NUCL 4077146 - Withdrawn

NUCL 4085120

Nuclide symmetry, stability, and cosmic abundance

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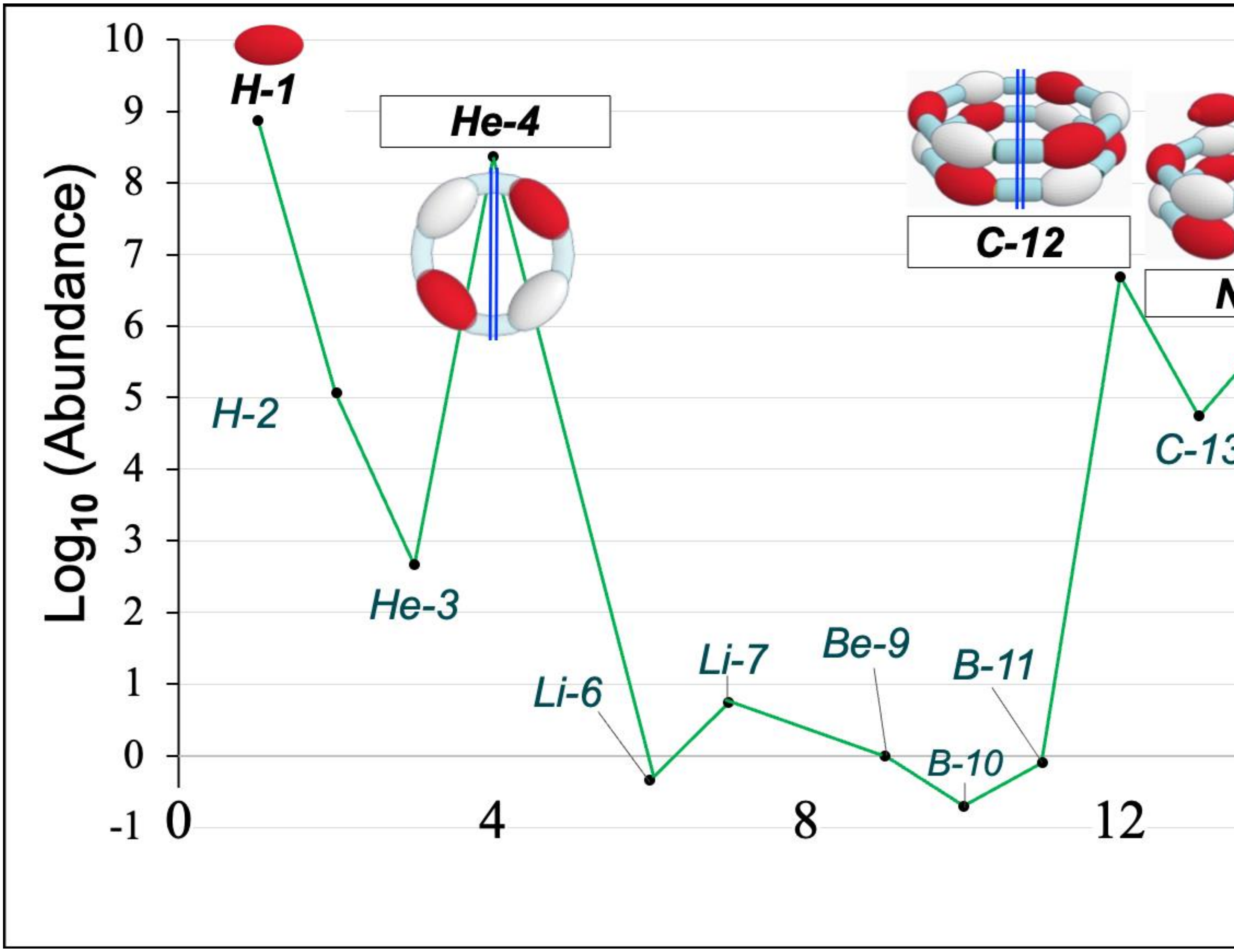
Protons and neutrons (nucleons) are baryons, the smallest particles with measurable size. The proton (^{1}H) constitutes 74% of ordinary baryonic matter in the universe. Within the remaining 26% of ordinary matter, protons tend to combine with neutrons in a 1:1 ratio. The stability conferred by the equality (or symmetry) of proton/neutron numbers within light abundant isotopes contrasts the relatively scares heavier isotopes, which tend to require an increasing ratio of neutrons to protons for stability. The structural basis of the numeric symmetry of nucleons with light nuclides, and its relationship to cosmic abundance, provide the basis for this investigation. The causal relationship between structural symmetry and stability is axiomatic throughout the sciences and engineering but has yet to be applied within the nucleonic realm. We propose a self-consistent model in which the symmetry in proton/neutron numbers manifests in structural symmetry as a basis for nuclide stability and abundance. In the proposed model, protons bound to neutrons alternate within the nucleus. This naturally produces equal numbers of each. Recent analyses of ground-state intrinsic quadrupole moments have determined a prolate shape for nucleons. From alternating prolate-shaped nucleons we predict unique structures for all stable isotopes through argon-36 consistent with accepted experimental charge radii. **Model nuclides demonstrating structural symmetry correspond perfectly to the most abundant nuclides in the cosmos.** Conversely, the rarest light nuclides *categorically demonstrate structural asymmetry!* We conclude that structural stability arising from symmetry is reflected in the unusual abundance of the eight most abundant light nuclides ^{4}He, ^{12}C, ^{14}N, ^{16}O, ^{20}Ne, ^{24}Mg, ^{28}Si, and ^{32}S, all of which contain equal numbers of protons and neutrons, and together comprise 99% of all polynucleonic matter. Each of these demonstrates a plane of symmetry, as shown in the attached image, a structural feature notably absent in the remaining stable light nuclides. In nucleosynthesis, the hypothesis that nucleons must alternate predicts the most stable light nuclides and radius predictions arising from elucidated alternating nucleon structures correlate nearly perfectly ($r(31)=.98$, $p<.001$) with accepted experimental radii.



NUCL 4087530

Adventures with Ken: Graduate school and beyond

***Jenifer Shafer**, jshafer@mines.edu. Colorado School of Mines, Golden, Colorado, United States*

Ken has been an exceptional career mentor and advisor. This presentation will cover adventures in Hanford, TALSPEAK, chromatography, hexavalent americium, amongst others. The actinide chemistry world has been well served by Ken's service and leadership over the decades.

NUCL 4087550

Modeling corrosion product migration and deposition in PWRs: A comprehensive approach

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In PWRs, the extensive contact area between the primary circuit coolant and structural materials facilitates the release of ionic and particulate corrosion products into the coolant. Some of the corrosion products deposited on the surfaces of fuel elements undergo activation. These activated corrosion products then migrate and deposit within the primary circuit, rendering the steam generator radioactive. This process impacts the operation, maintenance, and decommissioning of the reactor.

An integrated model for the simulation and analysis of corrosion product migration and deposition behaviors within the primary circuit of pressurized water reactors was developed and validated in this research. The effects of mass transfer processes and subcooled nucleate boiling on the deposition and release of both ionic and particulate corrosion products were incorporated. Furthermore, consideration was given to the diffusion of corrosion products within the coolant, as well as to convective mass transfer and phase transitions.

The model's precision was corroborated through juxtaposition with actual measurement data from the Callaway Nuclear Power Plant core. It was observed that concentrations of ionic corrosion products within the reactor's coolant experienced a marked decrease across both boiling and non-boiling zones of the core, whereas subcooled boiling exhibited negligible influence on ionic concentrations. Furthermore, the density of particulate corrosion products within the primary circuit's coolant demonstrated a degree of stability, albeit being substantially influenced by nucleate boiling—most notably within the subcooled nucleate boiling region situated at the core's upper section. The investigation further revealed that corrosion product deposition within the steam generator surpassed that in other sections, attributed primarily to its extensive heat transfer surface area. Additionally, alterations in the coolant's flow rate were found to significantly impact deposition caused by nucleate boiling, with an increase in flow rate markedly diminishing such deposition.

This research furnishes not merely a dependable instrument for the simulation of corrosion product migration and deposition within the primary circuit of reactor systems but also serves as a significant point of reference for the design, operation, and enhancement of safety and reliability in nuclear energy systems.

NUCL 4087642

Novel gamma secretase PET probe for Alzheimer's disease imaging

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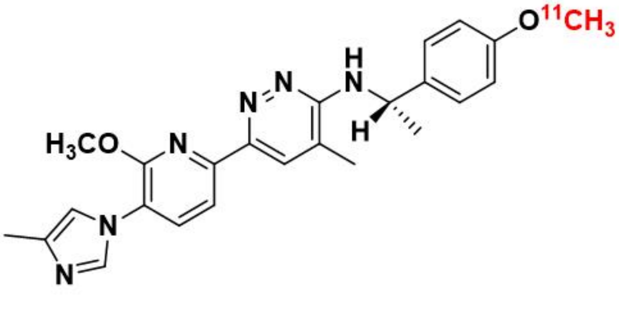
The increase in γ-secretase activity in the brain of Alzheimer disease (AD) patients and animal models of AD position this enzyme as a potential biomarker of the disease.

However, measuring γ-secretase activity both *in vitro* and *in vivo* presents challenges due to the limited fraction of catalytically active γ-secretase complexes and the lack of correlation between enzymatic activity and the quantity of the catalytic subunit, presenilin. We radiolabeled an analog of SGSM-15606, referred to as **[^{11}C]1** (IC_{50} of $A\beta_{42}$ = 6.5 nM), with carbon-11 and evaluated its potential as a γ-secretase PET probe in a three-stage validation process. Initially, we assessed the biodistribution, metabolism, and blood brain barrier (BBB) crossing capacity of **[^{11}C]1** in wild type (WT) mice and simultaneously gauged its potential to detect γ-secretase levels in AD mouse models through PET-CT imaging studies. Secondly, we undertook preliminary PET-MR imaging studies with **[^{11}C]1** in nonhuman primates (NHPs) to evaluate its brain permeability, regional distribution, and specific washout kinetics. Our findings indicate that using **[^{11}C]1** for PET neuroimaging effectively visualizes γ-secretase in brain regions of preclinical animals, underscoring its significant potential for clinical studies in AD patients.

[^{11}C]1 was produced in sufficient radiochemical yield and molar activity for the use in PET imaging. Metabolism and biodistribution studies confirmed sufficient stability in vivo, the ability of **[^{11}C]1** to cross the blood brain barrier (BBB) and slow washout from the brain. Blocking studies confirmed specificity of the binding. The PET-MR imaging in NHPs demonstrated high brain uptake (0.5 - 1.5 in SUV). The kinetic modeling results showed **[^{11}C]1** was expressed across different brain regions, and the levels in hippocampus and cortex displayed high levels and also with reduced VT in blocking study in brain regions, indicating the specific binding of **[^{11}C]1**. The imaging data in NHPs demonstrated that **[^{11}C]1** has a great potential for future study in AD patients. These results suggested that PET neuroimaging using **[^{11}C]1** allowed us to visualize γ-secretase in brain.



[^{11}C]1

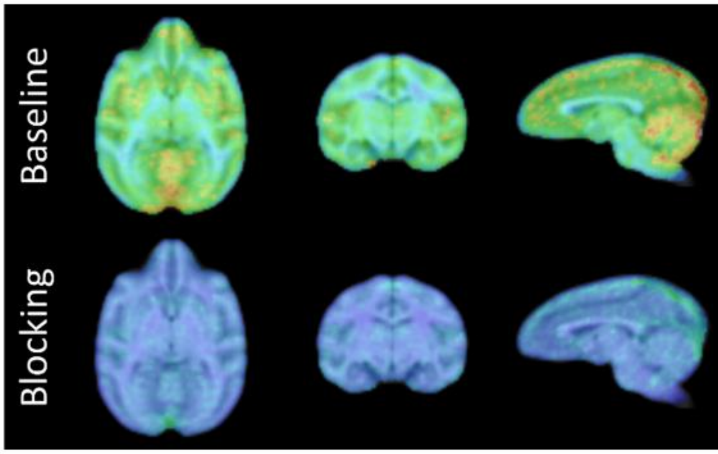


Figure. Chemical structure of [^{11}C]1 and NHP PET imaging in NHP.

NUCL 4087721

Raman spectroscopy and multivariate chemometrics for monitoring uranyl nitrate crystallizations

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One of the greatest challenges facing the nuclear power industry is achieving a sustainable nuclear fuel cycle by implementing the efficient recycling of used nuclear fuel (UNF). It is critical that the processes used to recycle UNF maximize energy utilization of the fuel while curtailing the waste destined for geological storage and addressing proliferation concerns. A single-step technology for recycling UNF, which can recover the bulk of U and other transuranic (TRU) species as the first step after dissolution in nitric acid media, would be an elegant and efficient approach. By leveraging the similar geometry and charge of the hexavalent actinides U(VI), Np(VI), Pu(VI), and Am(VI), we have developed an effective cocrystallization approach for the removal of TRUs that produce crystalline solid solutions. To support this work, chemometric analysis of U-based solutions using Raman spectroscopy directly quantified uranium(VI) from 10 – 300 g U/L and nitric acid 0.6 – 6 M concentrations. This demonstrated a feasible approach amenable to the remote and rapid analysis of processing solutions for production-oriented applications.

NUCL 4087737

Development of solution combustion synthesis capabilities at Oak Ridge National Laboratory

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Solution combustion synthesis is a unique method that offers a simple, rapid, and energy-efficient means to produce nanoscale materials. Taking advantage of the highly exothermic oxidation-reduction reactions of metal nitrates and organic reductants, these self-propagating reactions produce oxide, metallic, and alloyed products in seconds. Since initial reports in the mid-1980s, the use of solution combustion synthesis has produced materials spanning the periodic table. Within the past decade, research has pushed the field further into the realm of actinide materials with an emphasis on the study of uranium oxides. Recently, we have developed bench-scale reaction capabilities for the continued study and innovation of actinide oxide combustion syntheses. Current work is focused on the use of solution combustion synthesis to incorporate transition metal dopants in U_3O_8 for nuclear forensics research, investigating whether the introduction of elemental dopants (or taggants) produces a useful forensics signature.

Taggants of interest include Fe, Ni, and Cr, which are incorporated into a uranyl nitrate–glycine combustion system as their respective nitrate salts or through previously tagged uranyl nitrate. Subsequent sintering, hydrolysis and humidity experiments aim to evaluate the persistence of taggants within the material.

NUCL 4089774

Radiolytic generation of nitric acid in compromised nuclear fuel storage canisters

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Exploration of extended dry storage options for aluminum-clad spent nuclear fuel (ASNF) requires a full understanding of any adverse conditions that may occur over the storage lifetime of 50+ years. ASNF is intended to be dried and sealed in stainless-steel canisters backfilled with a helium atmosphere. Previous research has demonstrated that this storage method can be safely extended beyond 50 years. However, for copper-coated steel containers, the radiolysis of moist air was found to produce a significant amount of nitric acid (HNO_3) that contributed to ~9.4 μm of corrosion propagation over the permanent storage time of the canisters. This type of corrosion may occur under non-ideal extended dry storage conditions, such as in the presence of residual air or if the integrity of a storage canister is compromised. The formation of HNO_3 in these containers could potentially dissolve any protective corrosion layers on the ASNF cladding, leading to the exposure of bare aluminum metal, localized corrosion propagation, and ultimately the exposure of radioactive materials to the atmosphere. This research focuses on evaluating the impacts of such non-ideal conditions, specifically the gamma radiation-induced interactions of corroded aluminum coupons—ASNF cladding surrogates—in air and moisture containing environments. Backfill atmospheres of air, nitrogen, and helium at 0, 50, and 95% relative humidity were tested to determine their influence over the yield, suite, and distribution of HNO_3 and nitrogen oxide (NO_x) radiolysis products as a function of absorbed dose ($\leq$ 15 MGy). The total amount of HNO_3 generated in each sample was quantified by ion chromatography, while infrared spectroscopy and gas chromatography were used to measure each sample's headspace NO_x content. Scanning electron microscopy was also used to reveal changes in the morphology of the pre-corroded coupons after exposure to radiation and HNO_3. Under these investigated conditions, the yield of HNO_3/NO_x increased in the presence of humid air environments with absorbed gamma dose. The possibility of a steady-state HNO_3 yield, and the impact of a pre-corroded aluminum coupon on the yield were also investigated. These new data will be used to advanced and validate complementary computational modeling capabilities for the quantitative prediction of radiation-induced consequences under real-world extended dry storage scenarios.

NUCL 4089862

3D-printed microfluidic supported-liquid membrane systems for rare-earth element fission product separations relevant to nuclear forensics

Jake Bence[1], *bence1@llnl.gov, Nic Cicchetti*[2,1], *Narek Gharibyan*[1], *Kevin Glennon*[1], *Tashi Parsons-Davis*[1], *Jennifer Shusterman*[1], *Hector Valdovinos-Uribe*[1]. *(1) Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory Nuclear and Chemical Sciences Division, Livermore, California, United States(2) University of Nevada Las Vegas, Las Vegas, Nevada, United States*

Field-deployable, rapid chemical separation methods are advantageous for nuclear forensics in post-detonation scenarios to assay debris quickly compared to lab-based approaches. To accomplish this, the team at LLNL has developed a 3D-printed module used for microfluidic-scale separation chemistry based on a supported-liquid membrane system. This system has been previously demonstrated for reliable separation and characterization of U and Pu isotope ratios relevant to nuclear forensics. Current efforts aimed at the separation of trace rare-earth elements (REE) fission products purified from the U, Pu, and other fission products, as well as relevant sample matrices will be discussed.

NUCL 4090084

Solvent extraction behavior of iron(III) and tributyl phosphate in aqueous acidic media: Applications in nuclear forensic analysis

Madeleine Forbes[1], *mforbesmail@gmail.com, Penafrancia Monte*[2], *Ramsey Salcedo*[2], *Benjamin Burton-Pye*[2], *Lynn C. Francesconi*[2], *Deborah A. Penchoff*[3], *Nathalie A. Wall*[1]. *(1) University of Florida, Gainesville, Florida, United States(2) Hunter College, New York, New York, United States(3) The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States*

The authors want to recognize Kenneth Nash and his impact on separation chemistry. His pioneering efforts will continue to leave a legacy for future scientists. Nuclear forensic analysis requires elemental separation to quantify sample composition. Post-detonation debris may contain transition metals from building materials (i.e., concrete, steel, cement). Current separation techniques for nuclear forensic analysis include liquid-liquid extraction and ion exchange. Most separation techniques for actinides and lanthanides were developed for the civilian nuclear fuel cycle. However, transition metals present in post-detonation debris can interfere with f-element separations. For example, Eichrom’s TRU resin features the molecule tributyl phosphate (TBP) that selectively extracts Am(III) but also extracts Fe(III) from a highly acidic solution. A fundamental understanding of the extraction of transition metal elements will better inform radiochemical separation schemes and improve the timeliness of forensic sample analysis. Here, we will present results for the extraction of Fe(III) by TBP in nitrate and chloride media. Experimental results will complement computationally driven results to provide an in-depth understanding of coordination environments and complexation mechanisms. Batch solvent extraction experiments were conducted using

radioanalytical methods. Equal volumes of pre-equilibrated organic and aqueous phases were added to glass vials and spiked with radiotracer Fe-55/59. Vials were mixed to reach phase equilibrium. Aliquots of each phase were measured by liquid scintillation counting. The distribution ratio was determined as the concentration of metal species in the organic phase relative to the aqueous phase. We quantified the influence of extraction conditions, such as extractant concentration, acid concentration, salt concentration, time, temperature, and shaking method. Computational modeling was performed using electronic structure theory calculations and artificial intelligence tools. Elemental X-ray Absorption Spectroscopy (EXAFS) provided information on the extracted Fe(III) coordination environment. We quantified the stoichiometry of the extraction equilibria, the thermodynamics, and kinetics of the extraction.

NUCL 4090544

Formation of uranyl peroxide compounds via dissolution of studtite in ionic liquids

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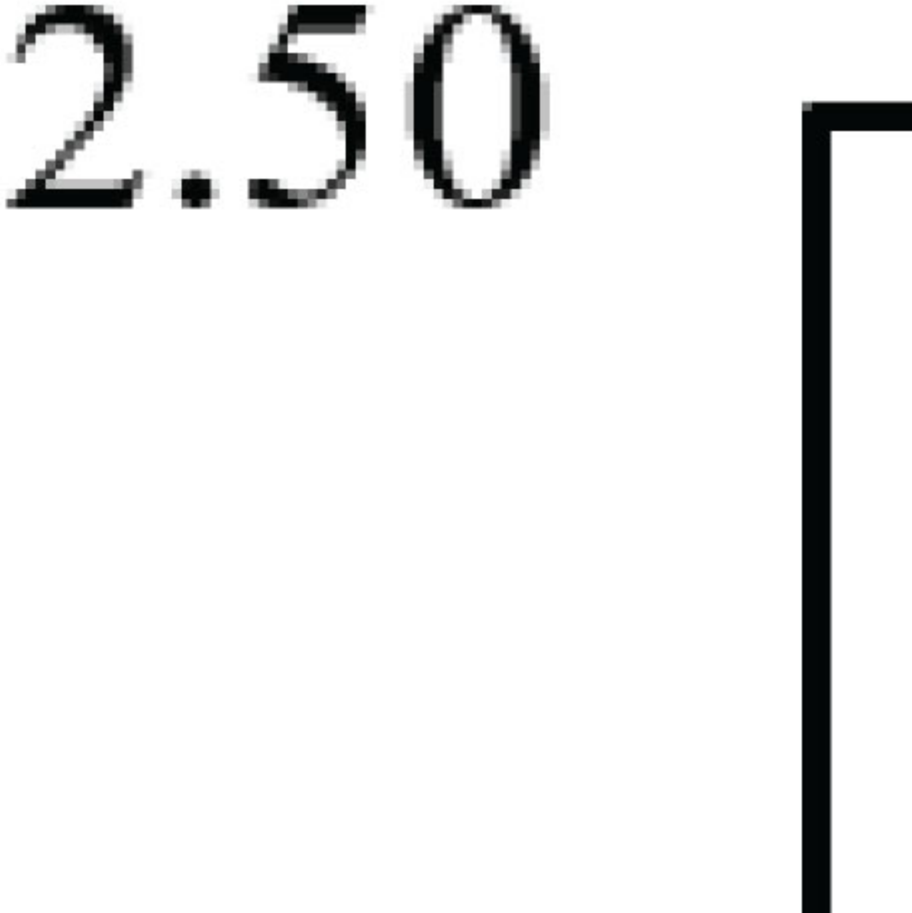
The uranyl peroxide mineral studtite plays an important role in the nuclear fuel cycle and has thus been a major component in research involving the synthesis of novel uranyl peroxide compounds, such as uranyl peroxide cage clusters (UPCs). The synthesis of uranyl peroxide species typically involves the decomposition of studtite in an alkaline, aqueous system using alkali metal hydroxides, and the resulting anionic uranyl peroxide species are charge-balanced by the alkali cations associated with the base used in the synthesis. Preliminary work has shown that studtite dissolves in a wide variety of ionic liquids, eliminating the need for a strong base and the presence of alkali metals in uranyl peroxide syntheses. The dissolution of studtite in ionic liquids allows for the formation of novel uranyl peroxide species with various terminating and bridging ligands, the incorporation of lanthanide cations in UPC structures, and an alternative synthesis technique for previously reported UPCs.

NUCL 4090783

Novel approach to calculate limit of detection of low-level neptunium and plutonium analysis by thermal ionization mass spectrometry multi-ion counter total evaporation (TIMS-MICTE)

will S. Fisher[1], *wfisher@lanl.gov, Jeremy Inglis*[1], *Rebecca Foley*[1], *Zsuzsanna Macsik*[1], *Joel Maassen*[2]. *(1) Chemistry-Nuclear Radiochemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States(2) Chemistry Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Environmental sample analysis is a pillar of the modern international nuclear safeguards and nuclear nonproliferation missions, and frequently requires ultra-trace actinide isotopic and assay measurements of elements like plutonium (Pu) and neptunium (Np). At the lowest analyte concentrations, measurements are performed using highly sensitive thermal ionization mass spectrometry (TIMS) techniques, which have been shown to detect Pu and Np at the femtogram level. At such low analyte concentrations there is a persistent concern about accurately defining the lowest quantity or concentration of a component that can be reliably detected, otherwise called the limit of detection (LOD). Here we report on efforts to calculate robust LOD values for both Pu and Np measurements by thermal ionization mass spectrometry multiple ion-counting total evaporation (TIMS-MICTE). To achieve this, representative environmental samples of Pu and Np were used to assess the full method detection limits (MDL); including ashing, dissolution, purification, chemical recovery, and mass spectrometry analysis. Single femtogram level $^{242-239}$Pu and ^{237}Np from CRM126A (Pu) and SRM 4341a[1](^{237}Np) were used for the tests and employed to calculate LOD values using several common approaches. In addition, we report on efforts to develop a TIMS specific internal LOD approach and compare it against Environmental Protecftion Agency MDL, the international standard LOD, and an uncertainty-based approach LOD. The internal TIMS LOD resulted in a ^{239}Pu detection limit of 0.154 fg and 0.259 fg for ^{237}Np. We believe this firmly establishes the detection limits that can be achieved for Pu and Np by the TIMS-MICTE technique.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Comparison of individual 1 fg swipe assay results (K=2 uncertainty) and internal TIMS LOD equation.

NUCL 4092164

Evaluation of SBMOF-1 and activated charcoal as potential adsorbents for collection of radioactive noble gases from FRIB's effluent gas streams

Vladyslav Bodnar[1,3], *bodnar@frib.msu.edu, Ate Visser*[2], *Xyla Kalman*[3], *Wesley Walker*[3], *Sung Ho Kim*[2], *Chloe Kleinfeldt*[1,3], *Chirag Vyas*[3], *Gregory Severin*[1,3]. *(1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Lawrence Livermore National Laboratory, Livermore, California, United States(3) Facility for Rare Isotope Beams, Michigan State University, East Lansing, Michigan, United States*

The Facility for Rare Isotope Beams (FRIB) is a unique accelerator laboratory complex for research in nuclear science. It will produce significant amounts of various by-product radionuclides of interest in nuclear medicine, plant biology, and stockpile stewardship. While most of the produced by-product radionuclides are aqueous, several of them will be present in the gaseous state. This project focuses on evaluation of different sorbent materials for collection of ^{76}Kr and ^{77}Kr radioisotopes whose radiobromine decay products are useful for preclinical nuclear medicine. To perform volumetric adsorption studies close to actual "harvesting" conditions, a closed-loop gas system was designed and constructed. The system includes temperature and pressure monitoring and real-time gas concentration measurements via quadrupole mass spectrometry. The effect of temperature on the adsorption of Kr on SBMOF-1 metal organic framework and activated charcoal pellets was investigated at temperatures ranging from 273 K down to 192 K. Both sorbents showed increasing adsorption with decreasing temperatures, ranging from 34.9 mmol/g/bar at 195 K to 6.2 mmol/g/bar at 258K for SBMOF-1, and 35.1 mmo/g/bar at 192 K to 3.9 mmol/g/bar at 250 K for activated charcoal. Preliminary analysis shows the enthalpy of adsorption for Kr with SBMOF-1 and activated charcoal pellets to be –11.6 kJ/mol and -14.3 kJ/mol, respectively. These data are necessary to determine optimal material and thermal conditions to achieve efficient collection of noble gases from the effluent streams at FRIB.

NUCL 4092164

Evaluation of SBMOF-1 and activated charcoal as potential adsorbents for collection of radioactive noble gases from FRIB's effluent gas streams

Vladyslav Bodnar[1,3], *bodnar@frib.msu.edu, Ate Visser*[2], *Xyla Kalman*[3], *Wesley Walker*[3], *Sung Ho Kim*[2], *Chloe Kleinfeldt*[1,3], *Chirag Vyas*[3], *Gregory Severin*[1,3]. *(1) Chemistry, Michigan State University, East Lansing, Michigan, United States(2) Lawrence Livermore National Laboratory, Livermore, California, United States(3)*

Facility for Rare Isotope Beams, Michigan State University, East Lansing, Michigan, United States

The Facility for Rare Isotope Beams (FRIB) is a unique accelerator laboratory complex for research in nuclear science. It will produce significant amounts of various by-product radionuclides of interest in nuclear medicine, plant biology, and stockpile stewardship. While most of the produced by-product radionuclides are aqueous, several of them will be present in the gaseous state. This project focuses on evaluation of different sorbent materials for collection of ^{76}Kr and ^{77}Kr radioisotopes whose radiobromine decay products are useful for preclinical nuclear medicine. To perform volumetric adsorption studies close to actual “harvesting” conditions, a closed-loop gas system was designed and constructed. The system includes temperature and pressure monitoring and real-time gas concentration measurements via quadrupole mass spectrometry. The effect of temperature on the adsorption of Kr on SBMOF-1 metal organic framework and activated charcoal pellets was investigated at temperatures ranging from 273 K down to 192 K. Both sorbents showed increasing adsorption with decreasing temperatures, ranging from 34.9 mmol/g/bar at 195 K to 6.2 mmol/g/bar at 258K for SBMOF-1, and 35.1 mmo/g/bar at 192 K to 3.9 mmol/g/bar at 250 K for activated charcoal. Preliminary analysis shows the enthalpy of adsorption for Kr with SBMOF-1 and activated charcoal pellets to be –11.6 kJ/mol and -14.3 kJ/mol, respectively. These data are necessary to determine optimal material and thermal conditions to achieve efficient collection of noble gases from the effluent streams at FRIB.

NUCL 4092718 - Withdrawn

NUCL 4092718 - Withdrawn

NUCL 4092849

EPR evaluation of ligands' radiation stability in nuclear waste separation

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Radical intermediates arising from key ligands in nuclear waste management, including di-n-Butyl N,N-Diethylcarbamoylphosphonate (DBDECP), N,N-Bis(2-ethylhexyl)butyramide (DEHBA), dioctyl phosphate (DOP), tributyl phosphate (TBP), N,N,N,N-tetraoctyl diglycolamide (TODGA), and octyl(phenyl)-N,N-diiso-butylcarbamoylmetliylphosphine oxide (CMPO), were systematically investigated using Electron Paramagnetic Resonance (EPR) spectroscopy at 77 K. Across all ligands, carbon-centered radicals originating from alkyl or amide compounds were identified in the experimental spectra (see Figure 1). Spectral assignments were performed by advanced quantum chemical calculations at the DFT(B3LYP)/L1a_3 level of theory, enabling the determination of approximate radical conformations. Kinetic measurements revealed a linear accumulation of radicals up to an irradiation dose of 1 kGy. Interestingly, the relative yield of stabilized radicals in organic phosphates (TBP, DOP)

was observed to be approximately three times higher compared to amide (DEHBA) or carbamoyl phosphonate (DBDECP) samples. This proposed method for evaluating radiation stability demonstrates potential applicability to a wide range of compounds or mixtures relevant to nuclear waste separation, as well as other substances of significant importance in related fields.

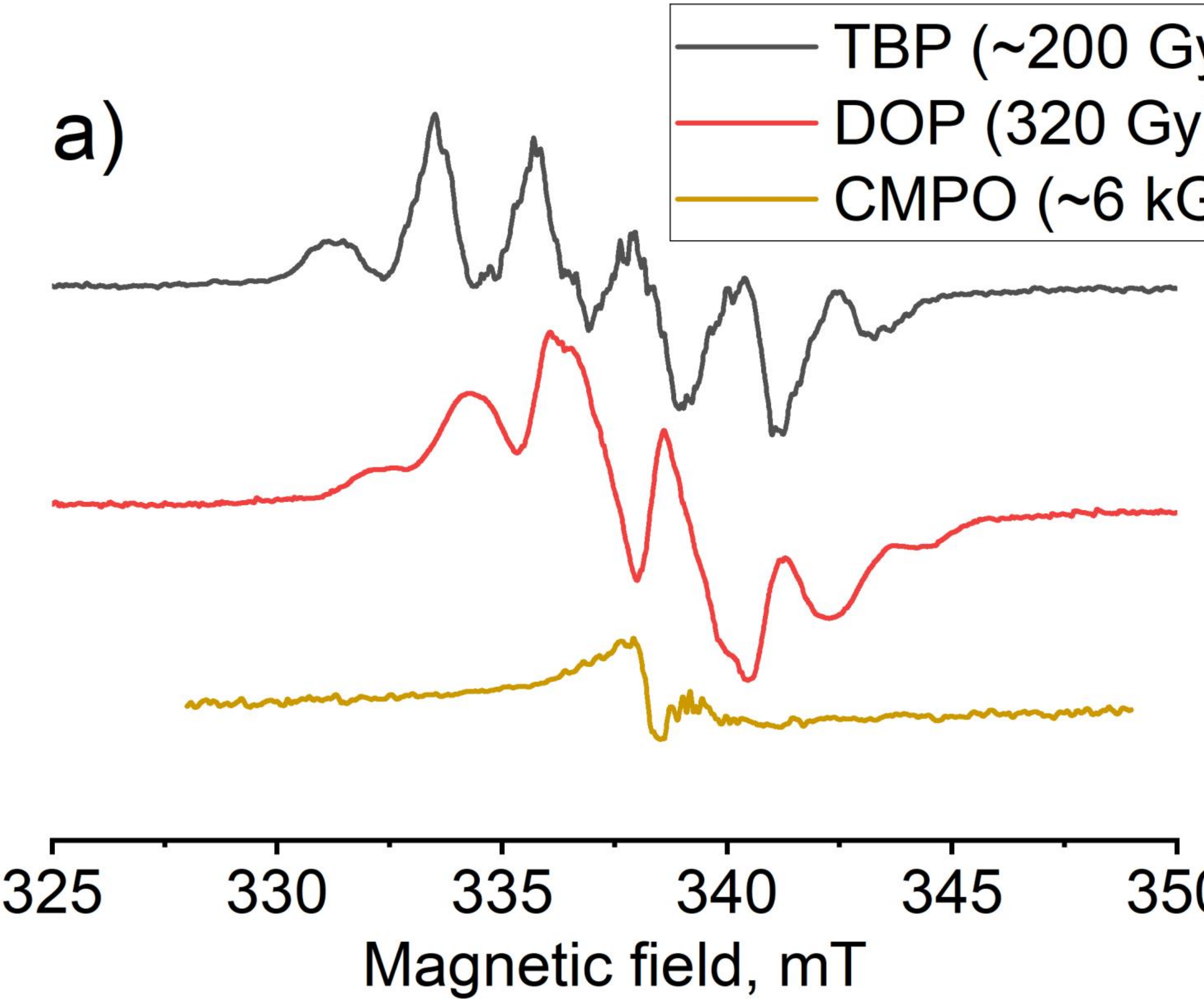

Figure 1. EPR spectra of irradiated TBP, DOP, CMPO (a) and DEHBA, DBDECP, TODGA (b) at 77K.

NUCL 4095026

Microfluidic separation platform for post-detonation nuclear forensic applications

Kevin Glennon[1]*, glennon5@llnl.gov, Hector Valdovinos-Uribe*[1]*, Jake Bence*[1]*, Nic Cicchetti*[1,2]*, Tashi Parsons-Davis*[1]*, Narek Gharibyan*[1]*, Jennifer Shusterman*[1]*. (1) Lawrence Livermore National Laboratory, Livermore, California, United States(2) University of Nevada Las Vegas, Las Vegas, Nevada, United States*

A microfluidic chemistry platform is under development to support post-detonation nuclear forensics. The microfluidic platform is designed to be compact, use a minimum amount of reagents, and utilize deployable technologies to support in-field use. The platform has been shown to separate U and Pu from realistic matrices using robust chemistry. After chemical separation, integrated UV-VIS, gamma spectrometry, and alpha spectrometry systems are used to perform online measurements of specific U and Pu isotope ratios. This platform is also being tested as a rapid separation chemistry front-end for ICP-MS analysis of U and Pu isotope ratios from post-detonation samples.

NUCL 4096414

TODGA extraction of cobalt (II) from aqueous chloride media

Rachel Wood[1]*, rachelwood@ufl.edu, Penafrancia Monte*[2]*, Ramsey Salcedo*[2]*, Benjamin Burton-Pye*[3]*, Lynn C. Francesconi*[2]*, Deborah A. Penchoff*[4,5,6]*, Nathalie A. Wall*[1]*. (1) Materials Science and Nuclear Engineering, University of Florida, Gainesville, Florida, United States(2) Hunter College, New York, New York, United States(3) Chemistry, Lehman College of CUNY Division of Natural and Social Science, Bronx, New York, United States(4) Nuclear Engineering, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States(5) Innovative Computing Laboratory, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States(6) Howard H. Baker Jr. Center for Public Policy, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States*

Dr. Kenneth Nash's impact on radiochemistry has made him an inspiration to aspiring young scientists. With his significant contributions to separation chemistry, radiochemical analysis can reach new heights. Nuclear forensic analysis will support law enforcement inquiries by analyzing evidence tainted with radioactive substances. Radiochemistry processes are used to identify and quantify actinides, fission products, and activation products in post-detonation debris, and separation techniques are used in this task. Transition metals, also present in post-detonation residues, have been observed to impact critical isotope extractions. For example, cobalt, ubiquitous in urban environments, particularly in corrosion-resistant alloys, paint drying agents, dyes, and pigments, can impact the separation of critical actinides and fission products. It is essential to understand the chemistry governing cobalt extraction. This work aims to quantify kinetic and thermodynamic parameters (ΔH, ΔS, ΔG) associated with cobalt extraction by tetraoctyl diglycolamide (TODGA), the ligand hosted by the commercial chromatographic resin DGA. TODGA is beneficial in separation chemistry as it adheres to the CHON principle classifying it as a greener extractant.We quantified the effect of time, acid and extractant concentrations, and the system temperature. We will present

thermodynamic parameters associated with cobalt separation by TODGA, coordination of the extracted complex, and kinetics. Binding preferences and coordination environments will be elucidated through computational modeling driven by electronic structure theory calculations and artificial intelligence tools. X-ray Absorption Spectroscopy (XAS) is an element specific technique. The EXAFS region will provide the cobalt-TODGA coordination environment of the extracted complex. The XANES region will provide oxidation state information. Computational modeling coupled with XAS experiments and thermochemical characteristics for Co binding obtained through experimental techniques provides an in-depth understanding of complexation mechanisms and metal binding competition between ligands and ions in solutions.

NUCL 4096414

TODGA extraction of cobalt (II) from aqueous chloride media

Rachel Wood[1]*, rachelwood@ufl.edu, Penafrancia Monte*[2]*, Ramsey Salcedo*[2]*, Benjamin Burton-Pye*[3]*, Lynn C. Francesconi*[2]*, Deborah A. Penchoff*[4,5,6]*, Nathalie A. Wall*[1]*. (1) Materials Science and Nuclear Engineering, University of Florida, Gainesville, Florida, United States(2) Hunter College, New York, New York, United States(3) Chemistry, Lehman College of CUNY Division of Natural and Social Science, Bronx, New York, United States(4) Nuclear Engineering, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States(5) Innovative Computing Laboratory, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States(6) Howard H. Baker Jr. Center for Public Policy, The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States*

Dr. Kenneth Nash's impact on radiochemistry has made him an inspiration to aspiring young scientists. With his significant contributions to separation chemistry, radiochemical analysis can reach new heights. Nuclear forensic analysis will support law enforcement inquiries by analyzing evidence tainted with radioactive substances. Radiochemistry processes are used to identify and quantify actinides, fission products, and activation products in post-detonation debris, and separation techniques are used in this task. Transition metals, also present in post-detonation residues, have been observed to impact critical isotope extractions. For example, cobalt, ubiquitous in urban environments, particularly in corrosion-resistant alloys, paint drying agents, dyes, and pigments, can impact the separation of critical actinides and fission products. It is essential to understand the chemistry governing cobalt extraction. This work aims to quantify kinetic and thermodynamic parameters (ΔH, ΔS, ΔG) associated with cobalt extraction by tetraoctyl diglycolamide (TODGA), the ligand hosted by the commercial chromatographic resin DGA. TODGA is beneficial in separation chemistry as it adheres to the CHON principle classifying it as a greener extractant.We quantified the effect of time, acid and extractant concentrations, and the system temperature. We will present thermodynamic parameters associated with cobalt separation by TODGA, coordination of the extracted complex, and kinetics. Binding preferences and coordination environments will be elucidated through computational modeling driven by electronic

structure theory calculations and artificial intelligence tools. X-ray Absorption Spectroscopy (XAS) is an element specific technique. The EXAFS region will provide the cobalt-TODGA coordination environment of the extracted complex. The XANES region will provide oxidation state information. Computational modeling coupled with XAS experiments and thermochemical characteristics for Co binding obtained through experimental techniques provides an in-depth understanding of complexation mechanisms and metal binding competition between ligands and ions in solutions.

NUCL 4096870

Nuclear forensics of americium-based samples using intra-elemental isotopic ratios

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Nuclear forensics has historically focused on uranium and plutonium. Americium, a byproduct of plutonium production, sees widespread civilian use but has not been a major focus of nuclear forensics. The oil and gas industries use ^{241}Am at scale, creating vulnerabilities for diversion/theft that potentially make americium an attractive option for nuclear terrorism. Furthermore, malicious state actors could potentially proliferate americium without violating existing safeguards treaties, a vulnerability made even more sensitive by modeling research showing that metallic ^{241}Am likely has a critical mass under 100 kg.

A previous collaboration with our group created a source reactor-type discriminator for plutonium samples, which combined MCMP modeling of several reactor classes with experimental validation via irradiation experiments and chemical processing. The method measures groups of intra-elemental isotope ratios, including $^{239\text{-}242}$Pu, ^{133,134,137}Cs, ^{153,154}Eu, and ^{149,150,152}Sm, which can be characteristic of the neutron spectra within specific reactor types and are resistant to past chemical purifications. Samples with known histories were created at Oak Ridge's HFIR and the University of Missouri's MURR reactors, and a historical plutonium sample was provided by Los Alamos National Laboratory. A PUREX-style chemical process for plutonium recovery of the irradiated samples simulated a typical forensic sample, and a lanthanide separation via column chromatography prepared samples for ICP-MS measurement. Modeled and experimental data were compared via a maximum-likelihood calculation, and yielded accurate values for reactor type, burnup, and time since irradiation.

The current work focuses on extending our sample criteria to include $^{241,\,243}$Am samples, since these are produced by the decay of $^{241,\,243}$Pu, respectively, and are primary contaminants in plutonium stockpiles. A collaboration with Dr. Robert G. Surbella III at Pacific Northwest National Laboratory has been created, to access and process multiple legacy samples of both $^{241,\,243}$Am. Initial steps will include column chromatography to

separate Am from lanthanide fission products for further lanthanide partitioning. This talk will give an overview of these methods and discuss the most recent results.

NUCL 4097388

Chlorination of aluminum using low-temperature sulfur chloride reagents

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In the United States, there is currently no strategy for the permanent waste disposal or recycling for used nuclear fuels from research reactors. For this reason, low-temperature reactions have been developed for the chlorination of the Al alloys and subsequent separation from used nuclear fuels to reduce the volume of high-level waste in storage. Three sulfur chloride reagents—sulfur monochloride (S2Cl2), thionyl chloride (SOCl2), and sulfuryl chloride (SO2Cl2)—were tested, and two were found to quantitatively chlorinate Al metal and Al alloys under mild conditions. These low-temperature reactions proceed between 298 and 411 K, and up to 5 g of metal is chlorinated in 1–3 h. Preliminary results indicate that the reactivity and exothermicity of the reaction between the Al and sulfur chloride reagents is highly dependent on the surface area-to-volume ratio of the metal and the volume of solvent. Elemental S is produced as a by-product during the chlorination with S2Cl2 but can be quantitatively rechlorinated under mild conditions to regenerate the initial chlorination reagent. Therefore, in this case, chlorine is the only element consumed in the reaction, thus minimizing the waste generated during the chlorination process. The AlCl3 may then be separated from other materials present in Al 6061 or Al 8001 because of its high solubility in the sulfur chloride reagents.

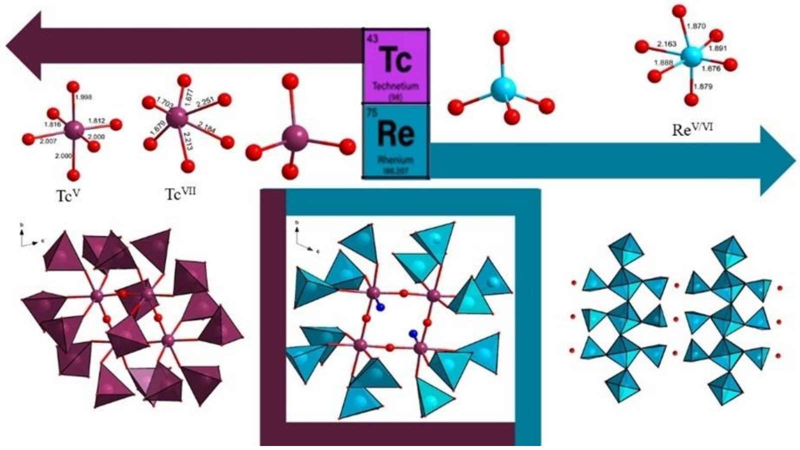
NUCL 4097654

Technetium mixed-metal clusters: Group 7 auto-reduction promoted by acidic media

***Jenna Bustos**, bustosj@oregonstate.edu, May D. Nyman. Chemistry, Oregon State University, Corvallis, Oregon, United States*

Technetium-99 (^{99}Tc) is a long-lived, high yield byproduct of Uranium-235 fission and a significant component of spent nuclear fuel and stored nuclear waste. Due to its long half-life, complex chemical and redox behavior, and mobility as the TcO_4^- ion, it is considered one of the most challenging radioactive contaminants. ^{99}Tc poses challenges with nuclear waste reprocessing as the TcO_4^- ion can co-extract with actinides of interest. The presence of lower valent ^{99}Tc has been observed in multiple forms in stored nuclear waste consisting of organics and complexants. Insight into the bonding and chemical behavior of technetium in solution is foundational to solving

nuclear waste remediation and reprocessing challenges.
In acidic aqueous solutions, pertechnetate is prone to auto-reduction, though the mechanism is not well understood. This phenomenon is well established in Mn chemistry, and is reported here for Re. In this work, we report single crystal X-ray structures of a reduced rhenium polymeric species, and a mixed Tc/Re cluster obtained from acidic aqueous solutions. By controlling the acidic aqueous conditions, different Re/Tc species can be obtained leading to coordination geometries advantageous for cluster/framework chemistry. Tc/Re speciation is studied in solution via 1) Small-angle X-ray Scattering (SAXS) to probe the size and shape of species, 2) X-ray absorption spectroscopy (XAS) to determine possible oxidation states, and 3) computation to explain the preferred topology and composition.



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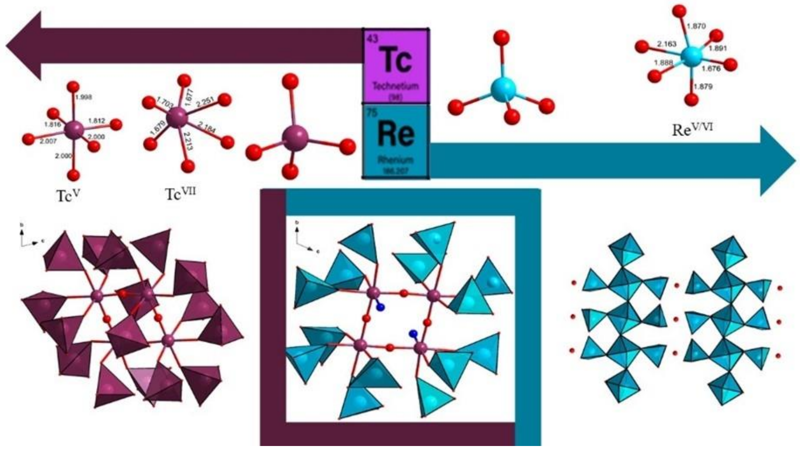

NUCL 4097701 - Withdrawn

NUCL 4099042

Early-time hole transfer to and damage of the UNF extractant TODGA

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Understanding the impact of ionizing radiation on extractants designed to separate out radioactive metals from used nuclear fuel (UNF) is important as it impacts the efficiency of separation process. *N,N,N′,N′* tetraoctyl diglycolamide (TODGA) is considered as one of the extractants with higher possibilities to be used to separate out trivalent minor actinides (specifically americium and curium) from the trivalent lanthanides. A tremendous effort has been put to understand the radiolytic damage of TODGA under various conditions, but the detailed mechanistic study on degradation of TODGA is poorly understood. In view of this, current work has focus on understanding the oxidation of TODGA by diluent molecules (n-dodecane, DD) following electron radiolysis, including subsequent hole transfer from $TODGA^{\bullet +}$ to low ionization potential (IP) solutes and possible pathways of degradation of $TODGA^{\bullet +}$ using pulse radiolysis and quantum chemical calculations. The results revealed that TODGA undergoes oxidation by $DD^{\bullet +}$ but only transfers ~8.5% holes to low IP solutes, most likely indicating either an inter or intramolecular proton transfer (PT) or rapid fragmentation of $TODGA^{\bullet +}$. Theoretical calculations indicate the etheric protons of $TODGA^{\bullet +}$ are more acidic enabling PT, plus after PT might lead to other fragmentation channels.

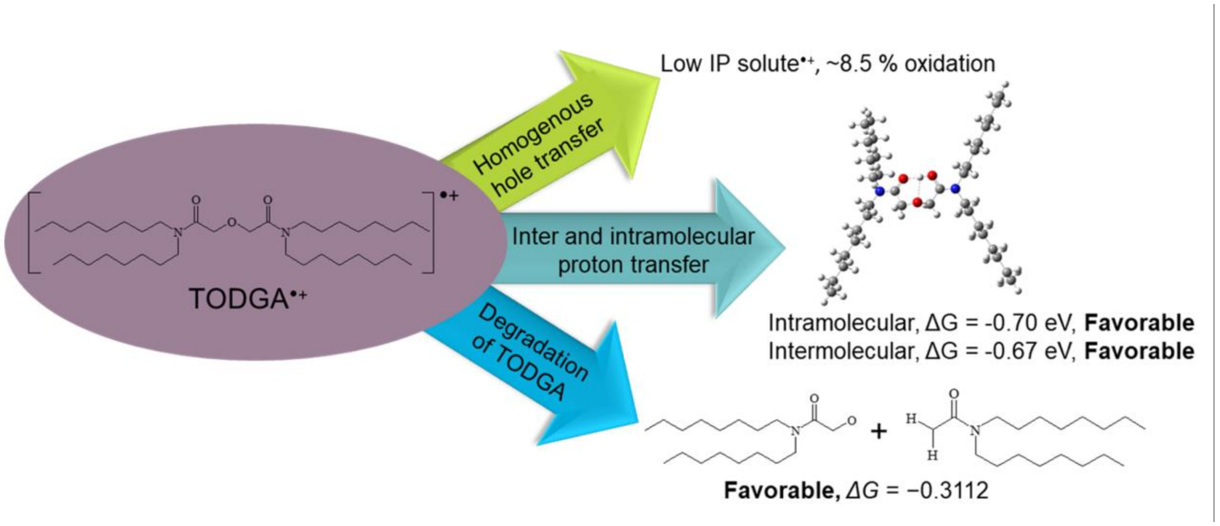

Figure. Different decay pathways of oxidized TODGA after irradiation are shown: 1) $TODGA^{\bullet +}$ transfers ~8.5% holes to low IP solutes, 2) $TODGA^{\bullet +}$ undergoes inter or intramolecular proton transfer with another TODGA, and 3) bond cleavage in $TODGA^{\bullet +}$ after oxidation.

NUCL 4099608

Kinetics of hydrogen production in gibbsite radiolysis: Effect of chloride as precursor

***Amita Bedar**[1], bedar.amita@gmail.com, Hanna Hlushko[1], Alejandro Ramos Ballesteros[1], Jay A. Laverne[1,2]. (1) Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, United States(2) Department of Physics and Astronomy, University of Notre Dame, Notre Dame, Indiana, United States*

Legacy waste from fuel processing includes significant amounts of aluminum compounds stored in underground tanks at the Hanford site, WA. Aluminum exists in solid oxyhydroxides (boehmite (γ-AlOOH)) and hydroxides (gibbsite (γ-$Al(OH)_3$)). Exposed to radiation, predominantly beta particles and gamma-rays from strontium-90 and cesium-137, the waste forms a complex multicomponent chemical mixture. This study focuses on the radiolytic species formed from irradiating gibbsite synthesized using chloride as precursor instead of the more common method using nitrate. Gibbsite particles were synthesized hydrothermally using aluminum chloride ($AlCl_3$) as a precursor, resulting in nanoplatelets with an average size of approximately 280 nm. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) revealed strong

stretching vibrations of structural hydroxyl groups, and suggested the dissociation of Al-O bond at higher radiation doses. X-ray photoelectron spectroscopy (XPS) confirmed the presence of chloride at an atomic concentration of 0.52%, affecting the bulk properties of gibbsite. During radiolysis, surface water and attached hydroxyl groups participate in generating radiolysis products, with hydrogen production increasing with radiation dose. Electron paramagnetic resonance (EPR) spectra of Cl-gibbsite showed distinct peaks of H atoms and O_2 radicals, indicating oxygen-centered species formation on gibbsite's hydroxyl groups. Irradiation of gibbsite derived from chloride produced trapped H atoms in contrast to the lack of observable H atom production from gibbsite derived from nitrate. Presumably, residual nitrate from its synthesis scavenges precursors to H atom formation. It is proposed that H atoms form through O–H bond breaking, followed by recombination to generate H_2.

NUCL 4099608

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NUCL 4099782

Mechanisms of action of a phase modifier - a physical chemists perspective

***Aurora E. Clark**, aurora.clark@utah.edu, Swarup Banerjee, Leonardo Da Silva Garcia Leite. Chemistry, University of Utah, Salt Lake City, Utah, United States*

It is well established that organic phase behavior during solvent extraction can have unanticipated consequences upon separations efficiency. The formation of a water-in-oil microemulsion may change stoichiometric coefficients for extraction reactions and as such, distribution coefficients and potentially separation factors. Further, phase splitting of the microemulsion (3rd phase formation) may initiate unanticipated and undesired reactivity like nucleation. Phase modifier additives (co-surfactants) have long been employed to modulate organic phase behavior, generally decreasing reverse-micelle size distributions and/or decreasing inter-aggregate interactions - thereby extending the compositional window before onset of deleterious phase transitions. Yet the physical underpinning of the mechanisms of action of phase modifiers are not well understood. To achieve new insight, molecular dynamics simulations have been employed to sytematically tune key intermolecular interaction energies of a variety of phase modifiers so as to better understand the role of interactions of the modifier with the polar core and including hydrophobic size and sterics. Complementary machine learning from a recently developed database of experimental solvent extraction data has been performed to elucidate the correlation of simulation data, the system composition and surfactant properties, with organic phase solution structure and separations characteristics.

NUCL 4099814

Educational resource development for uranium nuclear fuel cycle research

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The nuclear fuel cycle (NFC) remains a complex understanding of many areas in science, engineering, and health physics. The areas encompass but not exclusively the following: from geology, mining, chemical extraction, enrichment, fuel production, nuclear engineering, radioactive waste management, dosimetry, nuclear nonproliferation, and nuclear forensics. Over the years, with changes in research funding opportunities mainly from DOE, teaching and training in the NFC has been fragmented across the academic institutions. While individual courses are indeed given in various departments, an integrated pedagogical approach does not presently exist. The extreme interdisciplinary nature of the NFC makes it difficult to cover the all the critical facets. The objective of this educational endeavour is to create a blueprint for a

undergraduate and graduate level research and curriculum that can address a large fraction of these fundamental significant research areas.

NUCL 4101271

Improving uranium separation chemistry for environmental samples

***David L. Cook**, david.cook@lanl.gov, Kimberly Hinrichs, Andy Nunn, Allison Price, Kassey Christensen, Ron Amato. C-NR, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Post-detonation nuclear forensics are undertaken at Los Alamos National Laboratory for application to potential nuclear detonations or accidents (*e.g.*, Fukushima). Uranium isotopes, including the anthropogenic nuclide ^{236}U, provide a useful isotopic fingerprint to help elucidate the source and neutron exposure history of the nuclear material. Separation of trace quantities of U from environmental samples is routinely performed for treaty monitoring programs at Los Alamos National Laboratory.

The historic separation uses three anion exchange columns that require numerous reagents, including H_2SO_4. Using H_2SO_4 requires hot plate dry downs near the labware melting temperature, introducing unique hazards to the procedure. Ion exchange partition coefficients suggest that U could be sufficiently separated without the use of H_2SO_4. Another drawback of the current protocol is the use of H_2O_2 mixed with HCl. The presence of H_2O_2 often leads to bubble formation in the resin bed, which can cause channeling. Recently, we began investigating a new protocol with the following goals: to reduce the overall processing time needed for the chemical separation of U, to eliminate the use of H_2SO_4 and H_2O_2, to improve the reproducibility of the method among different chemists, and to potentially reduce the column blank by simplifying the overall procedure.

A new separation, using only HNO_3, HCl, and purified water as reagents, was developed. Calibration curves based on multi-element ICPMS standards showed a sharp elution peak for U. Subsequent tests using NIST 4350b (Columbia River sediment) confirmed high yields of U (*i.e.*, > 90%) that is well-separated from the matrix. Initial TIMS analysis of these purified U fractions agree well with previous data obtained using the historic separation chemistry. Chemical processing and TIMS measurements are underway on additional aliquots of NIST 4350b, as well as other reference materials (*e.g.*, USGS BCR-2, IAEA 410) and blanks, to fully validate the new method.

NUCL 4101679

High pressure study of uranyl silicate minerals with the uranophane sheet anion topology

***Carmen E. Chamberlain**[1], carmenhashope@gmail.com, Jennifer Szymanowski[2], Peter C. Burns[2,1]. (1) Chemistry and Biochemistry, University of Notre Dame, Notre Dame,* *Indiana, United States(2) Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

Numerous minerals are known to form on uranium dioxide under simulated repository conditions, including uranyl silicates, uranyl oxyhydrates, and non-uranium bearing phases. Uranyl silicates have a demonstrated ability to incorporate neptunium, fission products, and other metals into their crystal structures, thus limiting their environmental transport. Uranyl silicate minerals such as boltwoodite, $K_{0.57}Na_{0.43}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, and cuprosklodowskite, $Cu[(UO_2)(SiO_3OH)]_2(H_2O)_6$, form crystal structures with the uranophane sheet anion topology. The aim of this project is to probe the relative stability of uranyl silicates relevant to disposal of used nuclear fuel by subjecting samples to high pressures. Diamond anvil cells were used to achieve high, gigapascal range, pressures experimentally. The bulk modulus of boltwoodite has been determined and the response of polyhedral arrangement and geometry has been characterized. The high pressure X-ray diffraction and Raman spectroscopic techniques applied to boltwoodite are utilized in ongoing work.

NUCL 4101679

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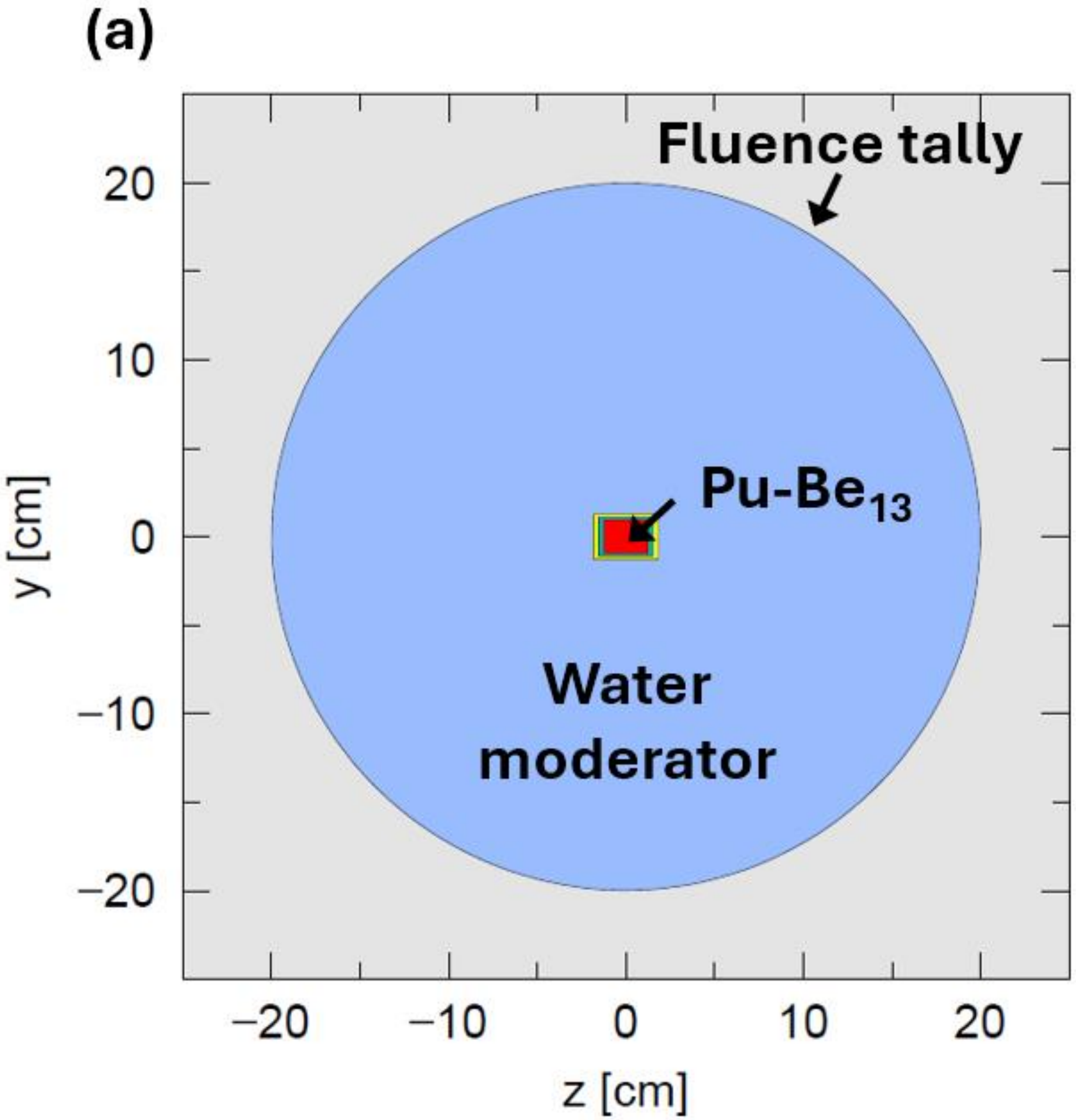
NUCL 4102080

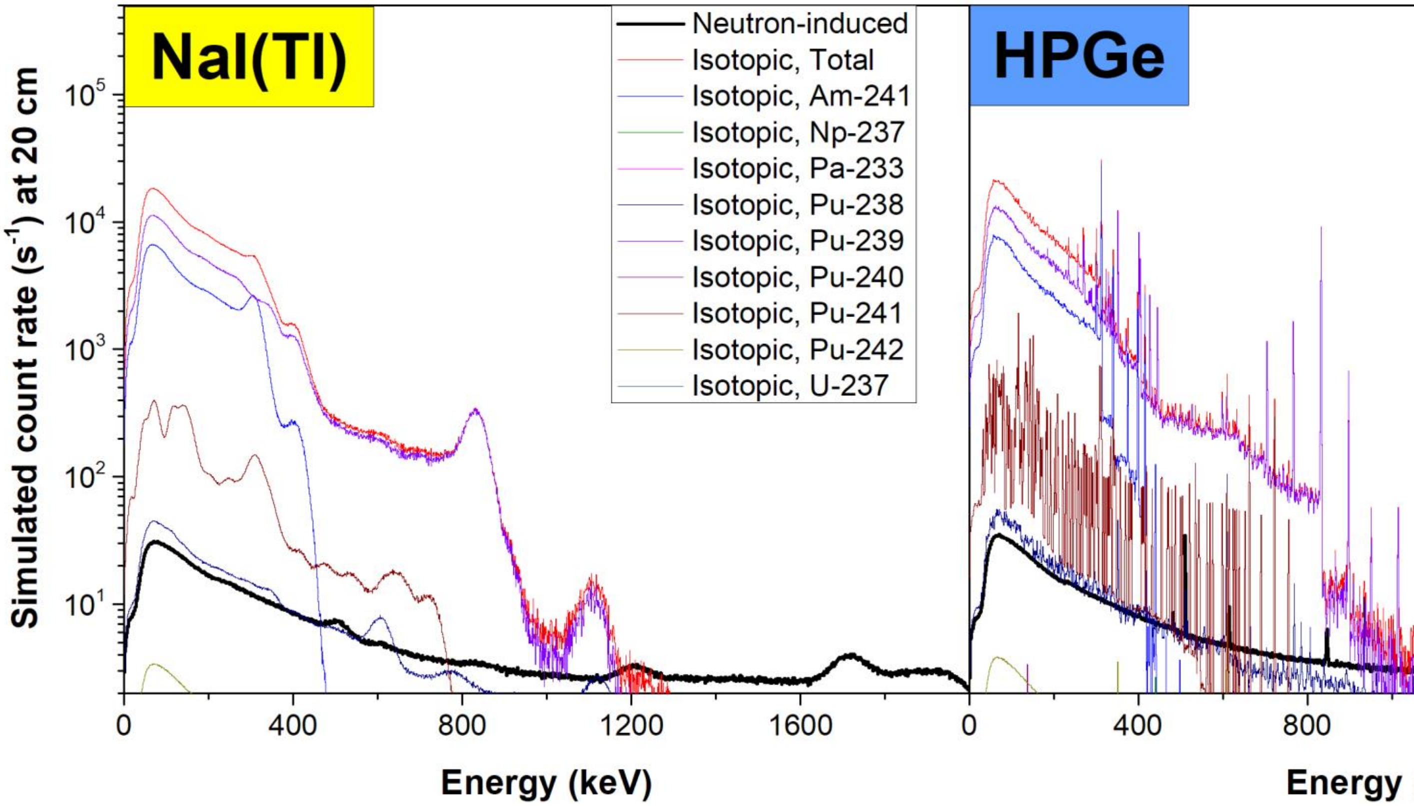
Monte Carlo simulations of detector responses to isotopic and neutron-induced Gammas in moderated plutonium-beryllium sources

***Frederick C. Hila**[1,2], fchila@pnri.dost.gov.ph, Candy C. Mercado[2], Alberto V. Amorsolo[2]. (1) Department of Science and Technology, Philippine Nuclear Research Institute, Quezon City, Metro Manila, Philippines(2) Department of Mining, Metallurgical and Materials Engineering, University of the Philippines Diliman, Quezon City, Metro Manila, Philippines*

Despite the discontinuation of ^{239}Pu-Be production, these neutron sources, with a half-life of approximately 24,000 years, remain prevalent. Given the long-lasting nature of these sources and the potential for exposure to neutron radiation, there is a pressing need for effective measurement techniques, such as gamma-ray spectrometry in a moderated configuration. This study utilizes Monte Carlo simulations to investigate gamma spectrometer responses to isotopic and neutron-induced gamma-rays from a Pu-Be source in both moderated and bare configurations, focusing on isotopic contributions and the impact of neutron-moderator interactions on the gamma spectrum quality. The research employs a three-fold methodology: using an internal decay chain calculator, PuChain, for plutonium-bearing materials to calculate decayed activities of gamma-emitting radionuclides; employing PHITS Monte Carlo transport to simulate the gamma-ray energy-fluence spectrum at 20 cm from the Pu-Be in both water-moderated and bare configurations; and using the resulting energy-fluence spectrum as a source term for subsequent Monte Carlo simulations for the responses of conventional HPGe and NaI(Tl) detectors. The simulations highlight HPGe detectors' effectiveness for spectrometric measurements in Pu-Be moderated or bare configurations, while acknowledging NaI(Tl) detectors' resolution limitations.



PHITS Monte Carlo models depicting a two-stage setup for variance reduction: (a) simulates Pu-Be interactions in a water moderator, and (b) applies the resulting energy-fluence to simulate detector responses.



Comparative simulation of NaI(Tl) and HPGe detectors' response to gamma-rays emitted from a 16-gram Pu-Be neutron source, illustrating the contributions of both isotopic and neutron-induced gamma-rays across a 2-MeV range.

NUCL 4102335

Optical vibrational spectroscopic signatures of ammonium diuranate process parameters

Tyler L. Spano[1], *spanotl@ornl.gov, Caleb Redding*[1], *Jordan M. Roach*[1], *Cody Nizinski*[2], *Evan Warzecha*[2], *Matthew Athon*[2], *Andrew Miskowiec*[1], *Rodney Hunt*[1], *Jennifer L. Ladd-Lively*[1]. *(1) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States(2) Pacific Northwest National Laboratory, Richland, Washington, United States*

Ammonium diuranate (ADU) is commonly encountered in the nuclear fuel cycle and may have significant variability in solid-phase products that relate to the procedures used to produce it. To elucidate structure-property relationships in ADU five samples were examined using powder X-ray diffraction, Raman and infrared spectroscopy, and scanning electron microscopy. We find that the primary solid phase resulting from ADU precipitations is similar to the uranyl oxyhydroxyhydrate mineral metaschoepite. Despite the significant phase contributions of a metaschoepite-like phase, spectroscopic evidence of both nitrate and ammonium are described for all samples. To gain a more

holistic understanding of spectroscopic features of process parameters in ADU, principal component analysis is employed and results in observable signatures that relate to the stir rate used during synthesis.

NUCL 4102351

Accelerating nuclear forensics through single-aliquot separations

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Destructive analysis provides information regarding the origin of a nuclear material out of regulatory control through quantifying the actinide species present. The elements of interest in a uranium material (Th, Pa, Pu, Am, and Np) are typically purified from the bulk U matrix into single-element fractions through column chromatography for analysis by mass spectrometry. Purification of these five analytes currently requires multiple weeks of effort from several chemists. Additionally, a balance must be struck between pulling enough sample aliquots for analysis and preserving the nuclear material for evidence. This work describes methods for expediting the purification of Th, Pa, Pu, Am, and Np from a single aliquot by taking advantage of the unique speciation and in some cases redox behavior of each element. A stacked TEVA/DGA column was utilized to isolate Pa, Np, Pu, Th, and Am from a nanogram-scale uranium matrix with recoveries for each element exceeding 75% as determined by mass spectrometry. Efforts to scale up the uranium content to reflect “real-world” quantities are discussed. This new separation approach could result in faster analysis times during a pre-detonation sample investigation, even when sample quantities are limited.

NUCL 4102478

Cross section for inelastic neutron scattering from ^{193}Ir at 6 MeV

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Two samples, one of natural iridium and the other of enriched ^{193}Ir, were irradiated with a monoenergetic neutron beam of energy 6.0 MeV at the Triangle Universities Nuclear Laboratory. The product of the ^{193}Ir(n, n′)^{193m}Ir reaction was determined by means of measuring X-rays following electron conversion of the isomeric state at 80.2 keV in ^{193}Ir. The cross section for inelastic neutron scattering is reported disagreeing with the literature data.

NUCL 4103091

Evaluation of interactions of uranyl cation under the influence of free radical initiators

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When aqueous solutions are subjected to ionizing radiation, a diverse array of free radicals emerges, complicating the precise elucidation of the interactions that can take place in the chemical system. This is of particular concern with nuclear materials used in energy production as radiolysis produces reactive free radicals that can impact the corrosion of uranium dioxide fuel, hamper radiochemical separations, and create soluble phases that will influence environmental fate and transport. While the presence of free radicals in these systems have been confirmed through previous irradiation studies, there remains a lack of atomistic level understanding regarding the formation, stability, and reactivity of actinide complexes with free radical species. Overall, we hypothesize that free radicals interact with the uranium to form metastable complexes that can participate in cascade reactions to form unexpected species. To test this hypothesis, we utilize chemical initiators to produce specific free radicals and identify the resulting metal complexes. In the current study, we have evaluated the speciation of uranyl cation under varying pH conditions in the presence of the radical initiators benzaldehyde/benzyl alcohol (peroxyl radical initiator) and persulphate (sulfate and hydroxide radical initiator). We utilize single crystal x-ray diffraction data in combination with Raman and Electron paramagnetic resonance spectroscopy to evaluate the interactions seen in both the solid state and solution. Overall, we observe that the peroxyl radical forms known U(VI) peroxide phases, whereas the persulfate system undergoes a radical cascade reaction to form other reactive oxygen species.

NUCL 4103091

Evaluation of interactions of uranyl cation under the influence of free radical initiators

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When aqueous solutions are subjected to ionizing radiation, a diverse array of free radicals emerges, complicating the precise elucidation of the interactions that can take place in the chemical system. This is of particular concern with nuclear materials used in energy production as radiolysis produces reactive free radicals that can impact the corrosion of uranium dioxide fuel, hamper radiochemical separations, and create soluble phases that will influence environmental fate and transport. While the presence of free radicals in these systems have been confirmed through previous irradiation studies, there remains a lack of atomistic level understanding regarding the formation, stability, and reactivity of actinide complexes with free radical species. Overall, we

hypothesize that free radicals interact with the uranium to form metastable complexes that can participate in cascade reactions to form unexpected species. To test this hypothesis, we utilize chemical initiators to produce specific free radicals and identify the resulting metal complexes. In the current study, we have evaluated the speciation of uranyl cation under varying pH conditions in the presence of the radical initiators benzaldehyde/benzyl alcohol (peroxyl radical initiator) and persulphate (sulfate and hydroxide radical initiator). We utilize single crystal x-ray diffraction data in combination with Raman and Electron paramagnetic resonance spectroscopy to evaluate the interactions seen in both the solid state and solution. Overall, we observe that the peroxyl radical forms known U(VI) peroxide phases, whereas the persulfate system undergoes a radical cascade reaction to form other reactive oxygen species.

NUCL 4103106

Aminopolycarboxylate journey: Tracing the footsteps of actinide separations giants

Peter R. Zalupski, *peter.zalupski@inl.gov. Aqueous Separations and Radiochemistry, Idaho National Laboratory, Idaho Falls, Idaho, United States*

Trivalent f-element separation is a challenging subset of separations field which Prof. Nash has mastered over the years. His multiple review papers on this topic have inspired radiochemists all over the world to carry on efforts on this subject. This contribution shares a story of one such effort of walking the path paved by the great actinide separations chemists.

NUCL 4104051

Defining the thermodynamic relationships between tetravalent actinide sulfates

Christopher J. Dye[1]*, cdye2@nd.edu, Teagan F. Sweet*[2]*, Kirstin Sockwell*[1]*, Peter C. Burns*[1,2]*, Amy E. Hixon*[1]*. (1) Civil & Environmental Engineering & Earth Science, University of Notre Dame, Notre Dame, Indiana, United States(2) Chemistry, University of Notre Dame, Notre Dame, Indiana, United States*

The chemical thermodynamics of solid-state transuranic actinide complexes remains sparsely explored despite their prevalence in the nuclear fuel cycle due to significant difficulties in handling transuranic materials. A side-effect of missing thermodynamic information is incomplete transport models for tetravalent actinides, adding complications to predictive modelling of the long-term storage or environmental remediation of high-level nuclear waste. High temperature drop solution calorimetry has been an effective tool in defining thermodynamic values for actinide materials due to the favorable solubility of actinide materials in the molten salt solvent. We used drop solution calorimetry to measure the heat of dissolution and calculate the heat of formation for $An(SO_4)_2(H_2O)_4$ (An = Np, Pu, Th). This data was then correlated to the

coordination environment of the metal cations and used to examine trends of tetravalent actinide coordination.

NUCL 4104101

Computational investigation of mono-uranium oxide anions in the gas phase

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The uranyl triperoxide (UT) monomer consists of a linear uranyl ion (UO_2^{2+}) coordinated equatorially to three bidentate peroxo ligands. The uranyl peroxide cage cluster (UPC) U_{28} $[(UO_2)_{28}(O_2)_{42}]^{28-}$ is a polyoxometalate composed of UT building blocks. The formation and speciation mechanisms between U_{28} and UT, along with other UPCs, are largely unknown due to the difficulty in isolating intermediates. Aqueous UPCs are observed with electrospray ionization mass spectrometry (ESI-MS), along with collision induced dissociation (CID). This area of focus in our group is used to study the speciation of UPCs in low concentration aqueous solutions. Current research shows ESI-MS of Li-UT and ESI-MS/CID/MS of Li-U_{28} produce the low mass gas phase anions UO_x^- (x=3-8) and $UO_xH_y^-$ (x=4-8, y=1-2). The electronic structure of many of the observed low mass anions is unknown, and their formation likely involves short-lived reactive oxygen species. Computational efforts involving actinides are complicated by relativistic effects and near degeneracy of valence orbitals. However, modern density functional theory (DFT) has been known to produce reliable geometric optimizations, and multi-configuration calculations can aid in the resolution of spin contamination issues. Geometry optimization calculations of various isomers of UO_x^- (x=6-8) and $UO_xH_y^-$ (x=6-8, y=1-2) suggest the inclusion of oxo and superoxo radical groups as well as unique hydroperoxo groups. Refined energy calculations help elucidate the relative stabilities of potential isomeric structures, and spin density and orbital population analysis help describe the character of the uranium centers and oxygen groups.

NUCL 4104275

Incorporation of fission by-products into carbonate mineral phases

Ilana Szlamkowicz*, iszlamkowicz2@gmail.com, Veronica Lara, Vasileios Anagnostopoulos. Chemistry, University of Central Florida, Orlando, Florida, United States*

In the past, fission products have been accidentally released into the environment from nuclear weapon testing and insufficient waste management practices. These contaminants are typically found at trace levels, which exerts controls over the environmental behavior of contaminants. However, most prior studies investigating the incorporation of fission products into carbonate minerals have only focused on calcium

carbonate. In the environment, other carbonate minerals are formed, such as manganese carbonate.

The two fission products investigated here are iodine and selenium, both of which are contaminants of concern. In the case of iodine, it exhibits a long half-life (16 million years), a biological affinity in humans, and is a known carcinogen. Selenium also exhibits a long half-life (110 thousand years), is both an essential micronutrient and is toxic to humans. Both fission products are highly mobile species, causing remediation strategies to be focused on immobilization methods.

Remediation methods that can be used for the immobilization of environmental contamination of fission products, is through incorporation into the mineral structure of carbonate minerals. Common carbonate phases include both calcium and manganese carbonate minerals, calcite and rhodochrosite, respectively. It has been previously shown that iodate, the oxidized form of iodine, incorporates within the calcite structure by replacing a carbonate molecule. However, these previous studies used artificially elevated concentrations of iodine, selenium, and the carbonate mineral components. In this study, the effects of environmentally realistic concentrations are investigated, to determine their influence on the incorporation of selenium and iodine into both calcium and manganese carbonate.

NUCL 4104839

Honoring Ken Nash: A solution chemistry extraordinaire, professor, mentor, and my friend

Travis S. Grimes, *Travis.Grimes@inl.gov. Aqueous Separations and Radiochemistry, Idaho National Laboratory, Idaho Falls, Idaho, United States*

Back when I was a graduate student, Professor Nash told me, “The easy stuff is OK, but don’t be afraid to take on the hard research problems.” Since then, I have embraced this approach to research, and throughout the years, it has emboldened me to not shy away from, or give up on research projects with significant challenges. This is just one example of Ken’s influence on not only me, but the many graduate students who studied under his guidance. This presentation will survey some of the projects I have been involved in at Idaho National Laboratory since leaving Ken’s research group at Washington State University in 2011. It is my hope that his influence shines through.

NUCL 4104897

Separation of actinides from soil matrices mass spectrometry

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Rapid determination of the concentration and ratio of actinides is important in nuclear forensics. Separation of the actinides from environmental constituents allows for higher confidence actinide data. In unseparated samples, polyatomic and isobaric interferences arise not only from the matrix but within the actinides such as, ^{232}Th and ^{232}U, and ^{238}UH^{+} and ^{239}Pu. Therefore, separations are needed to provide higher confidence actinide data. A single UTEVA column was used to separate Np, Pu, and U for purified fractions for inductively coupled plasma mass spectrometry (ICP-MS) quantification. The UTEVA column was tested with three different soil standard reference materials with and without additional actinide spiking. The proposed separation allowed for pure fractions from interferences with high recovery of the target actinides, with comparable ratios from published reports. All this from a single, simple, rapid column.

NUCL 4104986

Separation of divalent transition metal activation products

***Staci Herman**, Staci.herman@pnnl.gov, Dana Arbova, Bethany Lawler, Ean Arnold, Chelsie L. Beck. Pacific Northwest National Laboratory, Richland, Washington, United States*

In nuclear forensics, analytes of interest fall into one of three different categories: actinides, fission products, and activation products. However, activation products are difficult to measure since they can have short half-lives, low intensity gamma emission lines, and/or formed in relatively lower abundance with respect to fission products. This work presents the efforts to separate divalent transition metals (M^{2+} = Mn, Ni, Cu, and Zn) as well as Pt and V activation products using extraction chromatography. Two different resins were tested, DGA and AN, to determine if M^{2+} as well as V and Pt can be separated from the bulk matrix, and interfering fission and activation products. The ability of DGA and AN columns to separate these analytes will be presented in this work.

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different resins were tested, DGA and AN, to determine if M^{2+} as well as V and Pt can be separated from the bulk matrix, and interfering fission and activation products. The ability of DGA and AN columns to separate these analytes will be presented in this work.

NUCL 4105211

Improving Np extraction by TBP in used nuclear fuel: Studying the effects of radiolytically produced HNO_2

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

The CoDCon process is a modified Plutonium Uranium Extraction (PUREX) process that uses tributyl phosphate (TBP) in a long-chain hydrocarbon diluent designed for simultaneous co-extraction of U and Pu from used nuclear fuel (UNF) dissolved in nitric acid (HNO_3). Some Np is extracted during the CoDCon process but depending on experimental conditions, some Np remains in the aqueous phase owing to its presence as Np(V) which is not extracted by TBP. While Np(V) is the most stable oxidation state of Np when dissolved in low concentrations of HNO_3, some Np does exist as Np(IV) and Np(VI) which are extracted by TBP. Higher concentrations of HNO_3 can oxidize Np(V) to Np(VI). Low concentrations of nitrous acid (HNO_2), which is a product of the radiolysis of HNO_3, can catalyze the oxidation reaction. However, HNO_2 plays a complex role as at high concentrations it inhibits the redox reaction between Np(V) and HNO_3. The complete extraction of Np therefore requires conditions that favor the oxidation of Np(V) to Np(VI).

In this work, the effects of nitrous acid on the speciation and subsequent extractability of Np by TBP are studied. The radiolytic environment of UNF was simulated by irradiating aqueous HNO_3 solutions with beta radiation at dose rates similar to those found in UNF processing. Np dissolved in different concentrations of nitric acid and nitrous acid was extracted by 30% TBP in dodecane in batch and single stage counter-current centrifugal contactor experiments. Nitrous acid concentrations as well as Np concentrations were monitored in real time by in-line UV-vis-NIR spectroscopy. Herein, we report our findings.

NUCL 4105211

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NUCL 4105309

Comparative study of strontium-90 and cesium-137 analyses in freshwater fish near the Fukushima Daiichi Nuclear Power Plant

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In the wake of the Fukushima Nuclear Power Plant (FNPP) accident in Japan, commercially sold food products from the Fukushima prefecture have come under increased scrutiny by the public due to potential bioconcentration of radionuclides. The fish that are harvested from fresh and salt waters are one such product of interest. The main isotopes of concern in fish are strontium-90 (Sr-90) and cesium-137 (Cs-137). These are radioisotopes that have been found to substitute stable calcium and potassium in bone and muscle tissue, respectively. This research explores the concentration of Sr-90 and Cs-137 in freshwater fish sampled near the FNPP to determine if they are safe for consumption. This assessment is important in assuaging the fears of the public regarding the safety of products exported from the Fukushima region, allowing for commerce to flourish once again in the Fukushima prefecture. Fish have been sampled from the Ukedo River located northwest of the FNPP. Tissue and bone samples were separated for the fish and dried. Sample aliquots were divided between Colorado State University and Hirosaki University for a comparison study using the same dissolution and separation method. Tissue samples were dissolved in 8 M HNO_3 and measured via HPGe. Bone samples were ashed and dissolved in 8 M HNO_3 for separation of Sr-90 and yttrium-90 (Y-90) via Eichrom DGA resin. Analysis and determination of Sr-90 was completed using a gas flow proportional counter at Colorado State University and utilizing an inductively coupled plasma mass spectrometer at Hirosaki University. Sample results and method limits of detection will be compared to those obtained by our collaborators at Hirosaki University.

NUCL 4105445

Exploring phase modifiers in high-concentration monoamide separations systems

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In the United States advanced used nuclear fuel (UNF) recycling technologies are at a low TRL. With the continued use of nuclear as a source of energy in the US, advancing these technologies is necessary. Solvent extraction systems centered on monoamide extractants have demonstrated significant potential to meet the requirements to recycle UNF. These systems could be advanced by increasing the extractant concentration over what has been previously considered. Presently, the chemical properties and behavior of high-concentration monoamide (HiMA) systems are not well known. Ultimately, higher concentrations of the extractant will improve efficiency of the separations process through higher metal loading of the organic phase. It is expected this will come with a price possibly in the form of viscosity changes in the organic phase, solubility of the extracted complexes, and decreased phase disengagement. The research presented in this work will discuss attempts made to tackle some of these issues through the introduction of phase modifiers to the HiMA organic phases.

NUCL 4105472

Magnetic Particles as extractants for radionuclides

Jose M. Veleta, *jose.veleta@pnnl.gov, Ean Arnold, Staci Herman, Chelsie L. Beck. Pacific Northwest National Laboratory, Richland, Washington, United States*

Rapid separation of actinides, fission products, and activation products from environmental constituents is important to nuclear forensics, consequence management, and environmental remediation. Therefore, the ability to concentrate or extract radionuclides from environmental matrices is of interest. We propose the use of magnetic particles functionalized with carboxylic acid groups as an extractant for Pb in aqueous samples. Results from absorption capacity experiments show a strong influence of the matrix pH on the Pb adsorption, as observed from Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) analyses. Comparison of adsorption/desorption capacity of these magnetic particles with weakly coordinating

anion exchange resins will be presented. This work proposes a rapid method for environmental sample treatment for radiochemical analysis.

NUCL 4106175

Extraction and electrochemical behavior of Np in irradiated TBP

Joshua Dunbar[1]*, joshuadunbar@mines.edu, Mark P. Jensen*[1,2]*, Dean R. Peterman*[3]*. (1) Chemistry, Colorado School of Mines, Golden, Colorado, United States(2) Nuclear Science & Engineering, Colorado School of Mines, Golden, Colorado, United States(3) Aqueous Separations & Radiochemistry, Idaho National Laboratory, Idaho Falls, Idaho, United States*

Advanced nuclear fuel cycles require selective separation of the minor actinides in order to achieve full product recovery and purity. In this respect neptunium (Np) poses a challenge, as its variety of accessible oxidation states allow it to distribute between both the aqueous and the organic phase over a wide range of conditions. One complicating factor is the high radiation field found in reprocessing systems, which causes radiolysis of extractant molecules, creating degradation products that may have different chemistry with the minor actinides. In tributyl phosphate (TBP) based processes such as PUREX, UREX, COEX or CoDECON, the primary radiolysis product, dibutyl phosphoric acid (HDBP), is known to alter the speciation of extracted metals and complicate stripping in reprocessing systems.

We investigated the effect of solvent radiolysis on Np behavior in TBP through solvent extraction and electrochemical methods. In the absence of chemical valence stabilization, Np(VI) was readily reduced in the irradiated organic phase, resulting in depression of distribution ratios across the three acidities tested. Pentavalent neptunium, on the other hand, extracted better into irradiated solvent, and the Np(IV) distribution ratios increased greatly with dose. At higher doses and lower acidities, there were indications of Np(IV)-DBP precipitation. Distribution data for redox-stabilized Np(VI) will also be shown. The reduction potentials for the Np(VI/V) and the Np(IV/III) couples in TBP and TBP/dodecane organic phases will be presented, showing the influence of HDBP and TBP concentration on the reduction potential and demonstrating the viability of electrochemical characterization of metals in resistive nonpolar organic phases.

NUCL 4106212

Platform technology for purifying Ac-225 and other accelerator-produced isotopes

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Ac-225 is an alpha-emitting radioisotope with a short half-life of 9.9 days with promising clinical trials for Targeted Alpha Therapy (TAT). Although there is an increasing demand for Ac-225 in the medical field, there is a widespread shortage of this radionuclide. After production, the current state-of-the-art method for the selective separation of Ac-225 from lanthanide and actinide spallation products is through extractive chromatography using diglycolamide (DGA)-based resins. While effective on a small scale, this method faces multiple challenges as it is hindered by slow processing speeds and large elution volumes. This results in a significant amount of Ac-225 lost due to radioactive decay. An alternative approach is membrane adsorbers which may be more effective in purifying Ac-225 with faster separation times and smaller bed volumes.

In this work, a new class of membranes is synthesized through electrospinning poly(chloromethyl styrene) and covalently grafting DGA ligands to the membrane surfaces and pores. A series of adsorption experiments using a lanthanum as a non-radioactive surrogate for Ac-225 were conducted to determine the binding capacity and Langmuir constants of both commercial DGA resins and DGA membranes for 4 M, 6 M, and 10 M nitric acid. These acid concentrations are used in the loading/elution schemes for Ac-225 adsorption. In 4 M nitric acid, resins and membranes exhibit similar affinities, with Langmuir constants of 0.23 ± 0.01 and 0.28 ± 0.06 L/mg, respectively. Despite this similarity in affinity, there is a notable difference in adsorption capacity, with resins at 21.9 ± 0.4 mg/g and membranes at 0.37 ± 0.02 mg/g. Experiments focused on the dynamic adsorption and desorption of stable and radiolanthanum onto DGA resins and DGA membranes are underway. The independent variables are the pH and flowrate for loading and elution. We hypothesized that, due to diffusion-limited mass transport, increasing the process flow rate for resin-based separations would lead to lower dynamic binding capacities. Conversely, DGA membranes are convection-driven and would maintain constant dynamic binding capacities regardless of flow rate—resulting in faster loading and elution times compared to resins. This strategy lays a foundation for purifying Ac-225 using membrane adsorbers which has the potential to replace the conventional purification methods.

NUCL 4106238

Rapid high accuracy and precision analysis of uranium content in Texas ores using gamma-ray spectrometry

***Christopher Martin**, chrismartin47.87@utexas.edu, Sheldon Landsberger. The University of Texas at Austin, Austin, Texas, United States*

The nuclear fuel cycle relies entirely on the accurate and reliable quantitation of uranium content in naturally occurring radioactive material (NORM) or uranium mines. Typical analytical methods include inductively plasma atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS), x-ray fluorescence, atomic absorption, gamma-ray spectrometry, etc. We present two rapid non-destructive methodology in gamma-ray spectrometry to determine uranium concentrations in ore based on the decay of ^{238}U to ^{234m}Pa using the 1000.1 keV gamma- ray and the decay of ^{235}U to ^{231}Th using the143.7 and 163.3 gamma-rays using passive counting. Both decays belong to the first daughter

products Because of the high density of uranium at 19.1 g/cm^3 a ^{152}Eu point-source was used to determine the attenuation properties of the ore sample at varying gamma ray energies. Through the comparator method, we show a quantitative, non-destructive method for quantifying the total uranium content in a sample of NORM in the range of 8.207 wt.% in NORM with 2. % error within 2 hours utilizing only 1.4 grams of material after accounting for self-attenuation.

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NUCL 4106274

Pre-detonation nuclear forensics at Los Alamos National Laboratory, recent advances, and future research directions

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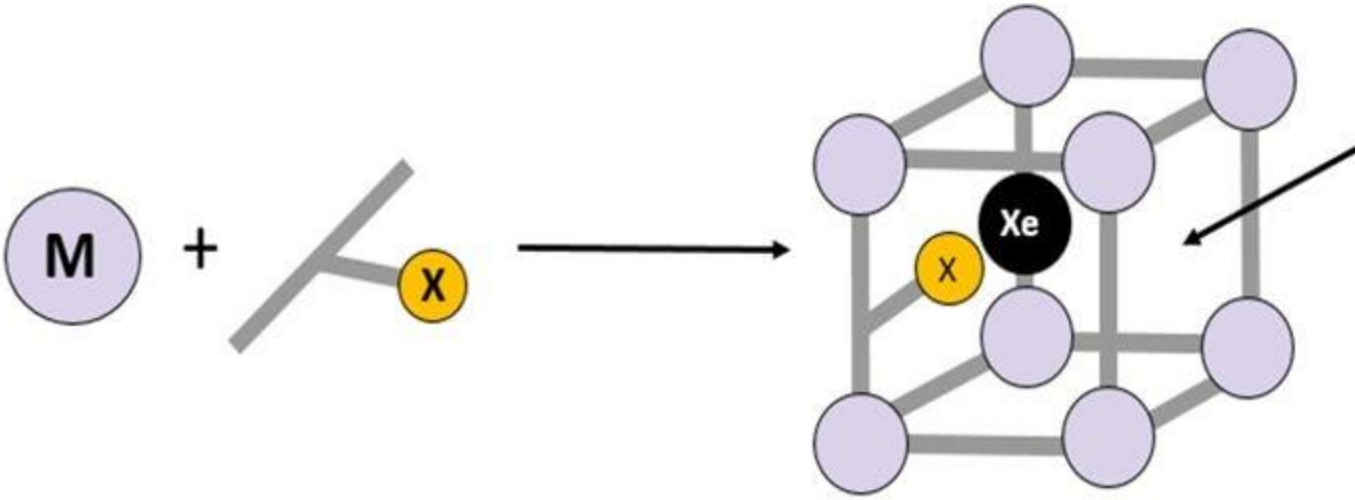
Los Alamos National Laboratory plays an important role in modern international nuclear safeguards, treaty monitoring, non-proliferation, and nuclear forensics. Advancing these missions involves interdisciplinary progress in a broad range of topics including investigating how forensic signatures are created in nuclear materials; how those signatures are distributed in the environment; what information they can provide about a particular process; and improved techniques for measuring those signatures. When considering the scope of understanding required across the nuclear fuel cycle, there is the potential to investigate an almost endless list of topics. Los Alamos National Laboratory is actively pursuing R&D efforts across a broad range of these subjects related to pre-detonation nuclear forensics. For example, experiments to recast well-characterized uranium metal is helping expand our understanding of radiochronometry investigations. Research into the bioaccumulation of radionuclides is furthering our knowledge of the fate of nuclear effluents in the environment. Other efforts are focused upon improving isotope ratio measurements in the wide variety of samples that can be encountered in pre-detonation mission areas, ranging from bulk uranium to environmental samples. These advances are part of our continued efforts to expand the broad nuclear forensic capability at Los Alamos National Laboratory.

NUCL 4106954

Lanthanide tetrafluoroterephthalate MOFs for use in optical detection of radionuclides

Elizabeth Decoteau, *edecoteau@gwu.edu, Claire Belatti, Christopher L. Cahill. Chemistry, The George Washington University, Washington, District of Columbia, United States*

Metal organic frameworks (MOFs) are porous materials comprised of metal cations and organic linkers to form 3-dimensional architectures. These materials have garnered interest among many scientific disciplines for use in gas storage, separations, chemical detection, and optical sensing. With an interest in nuclear forensics, we sought to synthesize a MOF that could trap and detect the presence of radioisotopes via scintillation. Lanthanides were candidates for the metal centers in these materials owing to their characteristic optical properties. We also employed a dual-ligand synthetic approach in an attempt to maximize porosity. Presented herein is a series of isostructural MOFs, $[Ln_2(TFTA)_3(2,2'\text{-bpy})_2(H_2O)_2]$ (Ln = Sm-Er), consisting of lanthanide metal cations bound to tetrafluoroterephthalate linkers and 2,2’-bipyridine capping ligands. The structures of these materials were determined using single-crystal X-ray diffraction and their purity was confirmed via powder X-ray diffraction. Initial void space calculations via the PLATON program show that these materials contain solvent accessible voids, indicating a potential for uptake capabilities. Current efforts consist of collecting thermogravimetric analysis data to understand the thermal decomposition of these materials and luminescence spectra to assess their optical signatures. We also plan to assess porosity and gas uptake capabilities via physisorption studies.



NUCL 4107135

Correlating the physicochemical properties of ionic liquids (ILs) with their behavior as extraction solvents: Toward the rational design of IL-based metal ion extraction systems

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Among the unique properties of ionic liquids (ILs) is their extraordinary tunability, with relatively minor structural changes often leading to substantial differences in physicochemical properties. Although widely cited as an advantage of ILs, this tunability, along with the enormous range of IL structures that accompanies it, also poses difficulties, particularly in their application in the solvent extraction of metal ions. That is, without principles to guide the selection of an ionic liquid appropriate to a given separation, choosing the IL is reduced to trial and error, clearly problematic when the number of potential candidates is large. Further complicating the use of ILs in this application is that metal ion partitioning between an aqueous phase and an IL is often far more complex than in a conventional solvent system, with undesirable ion-exchange processes frequently contributing significantly to the observed extraction. In an effort to address these problems, we have sought to identify quantitative relationships between the physicochemical characteristics of an IL and its properties as an extraction solvent. Studies of alkaline earth cation extraction by crown ethers from aqueous solution into various dialkylimidazolium-, pyridinium-, and quaternary ammonium-based ILs have shown that metal ion extraction efficiency is directly related to the water content of the organic phase. In addition, a clear correlation between the octanol-water partition coefficient of an IL and its propensity toward ion-exchange processes has been observed. Such relationships have the potential to serve as a valuable guide to the design of improved IL-based extraction systems for metal ions.

NUCL 4107255

Pressure induced phase changes in U_3O_8: Understanding a fundamental fuel cycle intermediate

***Ian Russell**, irussellmanatee@gmail.com, Jennifer Szymanowski, Amy E. Hixon. University of Notre Dame, Notre Dame, Indiana, United States*

U_3O_8 serves as a critical intermediate in the manufacture of nuclear fuel. It is a major component of yellowcake, the product resulting from the mining and milling of uranium. In these industrial processes, the U_3O_8 present mostly consists of the α-U_3O_8 phase. However, processing such as grinding or pressing can induce structural changes to ß-U_3O_8 or a fluorite-type high pressure phase. In this work, diamond anvil cells were used to study these phase changes under finely-controlled pressure conditions up to 20 GPa. Powder X-ray diffraction, Raman spectroscopy, and synchrotron-based absorption and emission techniques were utilized to identify at what pressures these phase changes take place and how the chemical environment changes as pressure increases. The research results will lead to a more robust understanding of how the electronic structure of uranium adapts to structural changes. Furthermore, identifying the pressure regions of these phase changes will bolster our understanding of how this critical intermediate changes during processing.

NUCL 4107350

Kinetic frontiers in *f*-element separations

***Mark P. Jensen**, mjensen@mines.edu. Chemistry Department, Colorado School of Mines, Golden, Colorado, United States*

Understanding the separations chemistry of the minor actinide elements in irradiated nuclear fuel, neptunium, americium and curium, is important to plans for advanced nuclear fuel cycles that minimize high-level radioactive waste through deployment of simplified separations. Equilibrium thermodynamic selectivity for particular target elements is widely understood as a critical component of generating selectivity in these chemical separations. However, separations of actinide elements are intrinsically dynamic processes, and the actual selectivity achieved in an implemented separation can be influenced by the kinetics of various processes as much as it is by equilibrium thermodynamics. The paucity of kinetic data available on actinide reactions currently

limits our ability to kinetically manipulate these separations, but Ken Nash's work in actinide kinetics defines much of the field. Important features relevant to the kinetics of actinide separations will be discussed in the context of Nash's essential contributions to actinide reaction kinetics as applied to solvent extraction systems. Building on that foundation, our new work in solvent extraction kinetics and the effect of stimuli responsive switching for controlling the kinetics will be discussed.

NUCL 4107788

Development of non-radiolytic radical assays for the prediction of the radiolytic stability of monoamide extractants

Dean R. Peterman[1], *dean.peterman@inl.gov, Brandon Wackerle*[2], *Madison R. Vicente*[2], *Fatema Zohara*[2], *Modi Wetzler*[2,3], *Julia L. Brumaghim*[2,3]. *(1) Aqueous Separations and Radiochemistry, Idaho National Laboratory, Idaho Falls, Idaho, United States(2) Department of Chemistry, Clemson University, Clemson, South Carolina, United States(3) Center for Nuclear Environmental Engineering Sciences and Radioactive Waste Management, Clemson University, Clemson, South Carolina, United States*

CHON-only extractants such *N,N*-di-2-ethylhexyl-isobutyramide (DEH*i*BA) as are a high priority for nuclear waste separations to facilitate incineration, minimize third-phase formation, and counter proliferation by only enabling uranium separation. However, to facilitate industrial-scale separations the radiolytic stability of potential extractants must be very well understood. Gamma radiolysis is the gold standard for characterizing the type of extractant degradation incurred during nuclear waste separations, but the technique is low-throughput and requires expensive capital equipment. Although DEH*i*BA itself is reasonably well-characterized in terms of its radiolytic stability, 2nd and 3rd generation monoamides are actively being developed, for example to improve selectivity against Tc. A higher-throughput technique that can pre-screen for radiolytic stability to narrow the potential pipeline would be highly advantageous. We are developing such a non-radiolytic, radical assay and will present results demonstrating semi-quantitative prediction of radiolytic degradation trends for monoamide extractants, correspondence of degradation products between radical and radiolytic assays, and the utility of DFT predictions of radical stabilities in marrying the two approaches.

NUCL 4107844

Development of database for machine learning driven rapid and sample specific radionuclide separations

Ethan R. Fix[1], *efix@clemson.edu, Marilú García*[2], *Theresa L. Windus*[3,2], *Musa Danjaji*[4], *Makendra Seawright*[4], *Katelyn Williams*[4], *Eric Brown*[4], *Brian A. Powell*[1,5]. *(1) Department of Environmental Engineering and Earth Science, Clemson University, Clemson, South Carolina, United States(2) Ames Laboratory, Ames, Iowa, United States(3) Department of Chemistry, Iowa State University of Science and Technology,* *Ames, Iowa, United States(4) Department of Engineering, South Carolina State University, Orangeburg, South Carolina, United States(5) Department of Chemistry, Clemson University, Clemson, South Carolina, United States*

Rapid separation of radionuclides is not only necessary for accurate measurements of concentrations and isotope ratios but is also essential for maximizing the amount of data collected for forensic analysis. When processing environmental samples, interference by competing native ions can reduce the efficiency of the separation and cause delays in the analysis. To determine the extent of interference by competing ions and to further facilitate rapid separation of radionuclides in the presence of these ions, our team has started development on a machine learning-driven algorithm that could determine the optimal separation method required. Such an algorithm requires a database with training data that includes distribution coefficients of radionuclides (Th, U, Np, Pu, Am, Tc) and system parameters such as the type of commercial resin used (TEVA, UTEVA, TRU, Dowex-50), interfering cations (Fe, Mn, Al, Ca, Mg, Na, K, Sr), interfering anions (phosphate, sulfate, oxalate, fluoride) and ionic strength. Ongoing efforts are digitizing current datasets in the open literature and performing batch uptake studies to fill gaps in the data. Training data will initially include Pu^{+4} sorption to TEVA with concentrations of 10^{-2} mM to 10 mM of interfering ions and 10^{-2} M to 10 M HNO_3. The database and associated model will predict the impacts of potentially interfering ions typical of natural systems. The model will thus aid in developing an optimized experimental method for separations in samples of known elemental composition

NUCL 4107875

Chelators for actinide radionuclides from a theoretical perspective

Cristian Celis, *celisbarroca@ornl.gov. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Targeted alpha therapy (TAT) and radiotheranostics offer a powerful alternative to treat late-stage cancers for which other therapies are limited. The delivery of alpha-particle radiation directly to cancer cells generally requires a radiometal, a targeting vector, and a metal chelator. The $^{225}Ac/^{213}Bi$ couple has shown to be a promising candidate for TAT, and studies are in an advanced stage. However, their progress has been hindered by their limited availability for widespread application. These limitations are overcome with the new and emerging $^{230}U/^{226}Th$ radionuclide couple, which is being considered as a novel alternative for TAT. Additionally, chelators are key to the safe implementation of TAT; they must show fast metal-complexation kinetics, high thermodynamic stability, and high in vivo stability. The lack of knowledge regarding the coordination chemistry of actinium and, to a lesser extent, thorium makes it difficult to accurately foresee which ligands will form stable complexes in vitro and in vivo without running experiments in the laboratory. Another challenge is that owing to the larger ionic radius of these ions compared with other radionuclides, kinetics and thermodynamics are decreased when using current chelators for TAT. To overcome these challenges, we propose to take a

theoretical and computational approach to understand the nature of the metal–ligand interactions with chelating agents that have been explored for use in ^{225}Ac/^{213}Bi-based TAT. The information collected intends to provide a starting point for researchers to gain understanding in the development of more suitable chelators for the new and emerging ^{230}U/^{226}Th TAT.

NUCL 4108517

Radiochronometric analysis of a historical ^{226}Ra pigment sample for nuclear forensics

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Radium pigments and paints were popular in the 1900s for their attractive, self-luminescent properties. However, after discovering their biological and environmental hazards, they were discontinued, with the last factory closure in 1979. In 2008, the International Atomic Energy Agency identified ^{226}Ra, the main radioactivity contributor in Ra pigments and paints, as a nuclear terrorism threat for its potential usage in dirty bombs (a type of radiological dispersive device (RDD)). Therefore, this work aims to establish the nuclear forensics field for ^{226}Ra pigments and paints by using forensic signatures such as the radiochronometric age and trace metal analysis to source attribute a historical ^{226}Ra pigment sample. This presentation will discuss the use of a ^{224}Ra mock pigment sample for all preparatory work to radiochronometrically analyze the historical ^{226}Ra sample. Thus far, a mock sample has been produced containing all radiotracers for this project and has been successfully dissolved in cocktail solutions containing phosphonium and ammonium salts. Furthermore, column chromatography separations of radiotracers have successfully used Chelex-100 resin for separating mixtures containing ^{226}Ra, ^{133}Ba, ^{212}Pb, ^{207}Bi, ^{209}Po, and ^{65}Zn. Additionally, the auto-deposition properties of trace amounts of Po on Ni foil have proven to be useful when assaying ^{209}Po, which is exclusively an alpha-emitter. In all, these results aim to pioneer future nuclear forensic analyses for ^{226}Ra radiological samples.

NUCL 4108588

Structural characterizations of neptunyl coordination with multidentate acyclic ligands

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The linear neptunyl ion ([NpO2]$^{1+/2+}$) as a stable aqueous species presents a unique opportunity to study the electronic, chemical, and ligating capabilities of transuranium elements. Recent attempts have utilized hard donor incorporated salophen systems to examine the participation of late actinide 5f electrons in chemical bonding, and recently the less explored softer donor porphyrin macrocycles have been applied to neptunyl as well. Herein, we explore the phenylene-substituted benzyl ester bis(pyrrole)phenylenediamine or pyrrophen ligand which features both hard and soft donor ligand types within an acyclic frame. This multidentate ligand is capable of binding to the metal directly through the equatorial plane while maintaining near ligand planarity. The coordination of functionalized pyrrophen (R1 = R2 = H (H_2L1); $R^1 = R^2 = CH_3$ (H_2L2)) with neptunyl has produced two stable hexagonal bipyramidal complexes. The structures and noncovalent interactions were determined and UV-Vis spectra measured. In one case it was determined the neptunyl ion exists as a Np^{5+} while in the other as a Np^{6+}, this difference in oxidation is despite identical synthetic conditions. This presents the first time pyrrophen has been utilized in Np chemistry and demonstrates a new platform to study 5f electron participation and coordination.

NUCL 4108589

Ab initio study of dopant incorporation into gamma-UO_3

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Uranium trioxide (UO_3) is a stable uranium oxide found throughout the nuclear fuel cycle. The γ-UO_3 phase is of particular interest as the most stable at ambient conditions. As such, the γ-UO_3 structure was selected for a theoretical investigation into the incorporation of metal dopants for nuclear intentional forensics applications. The two lattice types of this phase, tetragonal (I41/amd) and orthorhombic (Fddd) were investigated and found to be energetically identical, and as such the smaller tetragonal structure was selected for doping in this study. Three transition metal dopants (Cr, Fe, and Ni) were incorporated into the γ-UO_3 structure interstitially and substitutionally at a total of six different sites. The defect formation energy of each site was calculated. The most energetically favorable of these were investigated further through analysis of lattice parameters, bond distances, X-ray diffraction (XRD) patterns, and densities of states (DOS). These analyses led to the conclusions that interstitial doping of these three transition metals is much more energetically favorable than substitutional doping, and that Cr is the most likely candidate overall with a negative value for its defect formation energy.

NUCL 4108608

Enhancing nuclear forensics through radioelement speciation: Molecular nuclear forensics insights and techniques

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Characteristics of nuclear materials offer valuable signatures crucial for both safeguards and nuclear forensics. Recognizing this, there is a desire to enhance signature identification through the integration of radionuclide speciation in investigations through molecular nuclear forensics. This methodology proves to be a powerful instrument for scrutinizing materials of interest, providing insights into their chemical speciation, structural attributes, morphological features, and trace compositions. This route also leverages the identification of radionuclide chemical forms to expedite isotope evaluation through targeted separations and the intentional addition of signature to nuclear material. As radioactive materials undergo processing for various nuclear applications, discernible signatures emerge, providing information on their origins, separation dates, and chemical treatments. Examples are provided for plutonium-containing particles and uranium oxides, demonstrating the efficacy of molecular nuclear forensics rials. Microscopic analyses unveil crucial details concerning the genesis and processing conditions of actinide materials, while synchrotron spectroscopy elucidates speciation patterns and elemental correlations. These findings furnish a framework for evaluating materials and extracting forensic signatures, effectively bridging the methodologies employed in the nuclear fuel cycle with forensic applications. This integrated approach holds can increase existing capabilities of nuclear forensic science and underscores the potential for deliberate manipulation of signatures in nuclear materials.

NUCL 4108653

Alternative syntheses of metal ceramics for nuclear technologies

Alexander T. Chemey[1], *Alchemeyscience@gmail.com, Victoria Augustine*[1,2], *Esteban Espinoza*[1], *Devin McGlamery*[1], *S. S. Parker*[2]. *(1) School of Nuclear Science and Engineering, Oregon State University, Corvallis, Oregon, United States(2) Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Metal ceramics play a large role in current and proposed future nuclear technologies. Actinide oxides have been used for reactor fuels and explored as synthetic rock phases for long-term waste disposal, while advanced reactors are proposed that benefit from actinide nitrides and carbides. Metal borides also have promise for nuclear technologies, as they have unique properties that make them applicable in varied areas. Production of high-purity actinide nitrides, carbides, and some borides have been challenging, requiring alternative approaches. Solid-state reactions have many advantages, among them simplicity and direct access to the elements of interest with minimal competition. Molten salt-mediated reactions are slightly more complicated, but have the benefit of solution kinetics, resulting in chemical accessibility at lower

temperatures, and the production of novel phases. This presentation will discuss ongoing efforts at Oregon State University to synthesize metal ceramics for nuclear technologies via molten-salt synthesis.

NUCL 4108980

Impact of the major inorganic constituents of asphalt on the rapid determination of actinides

Raissa Chunko, *rchunko@colostate.edu, Ralf Sudowe. Environmental and Radiological Health Sciences, Colorado State University, Fort Collins, Colorado, United States*

In case of a nuclear incident, rapid and reliable radioanalytical techniques must be available to analyze radionuclides in unusual matrices. Radiochemical analysis of samples in standard matrices of soil, water, and air are very well established; however, much less research has been conducted on the effect of urban matrices such as steel, concrete, glass, and asphalt. The techniques used for plutonium separations from asphalt samples originating from roadways and roofing shingles must rigorously be tested to provide useful insight on the characteristics of the special nuclear material in the event of a detonation of an improvised nuclear device (IND) in an urban environment. Batch studies were used to determine the changes in uptake of plutonium on extraction chromatography resins in the presence of trace metal components found in asphalt including aluminum, iron, and manganese at possible ranges found in asphalt samples. In these studies, selected cations with a trivalent state or multiple oxidation states had salting out effects on the uptake of plutonium on the extraction chromatography resins. Metals with significant atomic radii may also contribute to sorption of plutonium synergistically on the extraction chromatography resins. Additionally, metals found in the asphalt were shown to interfere with the recovery of plutonium from column studies conducted. From this data, the contaminates found in asphalt with strong ionic strength give rise to a “salting out” effect with plutonium in solution that increases the sorption on the extraction chromatography resins and will need to be considered during the development of a rapid separation technique for plutonium and other actinides from asphalt samples.

NUCL 4108980

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NUCL 4109186

Surrogate nuclear explosive debris synthesis utilizing a CW CO2 laser

*Austin Burns, **David Rai II**, da097976@ucf.edu, Zachary Ronchetti, Vasileios Anagnostopoulos. Chemistry, University of Central Florida, Orlando, Florida, United States*

The formation of nuclear debris following a nuclear detonation is heavily influenced by the interactions that take place between the environment and the subsequent blast of energy and radiation from the explosion. Aside from the nuclear bombings of Hiroshima and Nagasaki, and the nuclear testing conducted during the Cold War, the number of nuclear explosive events have drastically fallen. This has resulted in a general lack of information regarding nuclear explosive debris and its properties, especially in urban environments. The aim of this work is to synthesize and characterize surrogate nuclear explosive debris (SNED) to advance the understanding of nuclear debris and fill significant knowledge gaps about the formation and characteristics of nuclear debris. The synthesis of SNED can be conducted using a high-powered continuous-wave CO2 laser to simulate the energy released during a nuclear explosion. Particles are lofted in a quartz tube containing the laser where they vaporize before condensing out of the apparatus. Some of the resulting samples resemble trinitite, the material collected following the Trinity Test of 1945, while the overall focus is on creating samples representing potential urban nuclear debris. A suite of nondestructive and destructive characterization techniques can be performed on the samples to gather physical and chemical characteristics about the synthesized SNED leading to a better understand of the mechanisms of the process, such as elemental and isotopic fractionation. This is the

first step toward the goal of creating a database of relevant SNED information, with more facets to be covered in the future.

NUCL 4109326

Studying neutron fluence in a pube neutron howitzer drum using experimental and computational techniques

***Anilu S. Diaz**, anilud@colostate.edu. Environmental and Radiological Health Sciences, Colorado State University, Fort Collins, Colorado, United States*

In the prosed work neutron activation will be utilized to measure the neutron flux at various positions in a Neutron Howitzer. Manufactured by Nuclear-Chicago Corporation, the Model NH-3 Neutron Howitzer Drum is constructed in such a fashion that a PuBe neutron source can be moved in and out of the irradiation position. In the irradiation position, two samples may be exposed to neutrons from the source by placing them in one of two horizontal ports in the drum. Both drum and ports are shielded with paraffin, which allows moderation of the neutron flux to thermal energies. The drum is to be modeled in Monte Carlo N-Particle transport code (MCNP), a program which simulates particle interactions in a given system. Based on the drum geometry and PuBe source, the code simulates and records neutron fluence and interactions at designated locations in the sample ports. In the proposed experimental procedure, multiple metal foils will be activated in the drum by irradiating them up to the point of saturated activation. Using a High Purity Germanium detector, the activity of the foils will be counted. The results of the measurements will be used to calculate the neutron flux using known neutron capture cross sections. The resultant measured neutron fluences are to be compared with the MCNP simulation results to estimate a function of expected neutron fluence in the sample ports per distance from the source.

By determining the neutron flux in the Howitzer drum, neutron irradiation at various intensities will become available for future research at Colorado State University. Additionally, the drum has proven to be an excellent teaching tool as it demonstrates neutron moderation, neutron shielding, material activation, and fluence measurement techniques.

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NUCL 4109459

Immobilization of molecular uranyl complexes on carbon electrodes with polycyclic aromatic hydrocarbons

Cecilia J. Paranjothi[1]*, cparanjothi@ku.edu, T. D. Curry*[1]*, Emily R. Mikeska*[1]*, Ronald Grimm*[2]*, James D. Blakemore*[1]*. (1) Department of Chemistry, The University of Kansas, Lawrence, Kansas, United States(2) Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts, United States*

Redox cycling of uranium is involved in reprocessing of spent nuclear fuel and represents an opportunity to control speciation and solubility. Electrodes can be used to oxidize and reduce uranium, but very few studies have directly examined the redox properties of uranium complexes on electrode surfaces. In this talk, the synthesis and characterization of uranyl complexes bearing different polycyclic aromatic hydrocarbons (PAHs) will be discussed, and the use of the PAH-appended complexes to directly interrogate interfacial redox cycling of uranium. Electrochemical studies have been used to elucidate differences in the apparent properties of uranyl complexes appended with PAHs of various sizes; complexes appended with larger PAHs appear most distinctive both in terms of their electronic absorption characteristics as well as surface stability. Recent work will be discussed, including analysis of the interplay between PAH structural characteristics and the factors that drive association of the complexes with carbon electrodes.

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NUCL 4109589

Molecular-scale understanding of diluent effects on ligand Assembly for actinide and lanthanide separations

Michael Servis*, michaelservis@gmail.com, Derrick Poe. Chemical Sciences and Engineering, Argonne National Laboratory, Lemont, Illinois, United States*

Solvent extraction is an important technique for selective recovery and recycling of lanthanides and actinides in various applications, yet diluent effects on extraction performance is not well understood. Experimental and empirical solvent parameters are often used to correlate extraction performance, such as the dielectric constant, but they are often poor predictors. We follow the hypothesis that the diluents' primary influence on extraction efficiency is in enabling or hindering assembly the bulky extracting ligands in solution into a geometry necessary for metal complexation. This behavior is readily accessible with molecular dynamics (MD), where the atomistic description of molecules can be applied to arbitrary extractant--solvent molecules and their mixtures. Several simulated quantities are considered, from both pairwise or graph theoretic analyses, and compared to experimental distribution ratio data for americium extraction by TODGA in a series of inert, non-interacting diluents. These simple properties, especially the formation of closed triplets corresponding to the 3:1 ligand:metal stoichiometric solvate, suggest potential predictive power of this approach. This methodology provides a path forward to comprehensively understand and predict diluent effects in more

complex systems involving different extracting ligands and multi-component diluent mixtures.

NUCL 4109613 - Withdrawn

NUCL 4109711

Towards predictive-quality electronic structure for heavy-element chemistry

***Edward F. Valeev**, evaleev@vt.edu, Samuel Slattery, Jonathon Misiewicz. Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States*

The critical challeneges for electronic structure modeling of heavy-element compounds include the increased prevalence of stronger-than-normal dynamical ("weak") correlation and more ubiquitous static correlation effects (due to partially-filled subshells). Furthermore, the increased numerical (basis set) errors for the heavy-element compounds are aggraved by the scarser coverage of the lower two-thirds of the periodic table. Here we will discuss our efforts to address some of these issues, by (1) designing self-consistent-field solvers that can be more reliably applied to the heavy-element compounds, and (2) development of correlated relativistic electronic structrure methods based on real-space numerical representations that allow confident control of the numerical error.

NUCL 4109989 - Withdrawn

NUCL 4110134

Small molecule organic glass scintillators for radiation detection

***Dina D. Liacopoulos**, dliacopoulos@mines.edu, Grant Bell, Alan Sellinger. Chemistry, Colorado School of Mines, Golden, Colorado, United States*

Often used for radiation detection, organic-based scintillators emit light when interacting with ionizing radiation. The fluorophores in these scintillators are responsible for the light emission and they tend to consist of materials with aromatic functionality. Solid-state organic scintillators come in several forms. Plastics have highly desirable mechanical properties, are relatively easy to fabricate and have good scintillation performance. Crystals like stilbene are difficult to produce, are extremely brittle, and exhibit excellent scintillation performance. A promising new material termed organic glass scintillators (OGS) has performance competitive with single-crystal stilbene scintillators, and an ease in production that rivals plastics. OGS can also efficiently differentiate between neutron and gamma radiation through pulse-shape discrimination (PSD). This is important in determining when there is a legitimate threat of special nuclear materials (SNM) since the gamma radiation from a container of bananas, avocados or granite could set off scintillators leading to costly and time-inefficient false

positives. However, current state-of-the-art OGS are quite brittle and tend to have low glass transition temperatures which would affect their usefulness in the real-world applications. Additionally, the current approach for preparing OGS includes a n-butyl lithium step, which is an extremely reactive and pyrophoric material. This poster will present and discuss relatively simple organic chemistry to create OGS materials that are less brittle with tunable thermal properties for radiation detection applications. Our OGS have shown promising initial results and competitive light yield and PSD properties.

NUCL 4110327

Radiochemistry, actinides, and separations: Reflection on 30 years of interactions with Ken Nash

Laetitia H. Delmau*, delmaulh@ornl.gov. Radioisotope Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Interacting with the right person at the right time can change an entire career. Those of us who have had the honor and privilege to work, collaborate, or just participate in stimulating discussions with Ken Nash know how true the statement is. Ken's impact on the entire actinide science and separation community spans several decades and his legacy will continue through the work of the new generation. Ken's work on the CMPO molecule at Argonne National Laboratory was the basis for the ligands I studied during my Ph.D. His in-depth study of the TALSPEAK system is a reference for trivalent actinide/lanthanide separation. I used his work to recover and purify promethium from waste solutions from the Pu-238 Supply Program and reestablish Pm-147 production in the US. Many other examples will be presented to show the impact of a life-long outstanding mentorship.

NUCL 4110490

High performance computing and artificial intelligence: Accelerating advances for Global Solutions

***Deborah A. Penchoff**[1], deborah.penchoff@ucf.edu, Charles C. Peterson[2]. (1) The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States(2) University of California Los Angeles, Los Angeles, California, United States*

This presentation will highlight the integration of High Performance Computing (HPC), data science, and Artificial Intelligence (AI) in advancing solutions to address national and global challenges. An overview of HPC resources, now having entered the exascale era of computing, will be discussed. Advances in AI facilitated by HPC will be addressed, focusing on needs in bias analysis and mitigation and ethics, ensuring responsible innovation across areas of research. Additionally, HPC and AI applications

to environmental remediation, nuclear forensics, sustainability, and circular bioeconomy systems will be addressed.

NUCL 4110536

Rare earth elements and their role in global sustainability

Deborah A. Penchoff[1]*, deborah.penchoff@ucf.edu, Charles Sims*[2]*. (1) The University of Tennessee Knoxville Tickle College of Engineering, Knoxville, Tennessee, United States(2) University of Tennessee Baker School of Public Policy and Public Affairs, Knoxville, Tennessee, United States*

This presentation will address the critical role that Rare Earth Elements (REEs) play in national security, including radiochemistry, and every day needs. The discussion will highlight REEs and their criticality in various domains, including technology, medicine, and green energy. The global distribution and deposits of REEs, production, and supply will be presented. In addition, national efforts and strategies to mitigate risks will be addressed. This includes initiatives to restart mining and processing capabilities, diversify supply sources, develop alternative materials, and foster international cooperation with countries that have significant REEs resources. Challenges and opportunities associated with these strategies, including environmental concerns, and the need for technological innovation will be highlighted.

NUCL 4110536

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NUCL 4110591

REACKT: Advancing separations of lanthanides and actinides

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The elucidation of the binding selectivity of lanthanides and actinides is quintessential for advancing nuclear and radiochemical applications, encompassing nuclear forensics, the design of separation agents, and the interpretation of spectra. Theoretical investigations employing molecular modeling methods, such as ab initio and Density Functional Theory (DFT), have been instrumental in simulating binding interactions, with computational protocols being refined for superior accuracy encompassing relativity, spin-orbit coupling, and core correlation effects. The integration of contemporary data modeling approaches, like Artificial Intelligence (AI) and Machine Learning (ML), further augments our understanding of binding selectivity properties. A notable stride in this domain is the advent of the REACKT program, which endeavors to bolster the precision and efficiency of computational methodologies. This presentation delineates the development and integration of computational protocols within the REACKT framework, illustrating how this program propels the frontier of lanthanide and actinide chemistry modeling. By leveraging the REACKT program, we elucidate how a synergistic blend of traditional computational chemistry methods and modern data analytics can significantly enhance predictive accuracy and provide deeper insights into the complex behavior of lanthanide and actinide systems.

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Radiochemists in non-chemistry departments

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This panel includes radiochemists currently working in academia, industry, and government sectors. Panelists will discuss the essential role experts in nuclear and radiochemistry play across various settings beyond traditional chemistry departments. Their diverse training and job experience highlight advances at the intersection of research and development toward public policy decisions that collectively address needs at the national and global levels for a sustainable and secure future. In addition, the panel will address the transformative potential of nuclear and radiochemistry to attain critical multidisciplinary solutions needed to harness its benefits for health, safety, and sustainability on a global scale.

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Fission product yield measurements of Pu-239 irradiated at the USGS TRIGA reactor

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Fission product yield measurements of the major actinides are essential for various nuclear applications. For instance, these nuclear observables are used to calculate the heat production of nuclear reactors at power, used to monitor the nuclear stockpile via computational modeling, and used to measure forensic signatures following detonation of a nuclear weapon. The relative uncertainties for current reported measurements impede the accuracy of these nuclear applications and therefore require additional measurements for proper nuclear data evaluation. Efforts aim to improve these measurements to better understand the energy-dependence of fission product yields. Specifically, the yields of valley nuclides (A ~ 120) are particularly sensitive to the energy of the incident neutron and provide the greatest insight towards the energy-dependence of the fissioning nucleus. Integral fission yield measurements were completed in the USGS TRIGA reactor at the Denver Federal Center located in Denver, CO. Two separate weapons-grade PuO_2 targets were individually irradiated in the Central Thimble under distinct neutron environments, and these experiments were designed to evaluate the behavior of a fissioning Pu-239 nucleus under a thermal and hardened neutron spectrum. Following irradiation, each PuO_2 target was individually dissolved and select fission products were radiochemically isolated for gamma analysis. This talk will summarize the experimental design used during irradiation, discuss significant radiochemical steps used, and feature the yields measured from Mo, Zr, Cd, Ag, Cs, Ba, and Nd fission products for each irradiated PuO_2 target. These experimental results will also be compared against currently reported measurements.

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Variations in the structure of unreported uranyl oxalate crystals correlating with counter-cationic radii

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Actinide oxalates are present in the nuclear fuel cycle and are frequently used to precipitate tetravalent actinides from solution, such as in used-fuel reprocessing. Following the PUREX process, plutonium(IV) is precipitated from solution using oxalate. Actinyl oxalates are found in the environment, due to the presence of oxalate in natural aqueous environments, from the degradation of humic and fulvic acid. There exist two uranyl oxalate minerals, uroxite ($(UO_2)_2(C_2O_4)(OH)_2(H_2O)_3$) and metauroxite ($(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2$), which were identified in 2020. More recently, the Pu(IV)-oxalate crystal structure was reported, demonstrating that although the actinyl oxalates are well studied, there still is much to be elucidated regarding their solid-state structures. Herein we present several new uranyl oxalate structures with monovalent

cations. These uranyl oxalate crystals were synthesized via hydrothermal techniques, where super-saturated solutions of the uranyl ion, oxalate ion, and monovalent cation are reacted in a Paar vessel, the supernatant is filtered from the remaining solid and allowed to crystallize. The resulting filtered solid and crystallized compounds were studied through X-ray diffraction, spectroscopic techniques, and calorimetry.

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Thiol functionalized metal-organic frameworks (MOFs) for mercury removal from waste tanks

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Mercury accumulation and separation has become a challenge in recent years as it is added to waste tanks for the catalytic acidic dissolution of aluminum cladding. Our goal is to understand the non-covalent chemical behavior and create adsorbents utilizing porous metal-organic frameworks (MOFs) to pursue high selectivity and achieve Hg separation in nuclear process waste tanks. Accessible thiol (−SH) functionalities installed in the MOFs provide wide-ranging reactivities, enhance MOF stability in the solid state, and promote higher selectivity toward mercury. The frameworks UiO-66, UiO-67 and UiO-68 type using Zr(IV) ions with linkers such as a) 2,5-dimercapto-1,4-benzenedicarboxylic acid, b) 3,3’-dimercaptobiphenyl-4,4’-dicarboxylic acid, and c) 2,5’-dimercaptoterphenyldicarboxyl-4,4’-dicarboxylic acid were tested in this study. These linkers feature both hard carboxyl and soft thiol functionalities, aiding and enhance mercury sorption. The efficacy of the thiol functionalized MOF was monitored by measuring the uptake and release kinetics of Hg(II) and the adsorption capacity of different Hg forms. Additionally, the radiolytic and pH stability of the MOFs was monitored by powder-Xray diffraction (P-XRD).

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Revisiting nuclear waste transmutation technologies for applications to energy / national security

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National security implications suggest that the United States must strengthen its internal availability of base-load sources of carbon-free power. This has led to renewed interest in fission reactors and continued deployment of nuclear energy. This is currently the only energy source that satisfies the needs of a modern economy and provides for the changing energy landscape of the future. This not only applies to the charging of electric vehicles, but also for extremely energy intensive processes such as desalinization of water, hydrogen production, affordable energy for citizens, etc.

We propose to investigate the design, development, performance requirements and cost of an accelerator-driven system (ADS) using molten salt (MS) technology as the working material for transmuting used reactor fuel. Recycling and transmuting used fuel in an ADS satisfies multiple needs: 1) Long-lived transuranic material is destroyed, thereby reducing the volume of radioactive waste, 2) Energy is produced by fission, and 3) The system is operated in a sub-critical configuration, which improves safety while minimizing criticality constraints. Establishing a domestic ADS effort will require a survey of the present technology status, development of an experimentally validated simulation of an ADS sub-critical waste burner, and a complete systems study to demonstrate the technological and economic feasibility of operating an ADS.