elements is well-established framework for studying the chemical behavior of the elements. However, the periodic trend seems to break apart in the heaviest members (Z >103) of the table, the superheavy elements (SHE), due to the onset of relativistic effects. This results in new and unexpected chemistry at the edge of nuclear stability. A novel experimental method utilizing the FIONA mass spectrometer at Lawrence Berkeley National Laboratory (LBNL) enables the chemical studies of these elusive elements. Before probing the fundamental properties of the SHE, analogous studies of their lighter group homologues need to be performed first. In this work, we report the results of experiments involving the gas-phase fluoride formation of three lighter elements (ytterbium, hafnium and tantalum) produced in nuclear fusion evaporation reactions. The relative production rate of MF_n^+ indicates the availability of electrons needed to reach a certain oxidation state, which is a characteristic of the group the element belongs to. The results agree with the findings of similar studies performed on stable isotopes of the same elements. This sets the stage for a future experiment involving SHE, aimed at understanding their chemical behavior and the trends that they are expected to break due to an energetic reorganization of the valence orbitals.

JOINT 4543644

Sorption and desorption isotherms of plutonium onto CST, goethite, and rutile

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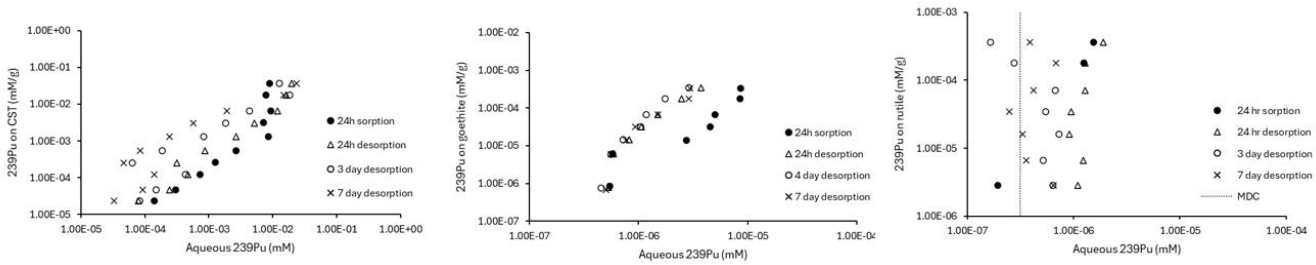
Sorption studies using crystalline silicotitanate (CST), goethite, and rutile show strong plutonium removal from solution for all three sorbents. Desorption studies show strong

retention of plutonium on the sorbent in the order of rutile > goethite > CST after 7 days. Comparing Kd values for the three sorbents shows a 3 order of magnitude larger Kd for rutile than the other sorbents, indicating greater solid phase plutonium concentration for that material. Desorption Kd values for rutile are also greater than those for CST or goethite, indicating greater retention of solid-phase plutonium after 7 days of desorption. Overall, these studies demonstrate CST, goethite, and rutile are effective sorbents for removal of aqueous plutonium and additionally demonstrate strong retention of plutonium to the sorbent, with rutile being the most effective of the three at retaining solid-phase plutonium.



JOINT 4543771

Solution dynamics of M-P coordination in MI(^{Ar}BiAMP^{tBu})(thf)$_3$ in THF-d_8

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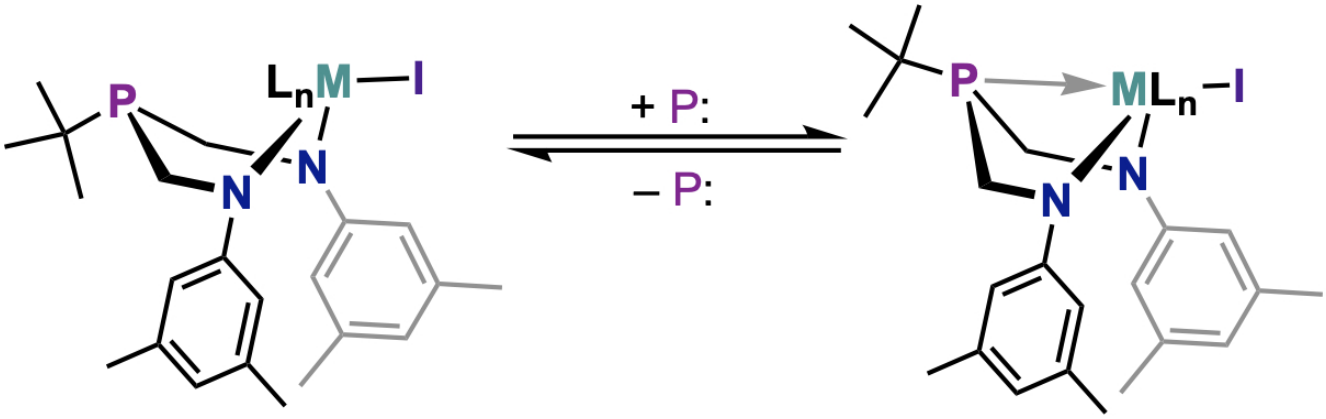
Given the observed differences in ^{31}P chemical shift between solid-state and solution NMR spectra, the solution dynamics of M-P coordination in MI(^{Ar}BiAMP^{tBu})(thf)$_3$ (M = rare earth element [REE] in the 3+ oxidation state) in THF-d_8 were studied using NMR spectroscopy. Solution-phase dynamic nuclear magnetic resonance (DNMR) techniques have been frequently employed to determine the rates of fluxional processes in small molecules through either line shape simulations in the fast, intermediate, and slow regimes of chemical exchange (typically corresponding to rates k_{ex} less than 5000 s^{-1}) or through spin saturation transfer experiments in the slow regime of chemical exchange. Uncertainties arising from unobservable chemical shift differences between exchanging sites (Δδ) have prohibited temperature-dependent rate studies of dynamic processes only observable at rates faster than the NMR timescale (k_{ex} >> Δδ). Here, we apply DNMR techniques involving variable spin-lock frequency $T_{1\rho}$ measurements typically used to measure fast protein dynamics to study the thermodynamics of phosphine association/dissociation in a diamagnetic REE compounds supported by ^{Ar}BiAMP^{tBu}.



The thermodynamic landscape of phosphine coordination/decoordination was studied using solution phase dynamic nuclear magnetic resonance (DNMR) techniques. The rapid equilibrium process induces changes to the ^{31}P resonance when complexes of the type MI(^{Ar}BiAMP^{tBu})(thf)$_3$ are dissolved in THF.

JOINT 4543808

Synthesis, structure, and reactivity of lanthanide and actinide Bis(amido)phosphine complexes

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Lanthanide and actinide complexes featuring coordination to neutral soft phosphine donors are an important class of molecules which serve to develop our understanding of fundamental bonding and covalency in the *f*-block — knowledge which has implications for *f*-element separations science. Bifunctional amido-based ligands featuring pendant phosphine donors have risen as a promising class of mixed-donor ligand framework for facilitating and studying *f*-element–phosphorus interactions. Furthermore, *f*-block complexes bearing more flexible phosphine-containing ligand frameworks may give allowances for phosphorus donor lability, inviting the potential for small molecule activation chemistry through cooperativity between the Lewis acidic metal and the Lewis basic phosphine, akin to intramolecular “frustrated” Lewis pairs (FLPs). While most lanthanides have demonstrated the ability to coordinate neutral phosphine donors, such complexes of the actinide elements have thus far been constrained to uranium and thorium exclusively. Additionally, phosphorous donor complexes of any kind involving the transuranium elements are exceptionally rare, and FLP-type chemistry involving the actinide elements remains poorly explored, with only two known examples reported in literature. This talk will present the application of the dianionic phosphine-containing ligand bis-({3,5-dimethylphenyl}-amidomethyl)-*tert*-butylphosphine (^{Ar}BiAMP^{tBu}) towards the synthesis of a series of trivalent lanthanide (i.e. La, Ce, Pr, Nd, Tm, Lu) and transuranium element (i.e. Np and Pu) complexes [(^{Ar}BiAMP^{tBu})MI(THF)$_3$], each featuring metal–phosphorous linkages. Trends in *f*-element–phosphine bonding will be

discussed with notable differences observed between near-isoradial Ln/An complex pairs in the series. The extension of the ^{Ar}BiAMP^{tBu} ligand to the tetravalent actinide metals U and Th will also be presented. The complexes were characterized by X-ray crystallography, multinuclear NMR spectroscopy, and UV-vis-NIR spectroscopy (where appropriate). The transuranic complexes [(^{Ar}BiAMP^{tBu})AnI(THF)$_3$] (An = Np, Pu) demonstrate the first examples of transuranium element–phosphine interactions, and only the second examples of molecular An–P (An = Np, Pu) bonds of any variety. Reactivity studies of the tetravalent uranium complexes with small molecule substrates will also be presented.

JOINT 4543910

Lessons from actinide chemistry: Towards the synthesis and characterization of hydrotris(3,5-Dimethylpyrazolyl)borate lanthanide(IV) chalcogenido compounds

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Based on our successful actinide work featuring pyrazolyl(borate) ligands, a family of lanthanide(III) complexes supported by the bis(Tp*) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) framework have been synthesized, characterized and studied. Their organometallic benzyl derivatives, Tp*$_2$LnBn, were proven to undergo interesting reactivity, forming the respective lanthanide(IV) terminal chalcogenido species. To understand how these compounds compare to each other, their electronic structure was studied using spectroscopic, structural and computational methods. Where applicable, compounds were characterized by multinuclear NMR spectroscopy, infrared spectroscopy, electronic absorption spectroscopy, and single crystal X-ray crystallography.

JOINT 4544146

Surveying protactinium coordination with X-ray absorption spectroscopy

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With its position on the periodic table, protactinium (Pa) serves as a nexus between transition metal (*d*) and actinide chemistry (5*f*). Even further, Pa holds relevance in both nuclear forensics (i.e., age dating of nuclear materials) and safeguards (i.e., fissile precursor to the formation of U-233). Taken together, a renewed interest in the fundamental chemistry of Pa has developed to inform nonproliferation missions. Despite foundational solution and solid-state studies over the past decade, Pa still remains deeply understudied, in part due to its high radiological toxicity and difficult solubility

properties. As a result, chemical separation schemes to separate and purify Pa remain challenging. To address this knowledge gap, this work probes Pa speciation during separations processes to fulfill needs in nuclear forensics and safeguards. Towards this aim, the bonding environment of Pa-231 was examined in the presence of various ion exchange and extraction chromatography resins used throughout actinide separation and purification processes. X-ray absorption spectroscopy (XAS) served as the tool of choice to interrogate the coordination chemistry and chemical speciation of Pa associated with these resins. Metal L_3-edge XANES and EXAFS measurements assessed the bonding and oxidation state of Pa retained with the resin particles. The results from these studies will aid in evaluating the chemical behavior of Pa in comparison to its periodic neighbors and further progress innovative strategies towards actinide separations and nonproliferation.

JOINT 4544191

Structural evolution and thermophysical properties of molten LiCl-$FeCl_2$ mixtures

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The electrolytic production of Fe from molten halide salt has received renewed interest as a low-energy-input alternative to traditional smelting that reduces reliance on metallurgical coal. However, the underlying liquid structure-property relationships remain underexplored. Here, we present a comprehensive investigation into the structure evolution of molten LiCl-$FeCl_2$ mixtures (5 - 50 mol% $FeCl_2$) using High Energy X-ray Diffraction (HEXRD), Empirical Potential Structure Refinement (EPSR) and complemented by Molecular Dynamics (MD) simulations performed with a Machine Learning Interatomic Potential (MLIP) based on an equivariant message passing MACE foundation model.
The results reveal that as $FeCl_2$ concentration increases, the Fe-Cl-Fe chain structure became more predominant. This structural shift is evidenced by the emergence of a pre-peak in the total structure factor as the $FeCl_2$ concentration reaches 25 mol%. The structure of the mixture is also compared with pure LiCl and pure $FeCl_2$ to elucidate the concentration-dependent coordination environment. Furthermore, MD simulations reveal that this increased polymerization leads to a concomitant increase in viscosity and a decrease in the Fe^{2+} diffusion coefficient. This study provides a structural basis for understanding the electrochemical plating behavior of iron in chloride-based melts, offering critical insights for the optimization of low-energy electrometallurgy.

JOINT 4544384

Reactivity and electronic structures of complexes with the smallest rare-earth element, scandium, in the +2 oxidation state

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The unexpectedly stable scandium(II) metallocene Cp^{ttt}_2Sc ($Cp^{ttt} = C_5H_2{}^tBu_3$) has proven to be a useful platform for discovering new structural types in rare-earth element coordination chemistry. These include the first isolable carbonyl complex of a rare-earth element and a complex containing a terminal side-on $(N=N)^{2-}$ ligand. The stability of these complexes may be attributed to the steric protection offered by the bulky tri-*tert*-butyl cyclopentadienide ligands and the moderate Sc(III)/Sc(II) reduction potential in these complexes. The reactivity of Cp^{ttt}_2Sc with a series of Lewis bases has been studied to generate information factors affecting hyperfine coupling constants of rare-earth metal complexes which is important for the design of new nd^1 qubits. The importance of the tri-*tert*-butyl substitution has been probed by examining the small molecule reactivity and spectroscopy of *tert*-butyl and di-*tert*-butyl cyclopentadienyl analogs.

JOINT 4544393

Coordination environment of rhenium ion in molten salt mixtures

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Understanding the speciation of fission products is necessary for successful deployment of molten salt reactors (MSRs) which is an emerging nuclear reactor technology. In the MSR, molten salt will be used as both fuel solvent and the coolant and heat transfer media. Technetium-99 (Tc) is a high-yield fission product in the nuclear fuel cycle which has a 210,000-year half-life. Understanding the oxidation state of and coordination environment of Tc-99 in molten salts is essential for optimizing nuclear fuel cycles, and especially important for fission product separation technology. Different salt matrices alter the speciation of the solute metal ion. The speciation also depends on temperature which influences kinetics behavior and transport property of metal ions. Rhenium (Re) is used as a non-radioactive surrogate for Tc-99 that offers similar coordination environments and reactivity. We explore speciation of variable oxidation states of rhenium ion in the molten salts LiCl-KCl and $MgCl_2$-KCl. Additionally, rhenium studies will inform future analogous studies with Tc. Here, we present ex-situ X-ray absorption spectroscopy (XAS) studies of the salt mixtures together with UV-Vis measurements to explore oxidation state changes and coordination environment of variable rhenium

oxidation states in different melts. These initial experiments provide the spectroscopic library necessary to identify mixed species produced under high temperature dissolutions.

JOINT 4544591

Translating decades of actinide science toward lanthanide separation: Sequential CMPO and TODGA sorbent systems for rare earth element purification

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Octyl-phenyl-N,N-diisobutyl carbamoylmethyl phosphine oxide (CMPO) and N,N,N′,N′-tetraoctyl diglycolamide (TODGA) are two of the most significant extractants in actinide partitioning chemistry, originally developed for the TRUEX (TRansUranium EXtraction) and ALSEP (Actinide Lanthanide SEParation) processes to recover minor actinides such as Am, Cm, and Np from spent nuclear fuel raffinate. Their bidentate and tridentate O-donor coordination chemistry underpin a generation of solvent extraction and solid-phase separation approaches for the f-block elements (lanthanides and actinides). Yet despite their nuclear origin, systematic solid-phase studies of CMPO and TODGA selectivity across the full lanthanide series in complex, multi-element matrices have remained limited. This gap carries direct implications for actinide science, where lanthanides serve as both chemical analogs and matrix interferences. This work presents two complementary solid-liquid extraction platforms that elucidate CMPO and TODGA coordination behavior with rare-earth elements (REEs) in detail and not previously accessible through solvent extraction alone. CMPO-impregnated silica gel (20 wt%) demonstrates pronounced selectivity for scandium and light REEs (La–Eu) over heavy REEs (Y, Gd–Lu). This behavior is consistent with the larger coordination numbers (9–10) of the lighter lanthanides and their preferred binding geometry with CMPO's bifunctional P=O and C=O donors. Stoichiometric analysis from Langmuir isotherm data supports a predominantly 1:4 REE–CMPO pseudo-complex. In contrast, TODGA-impregnated organosilica (20 wt%) exhibits the opposite selectivity profile, binding heavy REEs (Dy–Lu) with markedly higher affinity through a 1:3 REE-TODGA complex mediated by the tridentate ether-carbonyl backbone. Both sorbents achieve equilibrium via pseudo-second-order chemisorption, follow Langmuir monolayer behavior, and enable water-elutable recovery which eliminates the acid waste streams associated with conventional solvent extraction. More than 80% pure Lu was produced in a single pass through the CMPO column, and this complementary selectivity with TODGA now provides the basis for an integrated tandem sorbent strategy for staged light/heavy REE purification.

JOINT 4544609

Probing the dispersion state of magnetic nanoparticles in molten chloride salts at elevated temperatures using small-angle X-ray and neutron scattering

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Molten salts containing suspended magnetic nanoparticles (MNPs) have gained interest as potential heat transfer and coolant fluids in the energy sector, such as in concentrated solar power and Generation IV nuclear reactors. However, significant challenges for the stability of MNP suspensions arise from the high temperature and ionic nature of molten salts. For example, bare cobalt nanoparticles exhibit substantial instability due to their high surface energy and lack of stabilizing ligands. Destabilization mechanisms include aggregation (driven by diffusion and sintering), sedimentation from density differences, atmospheric oxidation, and ionic adsorption effects, all of which can contribute to nanoparticle loss from suspension. This work explores the use of small-angle X-ray and neutron scattering (SAXS and SANS, respectively) for inspecting the dispersion state of magnetic nanoparticle-doped molten chlorides in situ at high temperatures. Additionally, we use this technique to examine the effect of nanoparticle surface chemistry on the stability of these molten salt ferrofluids. Understanding the mesoscale interactions that govern colloidal stability in chloride nanofluid melts will lead to the development of more effective stabilization strategies for these materials, improving their efficacy as high-performance heat transfer fluids in extreme environments.

JOINT 4544655

Radiation-driven reactivity of Ce^{3+} in molten eutectic LiCl-KCl

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Cerium is a high-yield fission product, and it is often used as an imperfect but useful non-radioactive surrogate for investigating uranium and plutonium chemistry, particularly in the 4+ oxidation state that most other lanthanides cannot access. For both these reasons, it is important to study the chemistry of cerium in molten salts so that their behavior in the extreme, radiation-filled environments of molten salt reactors can be understood. In this study, we investigated the reactivity of Ce^{3+} ion with the primary radiation-induced transient species (the solvated electron $e^-_{(solv)}$, and the dichlorine radical anion $Cl_2^{\bullet-}$) in molten eutectic LiCl-KCl. Rate constants, the spectra of the resulting unconventional transient species, and the kinetics of subsequent delayed chemiluminescence, will be reported.

JOINT 4544960

Connecting molten salt structure to redox speciation and corrosion in chloride melts

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Molten salt composition influences both redox chemistry and corrosion, but the structural origins of these effects remain difficult to resolve. In this work, we combine in-situ synchrotron X-ray spectroscopy, electrochemistry, UV-Vis measurements, and molecular dynamics simulations to examine europium speciation and Ni-20Cr corrosion in LiCl-KCl and KCl-$MgCl_2$ molten salts. The experiments show that increasing $MgCl_2$ content makes the melt more chloroacidic, shifts the Eu(III)/Eu(II) apparent potential to more positive values, and changes the europium oxidation state observed under molten-salt conditions. Time-resolved XANES and XRF measurements further relate europium redox evolution to chromium dissolution during corrosion. A combination of PIM and MACE MD simulations were used to interpret these trends by examining how salt composition changes europium coordination, speciation, chloride sharing, and the local cation environment around Eu. Together, these results show that chloroacidity affects europium solvation and redox behavior, which in turn influences corrosion pathways in molten chloride salts. This work highlights how combining in-situ measurements with simulation can help connect molten salt structure to redox and corrosion behavior.

JOINT 4545030

Supporting the next generation of nuclear & radiochemists at SJSU

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The SJSU Nuclear Targetry Lab is a newly established, accelerator-independent nuclear targetry lab at San José State University. Recently, the nuclear science community has begun addressing the growing demand for well-made targets by re-investing in targetry. This shift is driven by the many currently thriving nuclear facilities,

the ramp-up of FRIB, the retirement of many seasoned targetry professionals, and the closure of several legacy targetry labs. In siting this laboratory at a primarily undergraduate institution (PUI), our team seeks to create exciting opportunities for supporting undergraduate student research in nuclear and radiochemistry through accessible and impactful targetry projects. This effort carries forward the spirit of mentorship and workforce development that Darleane Hoffman championed throughout her career. Current production techniques include physical vapor deposition (PVD), electrochemical deposition including the molecular plating of rare isotopes, cold rolling of ductile materials, solvent casting for deuterated plastic targets, and others. SJSU's target characterization capabilities include microscopy for surface morphology, FTIR / ICP-OES for elemental and chemical analysis, and α-energy loss for film thickness. In this way, we hope to help strengthen and broaden the next generation of nuclear chemists. SJSU is also home to the ACS / DOE Nuclear Chemistry Summer School (NCSS), an intensive, six-week program designed to introduce advanced undergraduate students to the fundamentals of nuclear and radiochemistry through a series of in-classroom lessons and laboratory experiments. The program has operated for over forty years, with both Glenn
Seaborg and Darleane Hoffman being early supporters. To date, we have introduced hundreds of undergraduates to nuclear & radiochemistry with many NCSS graduates now working as nuclear chemists at universities, national laboratories, and in private industry. In this talk, we present SJSU’s ongoing efforts to support, train, and educate the next generation of nuclear & radiochemists. This mission is very much in line with the career of Darleane Hoffman, and her legacy work in setting up the national labs’ Seaborg Centers & Institutions. Personal remembrances of Darleane will also be shared.

JOINT 4545034

Pursuing uranium clusters: Renewing a nuclear legacy at New Mexico State University

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The study of actinide clusters presents the opportunity to study electronic structure, bonding, reactivity, environmental speciation, materials, and more. While recent studies have focused on the use of highly reducing ions to activate small molecules causing clustering in the process, a novel route is by the use of protonolysis/C-C bond formation. Indeed, the benzyl ligand (Bn, $-CH_2C_6H_5$) can be leveraged for its strong basicity to form toluene, a strong nucleophile to form C-E bonds, or as part of a redox reaction to form bibenzyl (Bn_2) + $2e^-$. We have studied the reactivity of $(C_5Me_5)UBn_3$ with substrates featuring N-H and O-H bonds. The products can be classified as tetra- or hexanuclear clusters with three distinct structure types. The clusters follow general formulas of $(C_5Me_5)_4U_4(m_4\text{-}E)(m\text{-}E)_8(H)_x$, **$[U_4E_9]$**, $(C_5Me_5)_6U_6(m_6\text{-}E)(m_3\text{-}E)_8(H)_x$, **$[U_6E_9]$**, and $(C_5Me_5)_6U_6(m_3\text{-}E)_2(m\text{-}E)_{12}(H)_x$, **$[U_6E_{14}]$**, where x ranges from 0–24 dependent on the specific complex. In some cases, monomeric protonolysis products were isolated as

well. Beyond the synthesis, the structural and spectroscopic properties of these complexes will also be discussed. In particular the oxygen analogs may provide insight and comparison to environmental observations. Finally, some time will be spent discussing the nuclear legacy of NMSU-its connection to Darleane Hoffman, and how NMSU plans to move forward in the ramp up of increased nuclear chemistry research.

JOINT 4545231

Holistic understanding of actinide separations: A combined reaction network and interface engineering approach

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Liquid-liquid extraction (LLE) of actinides from complex mixtures is governed by both thermodynamic and kinetic factors. Thermodynamically, actinide ions undergo a series of reactions as they migrate from the bulk aqueous phase to the oil-water interface, generating a diverse population of species that interact with extracting surfactants. At the interface, the heterogeneous local environment significantly alters complexation energetics relative to bulk solution behavior. To capture this complexity, we are mapping the full thermodynamic reaction network of actinides during LLE by combining sampling from classical molecular dynamics with cluster-continuum embedding in heterogeneous dielectric models that represent the oil-water phase boundary. Alongside these thermodynamic considerations, temporal fluctuations of the thin oil-water interfacial film play a critical kinetic role. These fluctuations can directly influence the rate of actinide transfer from the aqueous to organic phase and may become rate-limiting under certain conditions. To quantify their kinetic significance, we apply capillary wave theory, characterizing the timescales of surface wave modes both before and during actinide transport across the interface.

JOINT 4545254

Microfluidic separation and assay of U and Pu for isotopic analysis

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A microfluidic method was developed as a potentially fieldable chemical U and Pu separation and assay platform. The 3D-printed platform performs an initial extraction using a supported liquid membrane (SLM) with tributyl phosphate (TBP) to separate U and Pu from the sample matrix, followed by an immediate acidification and reduction step to convert Pu to Pu(III). A second inline extraction step selectively separates U from Pu(III), enabling downstream radiochemical analysis with integrated alpha spectrometry, gamma spectrometry and UV-VIS. The Pu stream flows to a 3D-printed sample chamber for assay with an alpha spectrometer to measure the $^{238}Pu/^{239,240}Pu$

activity ratio. The U stream is coupled with PAR to form a U-PAR complex and measure total U content using an inline UV-VIS spectrometer. Additionally, the stream is analyzed with a CdTe gamma spectrometer for ^{237}U quantification. Performance was evaluated in presence of four representative matrices, neat solutions, soil, seawater, and cement to assess robustness against matrix effects. Isotopic analysis of matrixed samples with varying U and Pu concentrations were measured with inductively coupled plasma mass spectrometry (ICP-MS) to validate fixed laboratory measurements with reduced sample preparation time using the SLM method. The method achieved recoveries greater than 90% for U and greater than 40% for Pu. Total sample-to-result processing time is under one working day. Ongoing efforts to improve Pu recovery and purity using redox control will be discussed.

JOINT 4545563

Effects of niobium on phase stability and microstructure in uranium carbide fuel

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Uranium carbide (UC) has long been considered a candidate fuel for advanced reactor concepts because of its favorable thermophysical and neutronic attributes. However, UC is known to readily oxidize in air and oxygen containing atmospheres. Uranium carbide (UC) ceramic and ceramic composite materials, containing nominal 5, 10, 15, and 20 at% Nb were fabricated and heat treated for 25 days at 1000 °C to elucidate phase constitution and microstructure probing a possible miscibility gap. Powder X-ray distraction (PXRD) with Rietveld refinement shows systematic shifts of face centered cubic (FCC) UC reflections to higher 2θ with increasing Nb. Secondary phases increase with increasing Nb content, where
XRD detects α-U only at higher Nb contents, however SEM indicates it is present in all samples. Electron probe microanalysis (EPMA) reveals pronounced Nb-enriched grain centers and Nb-depleted regions near boundaries. Grain-boundary regions are U-enriched and C-depleted across all compositions. After annealing, Nb distributions homogenize and a secondary Nb-rich FCC carbide population appears in the 20 at% Nb alloy as discrete features within grain-boundary regions alongside a U-rich boundary phase. Scheil solidification simulations reproduce the observed coring behavior with the severity of segregation decreasing as nominal Nb increases. CALPHAD equilibrium calculations for 20 at% Nb at 1000°C predict coexistence the BCC phase with FCC miscibility gap, providing a thermodynamic basis for the experimentally observed U-rich metallic boundary constituent and two compositionally distinct FCC carbide populations after annealing. This is evidence of the initial formation of the FCC miscibility gap in the (U,Nb)C system at 1000°C.

JOINT 4545730

Synthesis, structural chemistry, and properties of tetravalent actinide complexes and clusters

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Speciation underpins the chemical behavior of the actinides, and is governed not only by metal ion oxidation state, but also other factors such as solvation, element-specific redox chemistry, and outer coordination sphere effects. Yet actinide speciation, solid-state structure, and properties remain difficult to predict due to persistent knowledge gaps. To address this need, systematic investigations into the synthesis, structural characterization, and properties of Ce, Th, U, and Pu solid-state phases have been undertaken, with emphasis on elucidating the effects of ligand identity, counterion, and solvent on species formation, stabilization, and reactivity. Studies spanning aqueous halide, nitrate, and carboxylate donor ligand systems have revealed that outer coordination sphere interactions play a decisive role in tuning structural chemistry, from discrete complexes to polynuclear clusters, as well as reactivity. Parallel investigations into aqueous and nonaqueous systems have further highlighted the importance of solvent identity, while more recent work has sought to establish the structural and compositional relationships between metal-oxo clusters and the size, shape, morphology, and assembly of AnO_2 nanoparticles.

JOINT 4545827

Exploring UCl_3-bearing molten salts with neutron scattering and Raman spectroscopy

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We aim to better understand the local structure of actinide–molten chloride salts using neutron scattering and complementary spectroscopic techniques, with the broader goal of linking atomic-scale structure to thermophysical properties. Neutron total scattering measurements collected at the NOMAD instrument at the Spallation Neutron Source (SNS) have enabled pair distribution function (PDF) analysis, providing insight into short- and intermediate-range order in NaCl, UCl_3, and the UCl_3–NaCl eutectic as a function of temperature. Building on our initial measurements, recent experiments have extended the temperature range examined toward a more comprehensive view of structural evolution in these systems. In parallel, we employ Raman spectroscopy as a complementary probe of local coordination environments and bonding in the melt. This talk will highlight recent progress, initial observations of temperature-dependent structure, and ongoing efforts to integrate neutron and spectroscopic data to advance understanding of actinide molten salt systems.

JOINT 4545867

Radiochemical recovery and separation of ^{244}Pu from legacy mark 18A targets, resource utilization and talent development with actinides

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The Mark 18A Target Material Recovery Program, established by the US DOE, was initiated to recover these strategically important isotopes to support nuclear forensic science, heavy element production, and national research priorities. The recovery effort requires the integration of advanced radiochemical separations designed to isolate plutonium fractions enriched in ^{244}Pu while simultaneously managing complex mixtures of actinides, fission products, and target matrix materials. The work involves dissolution chemistry, oxidation state control, selective precipitation, solvent extraction, ion exchange, and purification methodologies developed to achieve isotopic and chemical purity requirements. Processing activities leverage infrastructure and expertise at the Savannah River National Laboratory for target dissolution and initial separations, followed by material stabilization and long term storage capabilities at Oak Ridge National Laboratory. Beyond isotope recovery, the program provides a unique platform for the advancement of applied radiochemistry. The processing of high activity legacy materials requires refinement of actinide speciation knowledge, development of separation flowsheets, and demonstration of process scale radiochemical operations. These activities provide an important framework for training the next generation of radiochemists through university participation. Students engage in research addressing actinide separation science, analytical characterization, and process modeling, while gaining experience in handling complex nuclear materials and understanding the integration of radiochemistry with national mission objectives. The recovery of ^{244}Pu from Mark 18A targets demonstrates the continued relevance of radiochemical science in addressing contemporary nuclear challenges. The project illustrates how legacy nuclear materials can be transformed into critical national resources while simultaneously supporting education, talent development, and technological innovation in actinide chemistry.

JOINT 4547120 - Withdrawn

JOINT 4547365

Actinide separations tailored for Californium-252 and Promethium-147 campaigns

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Californium-252, plutonium-238, and promethium-147 campaigns are the main hot cell production activities conducted at the Radiochemical Engineering Development Center at Oak Ridge National Laboratory (ORNL). Each campaign comprises many process steps that had to be developed or improved upon to optimize the product quality or quantity. Californium campaigns are conducted every other year to produce nominally

~100 mg of californium-252, tens of milligrams of berkelium-249, and micrograms of einsteinium. Produced from the irradiation of curium targets in the High Flux Isotope Reactor, californium requires several processing steps to be obtained in a purity adequate for wire fabrication. Similarly, harvested during the plutonium-238 production campaigns and present in the waste solutions, promethium-147 is also produced at ORNL, which is the sole source of this isotope worldwide. In all cases, separation processes are tailored to obtain the desired isotopes with the target purity while meeting tight schedules. Overview of the processes and on-going improvements will be presented.

JOINT 4548455

Pulse radiolysis and DFT studies of sulfur-containing soft donor chelator candidates for the selective separation of trivalent actinides from lanthanides

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Soft-donor chelators containing sulfur donor atoms play an important role in the selective separation of trivalent actinides from lanthanides in advanced nuclear fuel recycling. Dithiophosphinic acids from the Cyanex class of extractants exhibit particularly high actinide–lanthanide selectivity, but their radiation stability and degradation pathways remain incompletely understood. Because many of these extractants are not readily accessible in simplified forms suitable for mechanistic studies, model compounds and structurally related soft-donor ligands were investigated to gain insight into radiation-induced transformation pathways.

In this work, we examined the radiation chemistry of bidentate dithiophosphates, their monothiophosphate analogs, and a recently proposed class of hydrophilic soft-donor ligands, 2,2′-thiodiacetic acid (TDA) and 2,5-thiophene dicarboxylic acid (TPA), under anoxic aqueous conditions. These structurally diverse ligands were selected as model systems and alternatives to Cyanex-type extractants. The radiation-induced transformations were studied using pulse radiolysis coupled with transient absorption (TA), transient conductivity (TC), and time-resolved resonance Raman (TRRR) spectroscopy across the pH range 4–10. Experimental observations were complemented by (TD)DFT calculations using the ωB97X-D/aug-cc-pVTZ method with IEFPCM solvation.

These studies were designed to characterize the early intermediates formed during indirect oxidative and reductive stages of ionizing radiation interactions with these chelators in aqueous solution. Rate constants for reactions with hydrated electrons, OH radicals, and one-electron oxidants were determined using TA spectroscopy. TC measurements provided insight into the pH-dependent protonation equilibria of transient intermediates, while TRRR spectroscopy was employed to obtain vibrational fingerprints of species exhibiting strong absorption bands. Computational results were used to

determine optimized geometries, predict optical absorption and vibrational spectra, assist in spectral assignments, and evaluate the regioselectivity of OH radical attack.