NUCL 3893673

Size and redox control for selective heavy element and inorganic isotope recovery

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Over the past decade, select isotopes of the lanthanide and actinide series of elements have emerged as promising therapeutic and/or diagnostic radiometals. To ensure the safe clinical use of these new – sometimes experimental – medical isotopes, it is imperative to establish reliable and reproducible purification and characterization procedures, which must be applicable to the different steps involved in radiopharmaceutical preparation and evaluation. From the determination of Ac-227 as a radionuclide contaminant in accelerator-produced Ac-225 to the routine purification of trace metal-free Th-227 and Ra-223 from Ac-227 generators, or the size- and charge-selective exclusion of daughter nuclides during radiolabeling with biological macromolecules, our focus has been placed on establishing simple, yet effective, separation strategies. Every step of our approach relies on a careful understanding of the radiological signatures and dynamic speciation of the isotopes at play. Separation examples following this approach will be presented, including the recent application of Ac-227 determination to the production of pure streams of Fr-223, which were used for targeted liquid-liquid extraction experiments to elucidate the chemical properties of the rarest and heaviest alkali metal.

NUCL 3899376

Mitigating the corrosive effects of molten salts through multi-layer ALD coatings for optimal material passivation

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Molten salts are extremely efficient heat exchange fluids, and have uses in applications such as molten salt nuclear reactors (MSRs) and concentrated solar power generators (CSPs). Because molten salts form stable ionic electrolytes at high temperatures, they also foster corrosion through electrolytic oxidation and dissolution. This makes safe, secure molten salt containment a challenge. Thin passivating layers are often employed to mitigate corrosion, however no perfect solution currently exists. The goal of this research is to intentionally employ multiple layered materials to achieve optimal corrosion resistance in highly corrosive environments, such as those in MSRs and CSP generators. This goal will be achieved through the systematic study of 1) layer material composition, 2) layer material thickness, and 3) number and order of layers. Using atomic layer deposition (ALD), multi-component, atomically precise anti-corrosive

coatings are prepared for iterative studies of early stages of corrosion at the interfacial scale. In situ analytical techniques such as attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and in situ SEM using WETSEM™ atmospheric control capsules are employed to characterize the chemical, compositional and morphological changes that occur during corrosion, to identify and eventually mitigate the deficiencies of these coatings. In summary, the proposed work has the potential to significantly enhance the resistance of materials used in manufacturing and infrastructure; not only for MSRs and CSPs generators, but more generally for materials at risk of exposure to highly corrosive environments.

NUCL 3903930

Improving uranium oxides processing history discernment with dynthetic data

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Recently, the quantitative morphological characterization of particles captured in scanning electron microscope (SEM) images has proven to be a valuable technique for determining the originating process of nuclear material. Specifically, the morphology features of particles with unobstructed edges have been used to discern processing history of an unknown uranium oxide. Previously, the particles with unobstructed edges were manually segmented using a software called morphological analysis for materials (MAMA). The manual segmentation step is tedious and time-consuming. Thus, a recent study had utilized a machine learning model, convolutional neural network (CNN) in particular, to automate the segmentation of particles. CNN is a data-driven approach. A large annotated dataset is required to achieve a reasonable performance with CNNs. However, obtaining such large annotated dataset is costly and time-demanding.Therefore, we propose to leverage simulated particles and their corresponding synthetic SEM images to enlarge the available annotated dataset in turn improving the overall performance of a CNN-based segmentation model. Concretely, we utilize a modified Monte Carlo Potts model to simulate the coarsening of uranium oxide particles. Next, we employ a generative model to synthesize the simulated particles into micrographs to create labeled pairs for training a CNN-based segmentation model. Through extensive experiments, we demonstrate that a CNN segmentation model is greatly benefited from the synthetic data. Furthermore, these results open a new research direction in how we can better incorporate synthetic data with experimental data to achieve a superior performance while lessening the overhead cost

NUCL 3906284

Lanthanide and actinide separation with graphene oxide membrane

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The separation of actinides from lanthanides is important for the management of nuclear waste, but is full of chanllenge due to the complexity of their chemical properties. The actinyl ions (U, Np, Pu, Am) are in the linear dioxo form while the lanthanides are spheric ions, which give a chance to separate them by using the size difference. Graphene oxide membrane with sub-nanometer interlayer nanochannel has been applied as ion cut-off filter. By tailoring the interlayer spacing, the hydrated actinyl ions could be blocked and the lanthanides could pass through, resulting an efficent group separation. This simple stratergy could realized a lanthanides/actinides separation factors up to ~400.

NUCL 3914327

Enriched isotopes of all shapes and sizes: A look at the stable isotope target laboratories at Oak Ridge National Laboratory

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The Stable Isotope Materials and Chemistry (SIMC) Group at Oak Ridge National Laboratory (ORNL) maintains and dispenses enriched isotopes from the National Stable Isotope Repository, a collection of more than 2,000 quality-controlled batches of 225 stable isotopes spanning 50 elements. In addition to dispensing the inventory forms, SIMC provides specialized technical services to convert materials to a customer's desired chemical form and fabricate a target of the desired physical form. These customized target forms are achieved through a suite of techniques that include the following: (1) pyrochemical and thermal conversions; (2) inorganic synthesis; (3) powder metallurgy by pressing, melting, and/or sintering; (4) hot and cold rolling; (5) wire casting, rolling, swaging; (6) arc melting, casting, alloying, and drop casting; (7) ion beam and plasma sputtering; and (8) high vacuum evaporation. Due to the high monetary value of these materials, low-loss variations of the group's techniques are emphasized and supported by a research and development program, which is designed to continually expand and improve upon these capabilities. This presentation will discuss the major processes and equipment used to manufacture a wide range of targets at ORNL and highlight the utility toward developing targets for nuclear physics measurements.

NUCL 3914473

Fission product analysis of ^{155}Eu for post-detonation nuclear forensics

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The cumulative fission product yield (CFY) of radionuclides on the wings and valleys of the typical nuclear fission split are sensitive to changes in neutron energy and fuel type. In this context, ^{156}Eu ($t_{1/2}$ = 15.2 days) is a ‘wing’ radionuclide that is often analyzed by the Chemistry - Nuclear and Radiochemistry group at Los Alamos National Laboratory. As radiochemical separations had previously been performed to purify europium for multiple irradiation experiments there was the potential to reanalyze these samples for ^{155}Eu, a fission product with a considerably longer half-life (4.753 y).
Radioanalytical counting protocols were developed using samples prepared from the irradiation of ^{235}U by thermal neutrons. The development of a satisfactory beta counting methodology was hampered by the necessity of requiring the samples to be aged (to allow for the decay of excess ^{156}Eu), the comparative low beta energies, and the low sample activity (long half-life coupled with low fission yield). While the low sample activity also impacted gamma-ray spectrometry analysis, two relatively high-intensity gamma-rays at 87 & 105 keV could readily be measured. As the 89 keV gamma line for ^{156}Eu would interfere with more recent samples a working method was based on the 105 keV emission. To minimize reliance on nuclear data, measured dpm values were divided by measured ^{99}Mo cpm values for a given ^{235}U(th) experiment to yield an ‘r’-value, and by extension a ‘k-factor’ in atoms/dpm.
Once developed, the ^{155}Eu analysis method was applied to samples prepared from irradiations using different fuels (^{235}U, ^{238}U & ^{239}Pu), and different neutron energies. Measured ^{155}Eu atoms values were as expected, coming between previously measured atoms values for ^{153}Sm and ^{156}Eu. Calculated fission yields were also in good agreement with literature values, many of which currently have high associated uncertainties.
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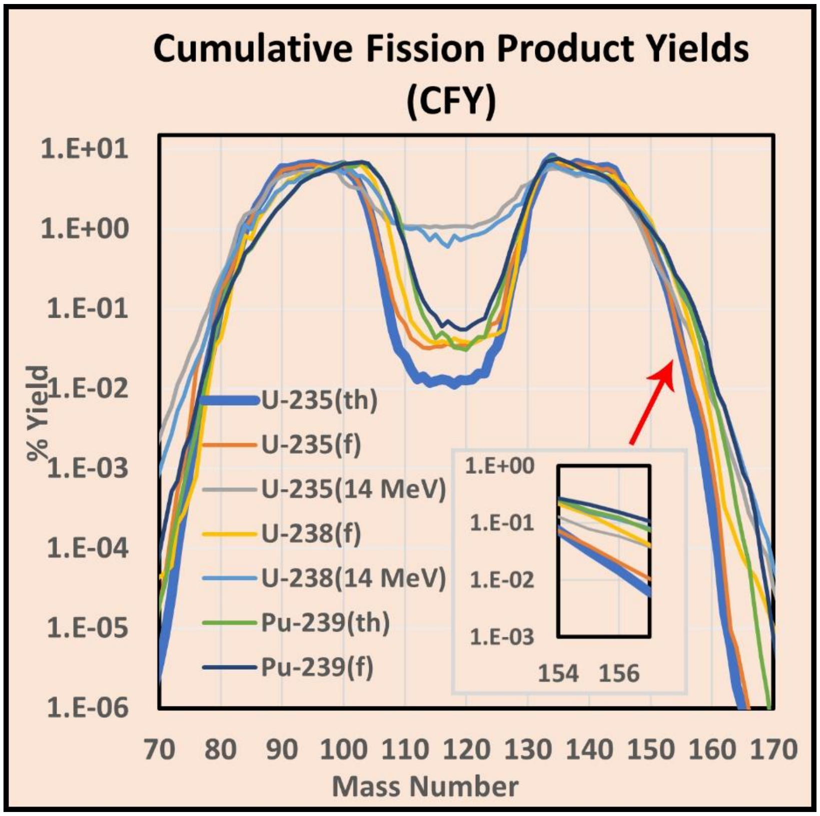

NUCL 3914916

Exploration of uranium tetrafluoride morphologic signatures for nuclear forensic science

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Current research has quantitatively proven the utility of uranium oxide morphology for identifying processing parameters such as precipitation conditions, thermal history, and storage conditions, among others. However, open-source literature regarding the morphology of uranium fluorides is limited, and similar morphologic attributes are expected to be observable in these materials. This study therefore examines the morphologic signatures of uranium tetrafluoride, UF_4, which is a common feedstock for the production of uranium metal and UF_6, and is thus of potential interest to nuclear forensic analyses and nuclear fuels production. To develop these signatures, UO_2 was synthesized from both ammonium diuranate (ADU) and ammonium uranyl carbonate

(AUC), which are common precipitation routes in commercial processing and have largely differing surface areas and morphologies (Figure 1). The UO_2 from each synthetic route was fluorinated in a fluidized bed reactor via ammonium bifluoride (ABF) to form UF_4. The morphology of the initial starting material, ADU and AUC, is anticipated to quantitatively affect the final UF_4 morphology. Powder X-ray diffraction was used to confirm the phase purity of the reaction product, while scanning electron microscopy in concurrence with Morphological Analysis of Materials (MAMA) software was utilized to quantify the material morphology. A response surface model design of experiment was additionally employed to interpolate between various factors of the fluorination and resulting morphology.

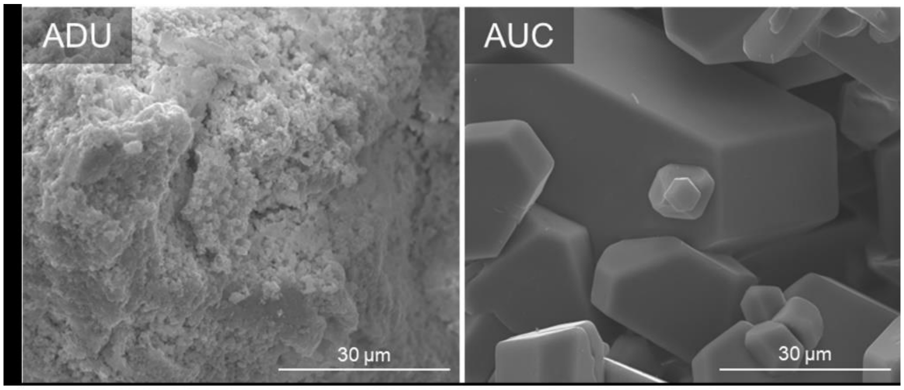

Figure 1. SEM-SE images of starting materials ADU and AUC at 10,000x magnification.

NUCL 3915018

Theoretical investigation of solvation of lanthanide cations in “dry” and “humid” room-temperature ionic liquids: A DFT study

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A DFT study has been carried out to explore the solvation of naked rare-earth (RE) cations (Yb^{3+} and Nd^{3+}) in “dry” and “humid” room-temperature ionic liquid (RTIL), 1,3-dimethyl-imidazolium$^+$, PF_6^-, designated as $[MMI]^+[PF_6]^-$. The entire solvation study was first explored in the gas phase and further extrapolated to water and IL medium employing continuum solvation models. As depicted in figure IL, in “dry” IL, the first solvation sphere is occupied by six PF_6^- anions followed by three $[MMI]^+$ cations in the second solvation shell. The scenario in “humid” conditions differs as the neutral H_2O molecules are directly bonded with Ln^{3+} cations in the first solvation sphere followed by PF_6^- anions forming the second solvation sphere. Nd^{3+} being relatively large, can acquire 9 and 10 coordination numbers (CN), whereas Yb^{3+} has been optimized to 8 and 9 coordinated species. From the binding energy (BE) analysis, it is noticed that irrespective of the CN and medium of study, all the complexes have the highest BE in the gas phase, followed by IL, and the least in the water medium. Moreover, it is also evident that for both “dry” and “humid” IL complexes, Yb^{3+} complexes have relatively higher BE than Nd^{3+} complexes. The results can provide some constructive information for the complexation phenomena of RE cations using IL, which can be useful for the practical extraction of REs using IL.

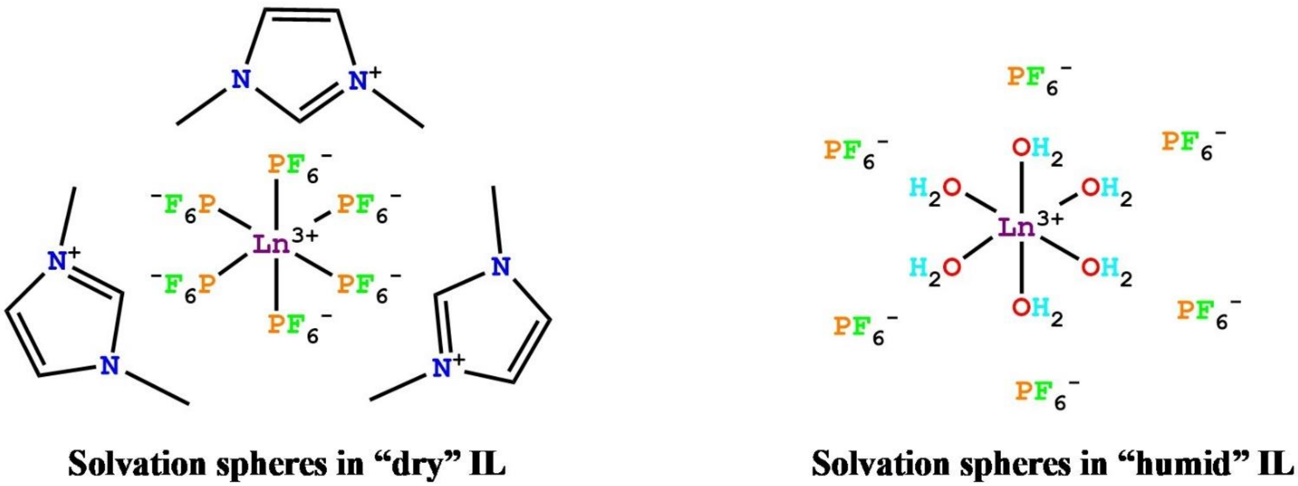

Figure IL. Pictorial diagrams of the lanthanide complexes formed with ILs in “dry” and “humid” conditions.

NUCL 3915544

True matched-pair heterodimers for treatment and diagnosis of prostate cancer

Grace Liles[1,2]*, grace.k.liles@gmail.com, Claudia Chambers*[1,2,3]*, Emily Lawler*[1]*, Terry Carmack*[1,3]*, Lisa Watkinson*[1,3]*, Michael Pun*[1]*, Michael Bellavia*[1]*, Katie Tucker*[1]*, Carolyn J. Anderson*[1,2]*, Charles Smith*[1,3,4]*. (1) Molecular Imaging and Theranostics Center, Columbia, Missouri, United States(2) Chemistry, University of Missouri System, Columbia, Missouri, United States(3) Harry S. Truman Memorial Veterans' Hospital, Columbia, Missouri, United States(4) Radiology, University of Missouri School of Medicine, Columbia, Missouri, United States*

Prostate cancer is the second most leading cause of cancer related deaths in men with a projected 34,700 deaths in 2023. Since 2014, the incidence rate of advanced-stage prostate cancer has increased by approximately 5% each year. Our goal is to develop a theranostic hybrid radiotracer that will effectively target the receptors or biomarkers expressed on prostate cancer cells.

Radiolabeled peptides and small molecules can be highly selective for receptors that are expressed on the surfaces of cancer cells. Gastrin-releasing peptide receptor (GRPR) and the prostate-specific membrane antigen (PSMA) are expressed in very high numbers on prostate cancer cells, which makes them ideal molecular targets for radiolabeled peptides and small molecules for diagnosis and therapy of prostate cancer. We have proposed GRPR-/PSMA- targeting DUPA-6Ahx-(NODAGA)-8Aoc-GRPR ANT and DUPA-6Ahx-(NODAGA)-Carboxypiperidine-GRPR ANT (DUPA → PSMA-targeting; GRPR ANT → GRPR-targeting) molecular hybrids and radiolabeled them with ^{64}Cu and ^{67}Cu. We have optimized the labeling conditions for these targeting vectors to improve the specific activity of our radiotracers for imaging and therapy. This was determined by high-performance liquid chromatography (HPLC). The radiolabeled, bivalent, heterodimers displayed high binding affinity and specificity in vivo to both PSMA and GRPR in our biodistribution studies, as well as high tumor uptake in our molecular imaging investigations. This study provides a promising approach for the development of dual targeting, radiolabeled, agents for prostate cancer imaging and therapy.

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NUCL 3915591

DFT Investigation of transition metal dopants in Beta-UO_3

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Early nuclear fuel cycle technologies involve the extraction and processing of uranium ore into nuclear fuel via milling techniques, enrichment of fissile material, and fuel fabrication. We focus on the addition of dopants, or taggants, to an early fuel cycle material, UO_3, as a means to add a nuclear forensics signature to these materials. This concept is generally known as intentional forensics.

A taggant is an element that is intentionally incorporated into the matrix of a material and further investigated for any obvious chemical interactions that develop with or without external stimuli. The beta phase of UO_3 is the principal polymorph for this study, formed by flash heating $UO_2(NO_3)_2 \bullet 6H_2O$ in air. With data collected from experimental X-ray diffraction (XRD), Raman spectroscopy, and previous density functional theory (DFT) calculations, modeling of β-UO_3 is done with the candidate metal taggants (Cr, Fe, and Ni) incorporated into the unit cell as defects.

The Vienna *Ab initio* Simulation Package (VASP) was used to conduct DFT calculations to determine the energies of incorporation for the three transition metal taggants in both substitutional and interstitial lattice sites and the site-dependence of changes in the electronic structure in the tagged materials. For the most stable doped structures, the lattice dynamics in the form of the vibrational modes were calculated and the Raman and IR active modes were determined by symmetry. Prediction of other experimental observables like powder XRD has also been performed. Comparison of these results to complementary ongoing experimental efforts will support the identification of the most likely incorporation sites and stability of the three candidate metals in β-UO_3.

NUCL 3917004

High-energy X-ray diffraction microscopy for nuclear forensic analysis

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The nuclear forensics community has long used traditional optical and scanning electron microscopy (SEM) techniques to observe morphological surface features. Recently, interest has increased in determining the sub-surface features of materials in

three dimensions. High-energy X-ray 3D imaging techniques using a direct beam (micro computed tomography) or diffracted beam (high energy diffraction microscopy) are well suited to providing qualitative and quantitative sub-surface morphological information and have the added benefit of being non-destructive. This work describes the synthesis, conventional characterization, and synchrotron characterization of morphologically different samples of U_3O_8 as well as the development of machine learning algorithms to decrease the time required to analyze the produced synchrotron data.

Three separate samples of U_3O_8 were synthesized in gram batches from the same UO_3 starting material while varying the calcination temperature from 600 °C to 800 °C. Each of these was then split into several analytical samples for analysis using powder x-ray diffraction (p-XRD) and SEM imaging. The results from these analyses confirmed that the morphology of the samples differed depending on calcination temperature and indicated incomplete transformation of UO_3 to U_3O_8 at the lower temperatures. Subsequent efforts have concentrated on analyzing the samples using high-energy x-ray diffraction microscopy (HEDM) and micro computed tomography (µ-CT). While the sample synthesis produced powders that have grains too small to individually resolve using HEDM, the collected diffraction patterns can be used to produce a 3D reconstruction of crystal phase distributions. Due to the small beam size and relatively high spatial resolution in 3 dimensions, a significant amount of data is generated causing reconstructions to be slow. For example, a single 1.5 µm thick layer of sample takes a few hours. The use of machine learning algorithms and unique analysis methods in this work has resulted in a significant drop of that reconstruction time to ~3 minutes. This work presents initial sample analysis results along with a discussion of the HEDM technique and how it may be beneficial to nuclear forensic analysis.

NUCL 3917254

Production of iridium radionuclides for nuclear forensics

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Radionuclides of iridium produced by neutron activation in a nuclear explosion can provide forensic information related to the neutron spectrum given the presence of Ir-190, Ir-193m, and Ir-192/194 from exposure of iridium material to neutrons of high (> 8 MeV), medium (1 < E < 8 MeV) or low (< 1 MeV) energy, respectively, while the presence of Ir-189 may arise from second order reactions. Producing reference materials with appropriate ratios of these radionuclides are needed for validation and verification of analytical measurement methods, and for capability demonstrations. Towards producing Ir with desired isotopic ratios, excitation functions were measured for osmium and rhenium targets irradiated with protons (8.2 < E < 15.5 MeV) and alpha particles (16.2 < E < 27.0 MeV), respectively. Separation methods were developed to isolate the radio-iridium from the bulk target materials. Measured cross-sections are consistent with TALYS simulations. Atom ratios around 10^4 for Ir-190/Ir-189 are achievable through irradiation of Re target with alpha particles while similar atom ratios for Ir-192/Ir-189 are achievable by irradiating enriched Os-192 with protons.

NUCL 3918160

Group hexavalent actinide separation via co-crystallization of isotopes found in used nuclear fuel

***Jennifer M. Pyles**[1], j2mpszz@uab.edu, Jeffrey Einkauf[2], Luke R. Sadergaski[3], Laetitia H. Delmau[3], Bruce Moyer[2], Jonathan D. Burns[1]. (1) Chemistry, The University of Alabama at Birmingham College of Arts and Sciences, Birmingham, Alabama, United States(2) Physical Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States(3) Isotope Science and Engineering Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

The burning of fossil fuels has been the primary source of energy for modern civilization. However, recently, the negative environmental impacts from these processes including, the emission of pollutats and greenhouse gases, which excellerate climate change, have garnered much attention. This has nesseitated the development of green, renewable energy, with one of the few energy sources that can be scaled to meet the growing demand being nuclear power. To enable the expansion of nuclear power several challenges need to be addressed. One of the main challenges is developing a separation/recycling scheme for used nuclear fuel (UNF) that enhances the recovery of the U, Pu, and other actinide (An) species. Sequentially, the ideal separation process should minimize the impact of waste bound for a geological repository, maintain the nonproliferation standards, and have the ability to scale the process for a diverse fleet of reactor fuels.
The aim of this research explores a single-step separation technology for the recovery of the Ans ranging from U-Am as a group, utilizing a co-crystallization with uranyl nitrate hexahydrate (UNH). Recent studies have shown the transuranic (TRU) species in their hexavalent state, Np(VI), Pu(VI), or Am(VI), which exist as the dioxo actinyl molecular ion, AnO_2^{2+}, have near proportional removal from solution to that of U(VI). The co-crystillataion approach has extremely high selectivity for the An(VI) species, while completely discriminating against fission products. Aspects of the separation of the hexavalent Ans from fission products will be discussed, with special attenetion on the problematic fission product species like Zr, Mo, Tc, and Ru.

NUCL 3918160

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NUCL 3918665

Focused ion beam for spatially resolved morphological and chemical analysis of nuclear materials

***Brandon Chung**[1], chung7@llnl.gov, Alexander Baker[1], Scott Donald[1], Tian Li[1], Rachel Lim[1], Uday Mehta[1], Debra Rosas[1], Shohini Sen-Britain[1], Donya Servando-Williams[1], Vanna Som[1], Nick Cicchetti[2], Alexander Ditter[3], David K. Shuh[3]. (1) Lawrence Livermore National Laboratory Physical and Life Sciences Directorate, Livermore, California, United States(2) University of Nevada Las Vegas, Las Vegas, Nevada, United States(3) E O Lawrence Berkeley National Laboratory, Berkeley, California, United States*

Nuclear forensics requires accurate identification of distinguishing material characteristics of interdicted nuclear materials. Local morphological and chemical variations in nuclear materials are nearly ubiquitous due to the varying provenance, process, and pathways. Conventional analysis using bulk nuclear material provides an overall analytical value, but a typical nuclear material is heterogeneous, requiring highly spatially resolved characterization. Consequently, averaging material characteristics may obscure critical forensic signatures resulting from local chemical and structural

variations. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for direct three-dimensional (3D) morphological analysis or to prepare site-specific material features to obtain spatially resolved characterizations using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Our work shows the internal morphological and chemical variations in host nuclear materials provide valuable information about the material's production processes and recent environmental exposures. We identified that internal microscopic features entrapped within bulk nuclear materials contain trace elements or chemical that are attributable to their origin, processing, and environmental exposures.

NUCL 3918665

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NUCL 3918700

Exploration of heavy actinide interactions with dipicolinic acid derivatives

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The exploration of fundamental chemistry of the heavy actinides (Am-Cf) through experimental and computational means is vital to waste remediation for the nuclear fuel cycle, further understanding of the periodic table, and intra-series separations of the trivalent actinides (An(III)). Periodic trends of the trivalent actinides remain elusive to the science community, but interesting trends in increasing covalency across the series have been found. Specifically, this has been observed with the mixed nitrogen and oxygen (N,O) donor, dipicolinic acid (DPA). Derivatives of DPA have been synthesized with various electron withdrawing and donating groups in the 4-position para to the coordinating nitrogen such as morpholine (mor) and hydroxymethyl (hm). While improving the solubility of DPA, these derivatives can also reveal electronic effects at the binding center which impact the mixing of the An(III)-L orbitals. Utilizing solvent extraction to inspect the binding ability of nitrogen and oxygen donors through obtaining stability constants is one key to unlocking the mysteries of the trivalent heavy actinides. Exploring the stability constants of actinides with DPA, mor-DPA, and hm-DPA through solvent extraction can also provide insight to intra-series separations. Experimental and computational studies have revealed higher stability constants and stronger bonding between the heavier actinides and more electron donating DPA derivatives. These results will be presented.

NUCL 3918931

Improving accessibility to DEHiBA through automated synthetic optimisation to support the advancement of nuclear reprocessing

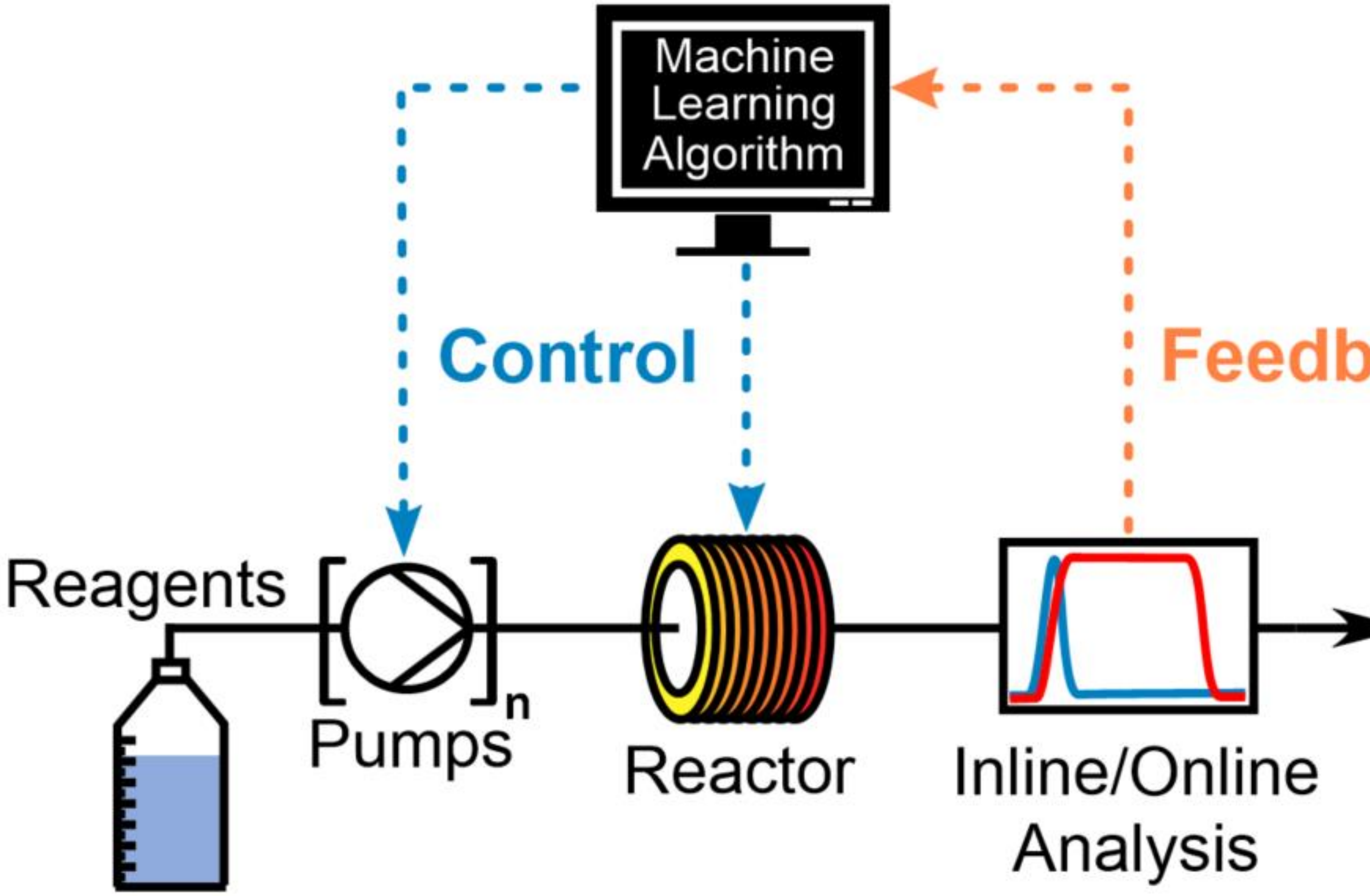
***Tom Shaw**, tomshaw2111@gmail.com, Bruce Hanson, Richard Bourne. University of Leeds, Leeds, West Yorkshire, United Kingdom*

Advanced hydrometallurgical reprocessing of nuclear fuel aims to further the recovery of troublesome and valuable radionuclides, thus reducing the burden of radiotoxic waste and facilitating the recycle of select elements. To achieve the selective recovery of radionuclides like uranium, specialised organic ligands like DEHiBA (N,N-di-(2-ethylhexyl)isobutyramide) are employed. Despite decades of research investigating the performance of DEHiBA for the selective extraction of uranium, there is little to no literature investigating an efficient, scalable synthesis of DEHiBA or other ligands. As the current high cost to purchase these molecules restricts access to large-scale testing of these processes, this work has developed a cost-effective process for the manufacture of DEHiBA. This has enabled the manufacture of large volumes of DEHiBA for pilot-plant testing of this otherwise costly ligand to aid further the technology readiness level of advanced nuclear reprocessing.

This work employs an automated, self-optimising flow reactor platform to facilitate the

efficient optimisation of process metrics such as reagent cost and productivity for the synthesis of DEHiBA. Our approach minimises chemical consumption and optimisation timelines whilst improving process understanding, this has resulted in the development of a cost effective route to DEHiBA whereby litres can be manufactured per hour. This powerful and effective methodology is also applicable to a multitude of ligands for advanced reprocessing to improve accessibility to these high value research materials. Consequently, we have been able to compare the effectiveness of DEHiBA for the extraction of uranium across a range of scales.

This work was undertaken within the institute of Process Research and Development (iPRD) at The University of Leeds, utilising machine-learning and flow chemistry to develop cost effective processes for the manufacture of DEHiBA and other ligands on demand. Ultimately we demonstrate improved accessibility to litres of ligands like DEHiBA to facilitate large-scale extraction testing and hence the adoption of advanced nuclear reprocessing in the future.



NUCL 3919320

New nuclear targetry lab at SJSU

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A new nuclear targetry lab has been established at San José State University. The last decade has seen a marked increase in the demand for well-made targets, driven by the many currently thriving nuclear facilities, the start of FRIB, the retirement of many seasoned targetry professionals, and the closure of several legacy targetry labs. To combat this trend, we recently established a broad program of stable and radioactive target production at SJSU. Focusing on thin film targets for low energy nuclear reaction studies, the SJSU targetry group are able to make and characterize nuclear targets for a variety of experimental applications. Current production techniques include physical vapor deposition via a resistive heating vacuum evaporator, molecular plating of rare isotopes, cold rolling of ductile materials, and solvent casting for deuterated plastic targets. SJSU's target characterization capabilities include microscopy for surface morphology, FTIR & XRD for elemental and chemical analysis, and α-energy loss for film thickness. As a primarily undergraduate and minority serving institution, a major motivation for our group's targetry efforts are to provide engaging research experiences for our students and help broaden the nuclear science pipeline. This talk will focus on introducing the different abilities currently available at SJSU by highlighting some recently produced targets for nuclear science experiments.

NUCL 3920039

Development of techniques for fabricating radioactive targets for nuclear data measurements

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One of the goals of the recently commissioned Facility for Rare Ion Beams (FRIB) is to study rare radioisotopes, including measuring nuclear reaction cross sections on these isotopes. There are numerous challenges associated with such measurements due to radioactivity of the target material, half-life limitations, and purity, both isotopic and chemical. This talk will discuss efforts to develop techniques for isotope harvesting, radiochemical separations and target fabrication to enable nuclear reaction measurements on radioactive isotopes that are relevant for national security applications. Isotope harvesting from FRIB is a key avenue to obtaining rare radionuclides in quantities and purities that are not readily achievable at traditional reactor or accelerator facilities. However, many isotopes are produced from beams at FRIB, necessitating extensive radiochemical separations to obtain a pure product of interest. Parent-daughter isotope pairs are a promising route to enable highly specific

isotope harvesting as the parent isotope can be harvested directly and the daughter isotope of interest separated with high isotopic purity from the parent. This route is currently in development for two key isotopes: ^{172}Lu and ^{73}As.
Once the isotopes of interest have been obtained, there are unique considerations for fabricating radioactive targets. The chemical purity of such targets must be extremely high as the number of target atoms will be significantly lower than typical targets, and the signal from reactions on impurities may be higher than the reaction products of interest unless rigorous steps are taken in the chemical processing to ensure the targets are highly pure. Timing for such experiments is also critical due to the potential short half-lives of the target material and reaction products. Typical chemical procedures for fabricating targets will not necessarily be applicable for radioactive targets as the samples will be carrier-free and some elements behave differently without mass present. Procedures must consider the chemistry of the element of interest as well, e.g. As is extremely volatile and cannot be heated to temperatures >100°C without losses. Efforts to develop experimental methods to meet these challenges are in development and recent progress will be discussed.

NUCL 3920045

Novel class of guanidium-based aqueous complexants for technetium management

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Technetium (Tc) is one of the harmful fission products developed during the reprocessing of spent nuclear fuel. Due to the long-term radiotoxicity of ^{99}Tc ($t_{1/2}$ = 2.1 × 10^5 years), and high solubility of TcO_4^- in water, it poses harm to the environment and human health. To mitigate this problem, Tc must be isolated from spent nuclear fuel. The proposed Tc management strategies utilize exchange resins and/or lipophilic host molecules. Hereby, we have designing novel aqueous complexants that are simple yet functional and show extraordinarily high affinity for TcO_4^- even in the presence of excess NO_3^-, offering simple solution to Tc management in aqueous environments. This talk will cover various fascinating findings from research conducted on guanidium-based complexants, including the development of more advanced structures that offer improved solubility and greater affinity.

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NUCL 3920055

Combustion synthesis of actinide nanoscale materials and thin films

***Khachatur Manukyan**, kmanukya@nd.edu. Physics & Astronomy, University of Notre Dame, Notre Dame, Indiana, United States*

The safe and economical preparation of robust target materials with desired thicknesses and uniformity remains challenging in nuclear science studies. Over the last few years, we implemented new methods for preparing nanoscale actinide oxides and thin film targets. The methods include combustion processes between actinide metal nitrates (oxidizer) with organic compounds (fuel) dissolved in different solvents.

The self-generated heat of these exothermic reactions eliminates or reduces the need for external heating to prepare nanoscale materials with high crystallinity. Our experiments show that the heat released and maximum temperature during combustion depends on the fuel-to-oxidizer ratio. For example, in the uranyl nitrate + glycine + water solutions changing the glycine-to-uranyl nitrate from 0.5 to 1.33 increases the reaction temperature from ~500 to 1,200 K. This ratio also influences the product phase composition. Lower glycine content in the solutions facilitates the formation of U_3O_8, while solutions with increased glycine consternation produce UO_2. The process also largely depends on the solvent used. Raman spectroscopy for the uranyl nitrate + acetylacetone solutions in water or 2-methoxyethanol shows the formation of distinct intermediate compounds. X-ray crystallography investigation of single-crystalline materials isolated from the solutions confirms that solvent has a unique role in forming intermediates. The thermal decomposition of these compounds determines the composition of products.

Combining combustion synthesis reactions with spin-coating and spraying techniques enables the preparation of isotopically pure and uniform thin film targets with tunable thicknesses deposited on different substrates. X-ray fluorescence, X-ray photoelectron spectroscopy, alpha-particle emission spectroscopy, and high-resolution transmission

electron microscopy investigations of targets irradiated with charged particles and neutron beams show high stability and robustness.

NUCL 3920118

How equatorially coordinated uranyl ligands affect metal-oxo interactions: a synthetic, crystallographic, and computational study

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Recently there has been much focus on the interactions of various species (halogens, organic cations, metal cations) with the uranyl oxo group and their influence on bonding, spectroscopic properties, and reactivity. While an understanding of these interactions is being built steadily, there remain knowledge gaps regarding the effects of equatorially coordinated species. Our current efforts to generate compounds where both the equatorial and axial interactions can be probed have produced six novel $[UO_2]^{2+}/Cd^{2+}$ complexes assembled through a combination of chelidamate and N-donor ligands. By changing the protonation state of the hydroxyl group we can modulate the electron donating ability of the equatorially bound chelidamate ligands, giving us an avenue to study the effects of differences in equatorial coordination. We observe a propensity to form Cd^{2+}-oxo interactions when the chelidamate ligand is unprotonated. This implies a previously observed “priming of the pump” wherein more electron donating equatorial coordination promotes oxo interactions. This demonstrates the influence of equatorial ligands on the uranyl oxo group’s tendency toward interactions and can give insight towards engineering uranyl-oxo contacts. Computational and spectroscopic analysis of these compounds is underway and a more in-depth understanding of the molecular effects of these interactions will be presented.

NUCL 3921289

Conversion of polymer coated UO_2 to UCO and UC via thermal processing

***Michelle Greenough**[1], greenough3@llnl.gov, Joey Griffiths[1], Maryline Ferrier[1], Bradley Childs[1], Chinthaka Silva[1], Silvina Di Pietro[1], Andrew Swift[1], Janae Burks[2], Aiden Martin[1], Kiel Holliday[1], Jason Jeffries[1]. (1) Physical Life and Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California, United States(2) Spelman College, Atlanta, Georgia, United States*

This work explores the fabrication of alternative fuel sources via a novel polymer coating and laser irradiation methodology. The conversion of polymethylmethacrylate coated uranium dioxide using laser irradiation at high temperatures (> 2000 °C) in argon and methane gaseous environments was investigated for production of uranium oxycarbide and uranium carbide material. Three different process parameters (laser power, gaseous atmosphere, and length of laser irradiation time) were varied to determine the

effect on the resultant material phase. Reaction dynamics was studied in-situ by residual gas analysis using a bench top mass spectrometer and the resulting laser irradiated material was analyzed using powder X-ray diffraction and scanning electron microscopy. This work realized the conversion of uranium dioxide into uranium carbide and oxycarbide phases at over 60 wt.% via the polymer coating and laser irradiation methodology.

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NUCL 3921498

Effect of Fe(III) and Cr(III) doping on radiolysis of gibbsite

Hanna Hlushko[1], *hanna.hlushko@aggienetwork.com, Alejandro Ramos Ballesteros*[1], *Xin Zhang*[2], *Kevin Rosso*[2], *Carolyn Pearce*[2], *Jay A. LaVerne*[1,3]. *(1) Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, United States(2) Pacific Northwest National Laboratory, Richland, Washington, United States(3) Department of Physics and Astronomy, University of Notre Dame, Notre Dame, Indiana, United States*

Legacy nuclear waste on the Hanford site contains about 2000 tons of radioactive waste sludge. One of the main metals presented in this waste is aluminum, which was accumulated from tubing and separations. During storage in underground tanks, aluminum was converted into various hydrolytic products, and one of the major phases is gibbsite or aluminum hydroxide. Under ionizing radiation in a highly alkaline environment, gibbsite platelets experience radiolysis causing changes in oxidation

states, which induce subsequent reactions between components of the waste. Various transition metal ions present in the sludge affect radiolytic behavior, resulting in variability of products forming in different tanks. This work explores the effect of Fe(III) and Cr(III) ions incorporated in the gibbsite on its radiolytic behavior under gamma radiation. The gibbsite was synthesized using a hydrothermal method, and various amounts of Fe(III) and Cr(III) were incorporated at the stage of crystallization. Samples were irradiated with cobalt gamma irradiation to 1, 5, 10, and 20 kGy. The stable radical formation was detected with electronic paramagnetic resonance (EPR). EPR spectra revealed oxygen paramagnetic centers growing in the gibbsite with an increase in radiation dose. At the same time, the presence of metal ions incorporated in gibbsite nanoplatelets affected the amount of oxygen paramagnetic species. In particular, Cr(III) decreases the production of oxygen species while being reduced to Cr(II). The reduction of Cr(III) was confirmed with diffuse reflectance UV-vis spectroscopy. Fe(III) demonstrated a similar effect; however, higher metal content was required to reach the same results as with Cr(III). This competition for excess electrons can affect the radiolytic behavior of the gibbsite and should be accounted for in waste processing.

NUCL 3921498

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NUCL 3922424

Machine-learning approach to separations of lanthanides and actinides

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Solvent extraction is the most used method to separate lanthanides and actinides. In this talk, I will discuss our approach to use data-driven machine-learning approach to predict distribution ratios. We collected experimental data of measured distribution ratios for various ligands, ions of lanthanides and actinides, organic phases, and reaction conditions. Then we used descriptors for the ligands, the Ln and Ac ions, and the extraction conditions. Then a deep-learning model was trained to predict logD values of Ln and Ac ions for any given ligand for a fixed set of separation conditions. The model could achieve very good accuracy. Our work shows great promise in leveraging data-driven machine-learning for predictive modeling of separations of lanthanides and actinides.

NUCL 3923018

Tracking the mineral evolution of a cementitious waste form for immobilizing ammonium containing wastes

***Joelle T. Reiser**[1], joelle.t.reiser@pnnl.gov, Miroslava Peterson[1], Jared M. Oshiro[1], Agathe Bourchy[1], Gary L. Smith[1], Grace Chen[2], Matthew Asmussen[1]. (1) Pacific Northwest National Laboratory, Richland, Washington, United States(2) Washington River Protection Solutions LLC, Richland, Washington, United States*

Over 56 million gallons of radioactive mixed waste at the Hanford site is slated to be vitrified to a glass waste form. The effluents from the off-gas management system within the vitrification plant will be treated to generate a liquid brine which will be immobilized as a cementitious waste form (CWF). However, this liquid brine will be an acidic solution of approximately pH 5 with a high concentration of ammonium (NH_4^+). Because most formulations used for CWF generate alkaline environments, the NH_4^+ would convert to ammonia (NH_3) gas, which presents toxicity and flammability risks. One option to mitigate NH_3 generation is to trap the NH_4^+ in a struvite ($NH_4MgPO_4 \bullet 6H_2O$) phase during fabrication of the CWF. An ammonia-tolerant grout (ATG) formulation currently under investigation for this CWF application is a sulfate-activated slag containing blast furnace slag and light-burned magnesia (MgO). However, in development of this CWF, deleterious expansion and cracking has been observed during curing. In this study, a matrix of grout formulations adjusting water to binder ratios and MgO content were fabricated to assess the cause of the expansion and cracking. The ATG matrix samples

were evaluated for mineralogical evolution of the ATG cement during curing (e.g., struvite, ettringite) using X-ray diffraction (XRD), differential scanning calorimetry – thermogravimetric analysis (DSC-TGA), electronic microscopy, and energy dispersive X-ray spectroscopy. This presentation will discuss the results and implications of the matrix variables on the final ATG properties.

NUCL 3923185

Particulate plutonium released from the Fukushima Daiichi meltdowns

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Traces of Pu have been detected in material released from the Fukushima Daiichi Nuclear Power Plant (FDNPP) in March of 2011; however, to date the physical and chemical form of the Pu have remained unknown. Here we report the discovery of particulate Pu associated with cesium-rich microparticles (CsMPs) that formed in and were released from the reactors during the FDNPP meltdowns. The Cs-pollucite-based CsMP contained discrete U(IV)O_2 nanoparticles, < ~10 nm, one of which is enriched in Pu adjacent to fragments of Zr-cladding. The isotope ratios, $^{235}U/^{238}U$, $^{240}Pu/^{239}Pu$, and $^{242}Pu/^{239}Pu$, of the CsMPs were determined to be ~0.0193, ~0.347, and ~0.065, respectively, which are consistent with the calculated isotopic ratios of irradiated-fuel fragments. Thus, considering the regional distribution of CsMPs, the long-distance dispersion of Pu from FNDPP is attributed to the transport by CsMPs that have incorporated nanoscale fuel fragments prior to their dispersion up to 230 km away from the Fukushima Daiichi reactor site.

NUCL 3923718

Novel technique for the production of actinide targets and the effects after Ion and Neutron irradiation

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Actinide targets are in great demand due to the importance actinides hold in nuclear science research and stockpile stewardship experiments. These targets are quite challenging to make since they are typically rare/low in abundance and radioactive. We have developed a new procedure in which solution combustion synthesis (SCS) is used in conjunction with electrospray deposition methods in order to produce uniform targets using the least amount of material for cost-efficiency. Chemically reactive solutions were deposited as layers that were then converted to actinide oxides by simple heat treatments. This method allows the control of the layer thicknesses while it provides excellent uniformity, producing thin (10-500 μg/cm^2) uranium oxide (UO_2) layers on thick (0.5 mm) Al or self-supporting thin (50-100 μg/cm^2) carbon backings.

The effects of ion irradiation on the UO_2 targets were investigated with an Ar^{2+} beam produced by the single-ended accelerator (5U) at the Nuclear Science Laboratory at the University of Notre Dame. The structural changes that took place and the overall stability of the targets will be reported. Additionally, the effects of neutron irradiation, the robustness and the purity of the targets were investigated using a neutron beam at the Los Alamos National Lab (LANL) LANSCE facility and the DANCE detector array and will be presented as well.

The newly developed techniques have been applied to other actinides such as americium. Americium is a chemically challenging isotope, and we initially developed approaches with Eu_2O_3 (targets with thickness ~ 2000 μg/cm^2), as surrogates for $^{243}AmO_2$. The Am targets will be used in a neutron capture cross-section measurement experiment utilizing the new spallation target (MARK IV) that was installed in 2022 at the LANSCE facility.

NUCL 3923828

Improvements in iridium target chemistry

***Athena M. Marenco**, athena@lanl.gov, Evelyn M. Bond, Gencho Rusev, Todd A. Bredeweg. Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

The purpose of this research is to optimize the dissolution and separation chemistry of iridium targets and prepare the iridium for analysis by a silicon drift detector. Iridium is important because it was used as a radiochemical detector in nuclear device tests to assist in the understanding of the neutron energy spectrum and is still used today as a spectral index for energy integral nuclear physics measurements at reactor facilities. Improvements in iridium chemistry techniques of irradiated iridium salt pellets and irradiated foils will be discussed.

NUCL 3924055

Leveraging spectroelectrochemistry to build chemometric models for monitoring Np(III/IV/V/VI) in HNO_3 by spectrophotometry

***Luke R. Sadergaski**, sadergaskilr@ornl.gov, Hunter Andrews, Adam J. Parkison. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

The visible/near-infrared electronic absorption spectra of aqueous Np species are not entirely documented in the literature. Spectral data sets must cover multiple Np oxidation states, disparate molar extinction coefficients, temperature effects, and solute–solvent and solute–solute interactions to enable online monitoring by spectrophotometry. Traditional methods for adjusting the valence of Np include the addition of chemical redox reagents, which complicate the medium or phase composition. Alternatively, spectroelectrochemistry enables in situ valence control without altering solution conditions. This method provides the opportunity to obtain representative spectral data sets that cover the range of anticipated conditions for the ^{238}Pu Supply Program at Oak Ridge National Laboratory. This work presents spectral features for Np species in +3, +4, +5, and +6 oxidation states at concentrations ≥0.01 M Np in HNO_3 (0.1–5 M). Key findings from multivariate statistical analyses will be discussed.

NUCL 3924068

Nuclear forensics at the Advanced Light Source: soft and tender spectromicroscopy

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Nuclear forensics is a field which has seen increasing importance in recent years. The development of new methods and signatures is crucial to ensure that nuclear forensics investigations remain effective. Synchrotron radiation analysis offers one way to expand the scope of forensics investigations in elemental, chemical, and structural analysis which all can be done in imaging modes that for some, reach to the nanoscale. X-ray techniques are particularly useful in this field with their elemental specificity and non-destructive nature. The ability to use tunable, focused beams makes synchrotron radiation sources a key tool in this arsenal, particularly when it comes to the investigation of particles or areas of interest in smaller samples. We will discuss here recent efforts at the Advanced Light Source to perform tender and soft spectromicroscopy using x-ray fluorescence (Beamline 10.3.2) and a scanning transmission x-ray microscope (STXM, at Beamline 11.0.2). X-ray fluorescence offers elemental analysis at the micron scale, whereas the STXM can probe chemical speciation with a spatial resolution of better than 25 nm. Several uranium and plutonium samples have been measured using these techniques and the potential signatures available from this data will be demonstrated. Potentials for the future of synchrotron radiation for forensics including the strengths and drawbacks of these techniques are also discussed.

NUCL 3924139

Development and evaluation of sodium bismuthate-based chromatographic systems for the separation of americium from curium

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The development of a successful and efficient americium (Am) and curium (Cm) separation method is necessary for stockpile stewardship science and for the simplification and improvement of the current used nuclear fuel reprocessing schemes. The nearly identical chemical properties of these radionuclides (e.g., ionic radii, bonding, and predominate trivalent oxidation states) makes this difficult to achieve; however, differences in redox chemistry can be exploited since Am can be oxidized in acidic media, while Cm cannot. Recently, the ability of solid sodium bismuthate ($NaBiO_3$) to quantitatively oxidize Am and its ion exchange properties have been demonstrated in solvent extraction and chromatographic systems. However, this approach was limited by AmO_2^{2+} instability, slow kinetics, and slow flow rates. This project focuses on evaluating and characterizing chromatographic systems that combine both the oxidation and ion exchange mechanisms into one material for a continuous separation process. This talk will highlight the batch extraction studies exploring the adsorption behavior of these radionuclides and its translation into chromatographic setups. In addition, the behavior of other radionuclides (U, Np, Pu, and Eu) will be discussed in view of a group hexavalent actinide/lanthanide separation pathway.

NUCL 3924143 - Withdrawn

NUCL 3924143 - Withdrawn

NUCL 3924355

Study of extraction chromatographic resins for the separation of alkaline earth elements and the extraction of radium from hydraulic waste produced by the oil and gas industry

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Abstract – The hydraulic fracturing industry produces a substantial amount of flowback water containing various amounts of dissolved naturally occurring radioactive material. Up to four million gallons of water-based fluid is injected per well, 10–70% of which is

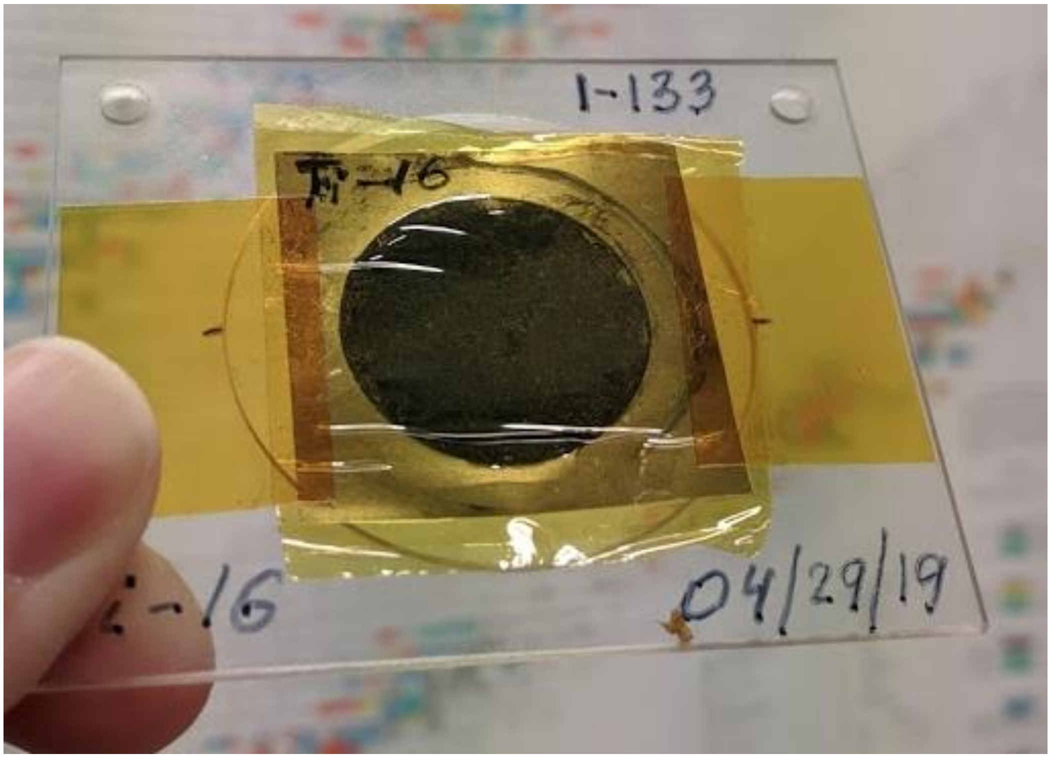
subsequently recovered as flowback. Improving the measurement and separation of "Technologically Enhanced Naturally-Occurring Radioactive Material" (TENORM) such as radium is a priority to ensure the appropriate disposal of flowback water as regulated or non-regulated NORM-containing wastes, or to develop treatment plans. The oil and gas industry produces water with large amounts of total dissolved solids, leading to a significant scientific and technical challenge in achieving the separation of radium due to the high concentration of interfering chemical analogues, such as calcium, strontium, and barium. A complete and selective removal of radium from the wastewater matrix would allow for a faster analysis while reducing costs associated with the handling, treatment, and disposal of the wastewater. Multiple proprietary extraction chromatographic resins developed by TrisKem Int. (Bruz, France) were investigated as a function of nitric acid concentration, contact time, and temperature to quantify and enhance the separation of radium from its chemical analogues.

NUCL 3924504

Methods for preparation and characterization of thin arsenic targets for stacked-target experiments

Andrew S. Voyles[1,2]*, andrew.voyles@gmail.com, Morgan B. Fox*[1]*, Jonathan T. Morrell*[3]*, Mike Zach*[4]*, Evan Still*[1]*, Lee A. Bernstein*[2,1]*, Wesley D. Frey*[5]*, Burton J. Mehciz*[5]*. (1) Nuclear Engineering, University of California Berkeley, Berkeley, California, United States(2) Nuclear Science Division, E O Lawrence Berkeley National Laboratory, Berkeley, California, United States(3) Los Alamos National Laboratory, Los Alamos, New Mexico, United States(4) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States(5) McClellan Nuclear Research Center, University of California Davis, Davis, California, United States*

Thin, uniform arsenic targets suitable for high-fidelity cross section measurements in stacked-target experiments were prepared by electrodeposition of arsenic on titanium backings from aqueous solutions. Electrolytic cells were constructed, capable of reliably and simply plating metallic arsenic deposits ranging in mass from approximately 1–29 mg (0.32–7.2 mg/cm^2 , 0.57–13 µm), with repeatable control over target thickness. Examination of electrodeposit surface morphology by scanning electron microscopy and microanalysis was performed to investigate the uniformity of produced targets. Brief studies of plating growth dynamics and structural properties through cyclic voltammetry were also undertaken. Alternative target fabrication approaches by vapor deposition were additionally conducted, but were unable to meet the demands and specifications needed for their application in nuclear physics measurements. We further introduce a non-destructive characterization method for thin targets by neutron activation, which is independent of neutron flux shape, environmental factors, and source geometry, while correcting for any potential scatter or absorption effects. These results, and the utility of this characterization technique for targets used in nuclear physics measurements, are presented in this talk, along with a roadmap for upcoming expansion of target fabrication capabilities at LBNL.



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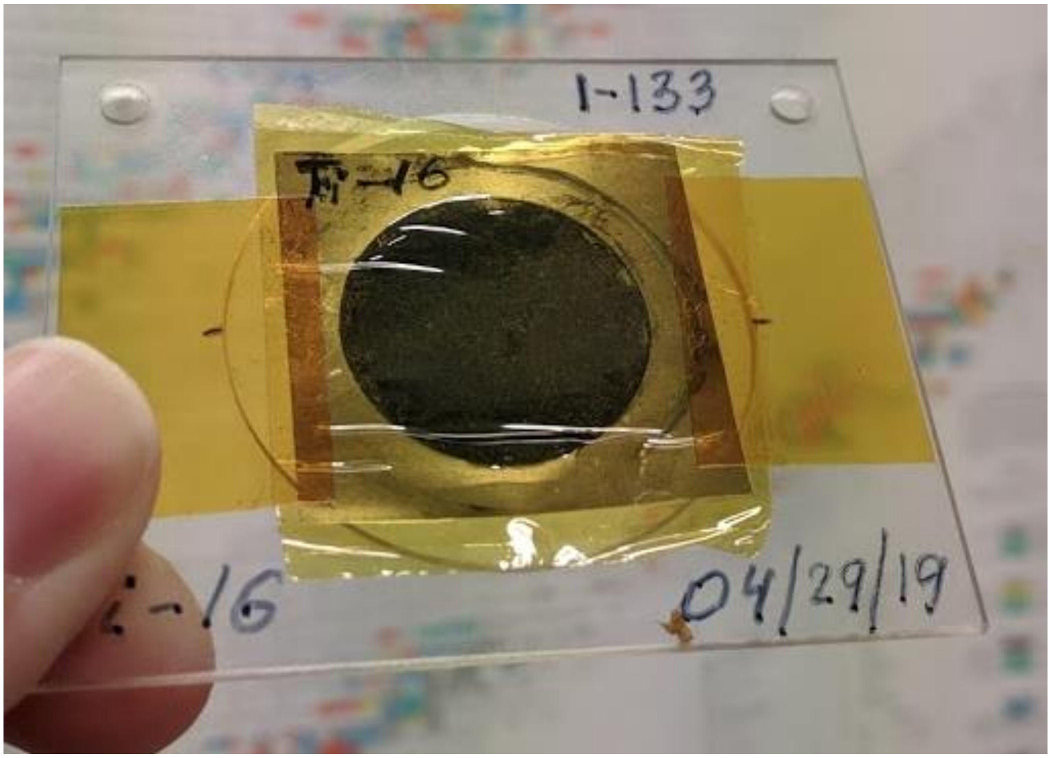

NUCL 3924573

Solid state photoreactivity of $[AnO_2X_4]^{n-}$ compounds: Insight into radical formation via anion oxidation

Christopher L. Cahill, *cahill@gwu.edu. Chemistry, The George Washington University, Washington, District of Columbia, United States*

Photoinduced quenching of uranyl luminescence has been observed in solid uranyl tetrachloride alkyl viologen compounds after prolonged exposure to UV radiation. Such atypical luminescent behavior may be explained by the formation of stable radical viologen species following an oxidation of the uranyl tetrachloride anion. This proposed

mechanism, which displays a second-order rate law, is supported by Rehm-Weller analyses, TD-DFT and EPR spectroscopy. The mechanism is in stark contrast to what is commonly observed in solution phase uranyl photoreactivity, which typically involves a reductive pathway. Moreover, our observations are consistent with those of other systems noting color changes or catalytic behavior upon exposure to radiation, yet provide a deeper mechanistic description of electron transfer and radical stabilization. Presented will be an experimental and computational overview of our efforts with UO_2^{2+} and NpO_2^{2+} bearing phases.

NUCL 3924670

Center for Accelerator Target Science (CATS): Current research efforts, target library and archives

***John P. Greene**, greene@anl.gov, Claus Mueller-Gatermann, Connor Mohs. Physics, Argonne National Laboratory, Lemont, Illinois, United States*

Research and development activities regarding target preparation techniques is one of the major thrusts of the Center for Accelerator Target Science (CATS) at Argonne National Laboratory (ANL). This is especially true for much needed targets currently not being manufactured. Several avenues and approaches are underway as part of this effort for providing access to these targets and are included for discussion. The availability of a significant storehouse of previously made targets are currently housed in the Argonne Target Library for dispersal to the low-energy nuclear physics community. The Physics Division Target Archives holds records of target preparation notes spanning over 60 years and are also compiled as part of this library. A description of all these activities will be presented.

NUCL 3924883

Soft and tender x-ray spectromicroscopy of focused ion beam sections from uranium dioxide aged under controlled humidity conditions

*Nicholas H. Cicchetti[1,2], Alexander Ditter[1], Danil E. Smiles[1], Joseph Pacold[1], Scott Donald[3], Lee Davisson[3], Artem Gelis[2], David Vine[1], Brandon Chung[3], **David K. Shuh**[1], DKShuh@lbl.gov. (1) E O Lawrence Berkeley National Laboratory, Berkeley, California, United States(2) University of Nevada Las Vegas, Las Vegas, Nevada, United States(3) Lawrence Livermore National Laboratory, Livermore, California, United States*

The nature of uranium oxidation is a critically important process across a variety of fields. It is a key component to understanding the nuclear fuel cycle, the fate and transport of uranium in the environment, and important signatures for nuclear forensics investigations. The oxidation of uranium dioxide is a complicated process, depending on factors including humidity, temperature and microstructure. The reactions of UO_2 with air and water vapor during storage and handling can provide useful insights into the

recent history of UO_2 materials; these reactions tend to form a layer of higher oxides at the sample surface, and the thickness, morphology, and composition of this layer are all promising potential signatures for recent storage conditions. At room temperature, the humidity of the environment is more important to oxidation than the oxygen content of the atmosphere, so understanding uranium oxidation can offer important insights into the provenance of a specimen.

The scanning transmission x-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2 is an instrument capable of chemical speciation mapping to the 25 nm scale, whereas the microX-ray fluorescence (XRF) Beamline 10.3.2 at the ALS can conduct chemical speciation and XRF with 2 um spatial resolution. UO_2 powder was allowed to age and agglomerate at 98% relative humidity for 378 days, then a focused ion beam (FIB) was used to section a thin slice of this agglomeration for study at the ALS STXM. Results at the oxygen K-edge and uranium N_5-edge identify a bulk, UO_2 phase and an interfacial, schoepite phase, located in distinct regions of the sample. Similarly, a UO_2 wafer was exposed to 20% oxygen for ~0.25 yr at 145 °C and a FIB section was extracted, yielding U_4O_9 and UO_2 phases via STXM. A modified non-negative matrix factorization (NMF) method was used to separate out the spectral components and identify the phases present. Use of the STXM to identify the uranium phases, particularly when coupled with FIB sectioning and NMF analysis is a promising method for the evaluation of spectromicroscopy result.

NUCL 3924991

Center for Accelerator Target Science (CATS): Target production and community education and outreach

Claus Mueller Gatermann*, cmuellergatermann@anl.gov, John P. Greene, Connor Mohs. Physics, Argonne National Laboratory, Lemont, Illinois, United States*

The Center for Accelerator Target Science (CATS) at Argonne National Laboratory provides targets in support of the ATLAS Accelerator Facility as well as to the low-energy nuclear physics community at large. It is one of the main thrusts of the Center. A description of some of the available target preparation techniques and current target production data will be discussed. Another, and somewhat equally important activities of CATS, is the sharing of the knowledge base through mentorship and training of students and other target practitioners. A recent example of this outreach culminated in the Student Target Workshop held recently at Argonne. Highlights from this and other educational activities will be presented.

NUCL 3925138

Microfluidics separations for field-deployable nuclear forensics

***Jennifer Shusterman**, shusterman1@llnl.gov, Kevin Glennon, Hector F. Valdovinos, Tashi Parsons-Davis, Narek Gharibyan. Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore, California, United States*

To expedite analysis of post-detonation nuclear debris, a small-scale chemistry and detection platform has been developed. This platform was designed for future field-deployable use, aiming to keep the footprint small, volume of reagents low, and reagents and detectors stable and operable in ambient conditions. Supported liquid membrane (SLM) microfluidic modules have been designed and 3D-printed for separation of uranium and plutonium from fission products, debris matrix elements, and other actinides. Online UV-Visible spectrophotometry and gamma spectrometry are used for uranium quantification and online alpha spectrometry to measure plutonium isotope ratios. The platform has been used to successfully separate and characterize uranium and plutonium constituents from various surrogate debris matrices containing actinides and fission products.

NUCL 3925155

Feedstock development for additive manufacturing of nuclear targets

***Jennifer Shusterman**[1], shusterman1@llnl.gov, Susana Herrera[1,2], Tashi Parsons-Davis[1], Andrew Pascall[3], John Wilkinson[4], Scott Tumey[4]. (1) Lawrence Livermore National Laboratory Nuclear and Chemical Sciences Division, Livermore, California, United States(2) Chemistry, Florida International University, Miami, Florida, United States(3) Materials Engineering Division, Lawrence Livermore National Laboratory, Livermore, California, United States(4) Atmospheric, Earth, Energy Division, Lawrence Livermore National Laboratory, Livermore, California, United States*

Thick targets (> 1 mg/cm^2) are often needed for isotope production irradiations to reach requisite product yields. Such targets need to be homogenous, robust enough to move in and out of the beam, and able to withstand the incident beam current. Traditional target preparation techniques, such as molecular plating, can produce homogenous targets of limited thickness on the order of a few hundred µg/cm^2, often cracking with thicker applications of material. The problem is further complicated with radioactive materials, such as actinides, which require higher efficiency deposition techniques to minimize radioactive contamination and loss of source material. To address these challenges, we are investigating additive manufacturing approaches to target preparation. Development of uniform nanoparticle feedstocks is needed for the additive manufacturing methodologies of interest. We are investigating the preparation of such feedstocks initially with Ce(IV) and will report on the status of this development and subsequent target preparation results.

NUCL 3925164

Smart and programmable sponges for separation applications

***Omar K. Farha**, omarkfarha@gmail.com, Madeleine Gaidimas. Chemistry, Northwestern University, Evanston, Illinois, United States*

MOFs are a class of porous, crystalline materials composed of metal-based nodes and organic ligands that self-assemble into multi-dimensional lattices. In contrast to conventional porous materials such as zeolites and activated carbon, an abundantly diverse set of molecular building blocks allows for the realization of MOFs with a broad range of properties. We have developed an extensive understanding of how the physical architecture and chemical properties of MOFs affect material performance in several applications. This talk will highlight what our team has been working on related to separations.

NUCL 3925248

Alternative methods for the production and purification of polonium-210 for use in industrial applications

***Jafar S. Ali**[1], jsa951624@yahoo.com, Ali Younes[1], Cyrille Alliot[2,3], Anne-Cecile Bonraisin[2], Marcel Mokili[2,4], Steffen Happel[5], Aude Bombard[5], Ferid Haddad[2], Gilles Montavon[4]. (1) Chemistry, Hunter College, New York, New York, United States(2) SUBATECH (UMR 6457), IN2P3-CNRS/EMN Nantes/Université de Nantes, Nantes, France(3) CRCNA, INSERM U892, Nantes, France(4) ARRONAX Cyclotron, Saint-Herblain, France(5) TrisKem International, Bruz, France*

Polonium (^{210}Po) is an alpha emitter with a half-life of 138.47 days that presents a radiation hazard when ingested due to the high energy deposited in biological tissue within a very short range. Despite its potent toxicity, it has found a variety of applications, such as in static eliminators during certain industrial processes, as well as radioisotope thermoelectric generators (RTGs), which are most prominently used as long-term power sources for space probes and satellites. Herein, a method for the production and purification of polonium from an irradiated bismuth target that minimizes processing time, cost, and generation of radioactive wastes, and increases recovery yield, is proposed. Production is done through two approaches: using a 37-MeV alpha particle beam to produce ^{210}Po, and using a deuteron beam of 16-MeV to produce ^{210}Po, ^{209}Po and ^{208}Po. Separation is performed using TBP resin, and batch studies were performed to optimize conditions. Bismuth is separated with 7 M HCl, and polonium is successfully retained on the TBP resin. Polonium was recovered using 8 M HNO_3 with a 99% yield.

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NUCL 3925260

Growth mechanism analysis of the uranyl peroxide synthetic route via in situ liquid phase TEM

***Nicholas J. Kurtyka**, nick.kurtyka@utah.edu, Luther W. McDonald. Nuclear Engineering Program, Department of Civil and Environmental Engineering, University of Utah, Salt Lake City, Utah, United States*

One of the main foci of nuclear forensics is identifying the processing history and potential origin of unknown nuclear materials. Understanding and predicting the morphology of Uranium ore concentrates (UOCs) is emerging as one of the main signatures for identifying the process history. Nonetheless, for morphology to advance, the underlying mechanisms involved in producing the morphological signatures need to be determined. Here we perform an in situ liquid phase transmission electron microscopy (lp-TEM) analysis, to see in real-time the formation of uranyl peroxide, studtite ($UO_2O_2(H_2O)_2(2H_2O)$). To do this, a starting solution of uranyl nitrate hexahydrate (UNH) was confined within a static liquid cell and used to precipitate uranyl peroxide by forming hydrogen peroxide by radiolysis via the TEM electron beam. The hydrogen peroxide concentration, directly controlled by the electron beam, was varied to create local environments of low and high concentrations to compare the impact of the saturation ratio on the nucleation and growth mechanisms. The subsequent growth mechanisms were observed in real-time by scanning TEM (STEM) imaging. After the initial precipitation reaction, a postmortem TEM analysis was performed on the samples to obtain high-resolution TEM images (HRTEM) and selected area electron diffraction (SAED) patterns to investigate crystallinity, as well as energy-dispersive x-ray

spectroscopy (EDS/EDX) spectra to ensure that uranyl peroxide was produced and that there was no contamination of the sample. Results from this study aid in evaluating the thermodynamics and kinetics governing particle nucleation and growth and subsequently the morphology signature on nuclear forensics.

NUCL 3925500

Tailoring solid-liquid interfaces for efficient electrochemical separation of lanthanides

Manh Thuong Nguyen, *manhthuong.nguyen@pnnl.gov, Venkateshkumar Prabhakaran, Shuai Tan, Grant E. Johnson. Pacific Northwest National Laboratory, Richland, Washington, United States*

In the United States, chemical separations currently consume around 15% of the energy used in industry. At the same time, separation of critical minerals, like rare earth elements (REEs), poses a grand scientific challenge due to their similar chemical and physical properties. Therefore, it is important to develop energy- and material-efficient processes for the selective extraction and purification of these metals which are increasingly needed for clean energy technologies. Electrochemical separation is considered as one of promising approaches to increase the efficiency and selectivity of the separation of heavy metal cations. In this presentation, we demonstrate the use of hydrophobic ionic liquid molecules, including 1-ethyl-3-methylimidazolium chloride, as a minor solvent component to increase the efficiency of the desolvation of lanthanide cations in cathode-electrolyte interfaces. We investigate the nano-scale structure of hydrophobic domains formed under applied potentials, and how the chemical and physical properties of the minor solvent composition affect these regions, employing a combination of theoretical (density functional theory, molecular dynamics, machine learning) and experimental (electrochemical impedance spectroscopy) methods. We also correlate the structural properties of the minor solvent component with the thermodynamics and kinetics of potential-driven targeted metal cation enrichment at interfaces. This work demonstrates that hydrophobic molecules may be used as a minor solvent component of electrolyte in a novel approach for the rational design of electrochemical separation processes for REEs.

NUCL 3925660

Washing U(VI) and Zr(IV) ions from contaminated Purex solvent by hydrazine carbonate

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The contaminated solvent from the Purex process is washed with alkaline detergents such as sodium carbonate, which generates a large amount of secondary wastes.

Therefore, hydrazine carbonate as a salt-free reagent deserves to be studied in depth. In this study, the U(VI), and Zr(IV) metal ions in organic phases containing HDBP of 30% TBP-dodecane were washed with hydrazine carbonate. The effects of the oscillation time (1min-15min), cumulative number of washes (1-4 times), mass fraction of hydrazine carbonate (0.1%-20%), the volume ratio of the aqueous phase to the organic phase (0.2-5), HDBP concentration (0-0.4 M), HNO_3 concentration (0.05 M-8 M), and the concentration of U(VI) and Zr(IV) metal ions on the removal percentages of U(VI) and Zr(IV) metal ions in polluted solvents were studied. The results showed that the organic phase containing 0.02 M HDBP was washed three times with 5% hydrazine carbonate at 25 °C, and the removal percentages of U(VI) and Zr(IV) ions were 96%, 98% and 94%, respectively. Meanwhile, the retention concentrations of the three in the organic phase were 35 mg/L, 28 mg/L and 78 mg/L, respectively. The increase of the mass fraction of hydrazine carbonate leads to the enhancement of the washing ability. High acid is not conducive to the alkaline washing of metal ions. The increase of HDBP concentration not only promotes extraction but also increases the retention capacity of the organic phase and has the most significant effect on Zr(IV).

NUCL 3925916

Innovative application of molten salts: Cleaning of uranium-containing radioactive contaminants from stainless steel surfaces

***Huitao Lv**, lvhuitao@yeah.net, Yun Xue. Harbin Engineering University, Harbin, Heilongjiang, China*

A molten salt cleaning method was developed to decontaminate stainless steel surfaces with radioactive uranium-containing contaminants. Based on a theoretical analysis of the feasibility of molten salt cleaning toward radioactive materials, NaOH molten salt was used to treat specimens contaminated with UO_3. Remarkably, the addition of Na_2CO_3 and NaCl to NaOH exhibited superior decontamination performance, with a decontamination rate of 93.8% within 12 min, outdoing the performance of the single NaOH molten salt. The experimental results demonstrated that the synergistic effects between CO_3^{2-} and Cl^- promoted the corrosion efficiency of the molten salt on the substrate, which accelerated the decontamination rate. Furthermore, the optimized experimental conditions were gathered by the response surface method (RSM), and the best experimental conditions included: a cleaning temperature of 746.80 K, a cleaning time of 13.61 min, and the molten salt formulation of NaOH, Na_2CO_3, and NaCl ($NaOH:Na_2CO_3:NaCl=85:6:9$wt.%), under which the experimental decontamination efficiency of 94.9% could be achieved. The decontamination ability of molten salts under optimal conditions was evaluated on specimens with different radioactivity and contaminated with different radioactive materials. The results showed that the molten salt cleaning method had more significant removal efficiencies for samples with high activity levels. Impressively, the radioactivity levels of all decontaminated samples achieved the requirements for reuse in the nuclear domain. In addition, XPS and hardness tests proved those corrosion products were produced on the surface of the samples after decontamination, but they did not negatively affect the hardness of the

stainless steel. We believe the findings here are a crucial step toward the widespread implementation of molten salts for the decontamination of radioactive metallic materials.

NUCL 3925965

Rapid separation of yttrium radionuclides from uranium fission products

***Malik J. Oliver**[1,2], malikjoliver@gmail.com, John Despotopulos[2], William M. Kerlin[2], Nicholas E. Esker[1]. (1) Chemistry, San Jose State University, San Jose, California, United States(2) Lawrence Livermore National Laboratory, Livermore, California, United States*

Rapidly separating fission products is of interest to the nuclear security and energy communities. New techniques could reduce activity exposure, and be used for isolating shorter-lived species rapidly. A method for isolating fission produced yttrium radionuclides using a single column of Eichrom Ln resin with hydrochloric acid was developed using a gravity separation technique. While this method yields a highly pure yttrium fraction free of many salts, this column can take up to 7 hours to run under gravity. We have further developed this technique to understand this separation under forced fluid conditions and to assess how fast this separation may be performed. Batch and kinetic studies have been performed from hydrochloric acid solutions to assess the best parameters for a yttrium fission product separation. Results will be presented on how these rare earth elements behave in a hydrochloric acid matrix and how fast these separations may be performed. The goal of this systematic study is to minimize reaction time. Results from the study will be used to further develop an automated system that uses forced fluid for separations.

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NUCL 3926190

Novel recycling protocol for zirconium alloys in uranium dioxide fuels

Breanna Vestal[1,2]*, vestalbk@ornl.gov, Craig E. Barnes*[2]*, Joanna McFarlane*[1]*, Richard T. Mayes*[1]*, Rodney Hunt*[1]*. (1) Fuel Cycle Chemistry Technology, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States(2) Chemistry, The University of Tennessee Knoxville Department of Chemistry, Knoxville, Tennessee, United States*

The Zircaloy cladding found on used nuclear fuel rods constitutes approximately 25% of the high-level waste from light water reactors. Significant socioeconomic benefits would come from separating the zirconium from the fuel and either reprocessing as low-level waste or recycling the zirconium. For this purpose, a potential new zirconium recycling protocol has been developed for the chemical removal of the Zircaloy cladding. This protocol is based on the application of three new scientific findings. First, a new lower temperature chlorination reaction of zirconium with sulfur monochloride. Second, the high solubility of zirconium chloride in thionyl chloride which can be used to separate it from uranium dioxide. Finally, the zirconium chloride can be purified by simple recrystallization from thionyl chloride. Utilizing sulfur chloride solvents for a lower temperature liquid-based chemical digestion and purification of zirconium alloy claddings reduces technical complications experienced by current high temperature gas phase chlorination strategies. A preliminary description of an industrial protocol to recycle zirconium will be presented.

NUCL 3926190

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from uranium dioxide. Finally, the zirconium chloride can be purified by simple recrystallization from thionyl chloride. Utilizing sulfur chloride solvents for a lower temperature liquid-based chemical digestion and purification of zirconium alloy claddings reduces technical complications experienced by current high temperature gas phase chlorination strategies. A preliminary description of an industrial protocol to recycle zirconium will be presented.

NUCL 3926303

Paired synthetic and computational effort to explore the effect of hydrogen bonding and cation interaction on electronic structure, thermochemistry, and spectroscopic signals of neptunyl (VI) tetrahalide compound

***Harindu Rajapaksha**[1], harindurajapaksha@gmail.com, Grant Benthin[1], Dmytro V. Kravchuk[1], Logan J. Augustine[1], Sara E. Mason[2], Tori Forbes[1]. (1) Chemsitry, The University of Iowa, Iowa City, Iowa, United States(2) Brookhaven National Laboratory, Upton, New York, United States*

Although columbic forces drive the assembly of supramolecular solids and coordination compounds, non-covalent interactions (NCIs) govern the molecular level structure of these materials. Within actinyl (AnO_2^{2+}) hybrid materials, NCIs can specifically influence the actinyl bond and results in changes to the spectroscopic signals and overall energetics of the system. In this work, we investigated the effects of hydrogen bonding and cation interaction on electronic structures, thermochemistry, and spectroscopic signals of neptunyl (VI) tetrahalide hybrid phases. We chose $[NpO_2Cl_4]^{2-}$ species because they have simple molecular assemblies that engage in charge assisted hydrogen bonding and cation interaction. Solid phases were prepared by slow evaporation of neptunyl (VI) chloride solution in the presence of various heterocyclic ligands and alkaline metal cations capable of participating in charge assisted hydrogen bonding and cation interaction respectively. Crystalline materials were characterized by Single-Crystal X-Ray Diffraction (SC-XRD) and Raman spectroscopy. The electronic structure and formation enthalpies (ΔH_f) of solid phases were analyzed through Density functional theory (DFT) calculations performed using Vienna Ab initio Simulation Package employing PBE functional and Hubbard U corrections. The calculated ΔH_f were validated by performing isothermal acid calorimetry on two selected systems. Overall, neptunyl (VI) phases with varying degrees of hydrogen bonding and cation interactions were observed. Our results show that NICs play an important role in altering the thermochemistry, bonding, and spectroscopic signals of neptunyl (VI) solid phase.

NUCL 3926371

Design of high-purity uranium recovery strategy in complex radioactive wastewater

***Jianzhang Gao**, gaojianzhang@hrbeu.edu.cn, Yun Xue. Harbin Engineering University, Harbin, Heilongjiang, China*

Nuclear energy applications inevitably generate large amounts of uranium-containing wastewater, and the treatment of uranium-containing wastewater is crucial for environmental protection and sustainable development of nuclear energy. Herein, a strategy was developed for the extraction of high-purity uranium oxide from the complex uranium-containing wastewater. A comparison of the separation effects of different systems revealed that carbonate could separate uranium and impurity ions well. The carbonates were used to retain more than 70% of the uranium in the liquid phase and limit more than 99% of Fe^{3+}, Cr^{3+}, Ni^{2+}, and Mn^{2+} in the solid phase by the complexation of CO_3^{2-} with UO_2^{2+}. The initial separation of uranium and impurity ions was achieved based on the above process. And the increase in pH could improve the retention of uranium in the liquid phase. In addition, the purity of uranium was further improved by electrochemical purification. By comparing the electrochemical purification ability of different electrodes, it was found that the Ti electrode had the best electrochemical purification ability and separation rate. The results of the electrochemical behavior analysis of uranium indicated that U(VI) in solution was converted to uranium oxide by a single electron transfer process and disproportionation process when the Ti electrode was employed. The combined system and electrochemical separation ultimately resulted in the recovery of uranium with a purity exceeding 99.9%. To improve the recovery efficiency, the solid-phase uranium recovery process was introduced, and the recovery efficiency of uranium has been improved to over 98%. Surprisingly, the concentration of heavy metal ions reached WHO guideline values through this strategy, which is of great importance for environmental protection. This strategy provided new insight into the treatment of uranium-containing wastewater and the sustainable development of nuclear energy.

NUCL 3926471

Novel preorganized ligands for selective and efficient separation of f-elements

Santa Jansone-Popova*, jansonepopos@ornl.gov. CSD, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

The selective separation of f-elements poses a significant challenge due to their similar properties. To overcome this challenge, ligands capable of selectively recognizing one element over another are highly sought after. Neutral organic ligands decorated with at least four donor atoms (oxygens and/or nitrogens), designed to complex with metal ions and that do not undergo a conformational change in the process, demonstrate exceptional size selectivity. The innate rigidity and size of the cavity and the electronic structure of these ligands provide the means to control selectivity across the trivalent f-element series by design. In contrast, organic ligands with donor groups connected to freely rotating single bonds exhibit a high affinity for metal ions that are more Lewis acidic. The superior performance of preorganized ligands in two immiscible solvent systems in selectively separating adjacent lanthanides and/or lanthanides from actinides will be discussed in detail. The performance of rigid ligands decorated with one to four donor atoms will be shown and compared to their non-preorganized counterparts.

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NUCL 3926480

Efficacious selective separation of U(VI) over Mo(VI) using novel 2,9-diamide-1,10-phenanthroline ligands: Liquid-liquid extraction and coordination chemistry study

Taoyuan Xiu[1,2,3]*, 1908687440@qq.com, Liyong Yuan*[2]*, Meng Zhang*[1]*, Guoan Ye*[3]*, Caishan Jiao*[1]*, Weiqun Shi*[2]*. (1) College of Nuclear Science and Technology, Harbin Engineering University, Harbin, China(2) Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China(3) China Institute of Atomic Energy, Beijing, China*

With the development of nuclear medicines, medical radioisotopes play a very important role in the diagnosis and treatment of diseases, among which ^{99m}Tc is widely used in nuclear medicine. ^{99m}Tc is mainly prepared from its parent nuclide ^{99}Mo by ^{99}Mo/^{99m}Tc generator. At present, ^{99}Mo is mainly produced by fission of HEU (highly enriched uranium) and LEU (low enriched uranium) targets in reactors. Methods for separation of U(VI) and Mo(VI) from solution include precipitation, extraction, ion exchange and others. The first three methods are commonly used at present, while the others have been studied but not applied in industry, such as liquid membrane extraction method and ion flotation method. Solvent extraction is widely used in the front and back ends of the nuclear fuel cycle because of its mild conditions, simple operation and easy industrialization. In this study, the four phenanthroline diamide ligands were synthesized, and extraction and stripping experiments were performed under different

conditions to evaluate the potential application of these ligands for separation of U(VI) over Mo(VI). With the growth of alkyl chain, the solubility of ligands could be greatly improved, and the separation effect of U(VI) over Mo(VI) gradually increased. The $SF_{U/Mo}$ were around 10000 at 4 mol/L HNO_3. Three stripping agents were tested with the stripping efficiency of Na_2CO_3 (5%)>H_2O>HNO_3 (0.01 mol/L). The stripping percentages of the three stripping agents were all close to unity, indicating that the ligands had the potential to be recycled. The chemical stoichiometry of U(VI) complexes with ligands was evaluated as 1:1 using electrospray ionization mass spectrometry, ultraviolet visible spectroscopy and single-crystal X-ray diffraction. The consistency between theoretical calculation and experimental results further explains the coordination mechanism.

NUCL 3926698

Challenges in developing predictive thermodynamic models for complex molten chloride salts

Juliano Schorne-Pinto, *julianos@mailbox.sc.edu, Jacob Yingling, Ted M. Besmann. Mechanical engineering, University of South Carolina System, Columbia, South Carolina, United States*

In the development of the *Molten Salt Thermal Properties Database - Thermochemical* (MSTDB-TC), the lack of thermodynamic data prompted the development and/or expanded use of semi-empirical and constraints-based approaches. These methods allowed the prediction of enthalpies of liquid-liquid mixing ($\Delta_{mix}H$) and melt heat capacity for AkCl-UCl_3 and AkCl-$PuCl_3$ (Ak = alkali element) systems. The approaches have been validated using comparisons with reported experimental $\Delta_{mix}H$ values for NaCl-UCl_3 and those for the excess heat capacity for NaCl-$PuCl_3$ at the eutectic composition. This presentation will also consider the useful example of the evaluation of phase equilibrium data, thermochemical values, and differential scanning calorimetry measurements for the LiCl-NaCl-UCl_3 system and the development of thermochemical models.

NUCL 3926970

Effects of Xylenes isomers for Aliquat 336® actinide solvent extractions from acidic and salt-rich chloride waste streams

Hope Rasmussen[1]*, hope.ut@gmail.com, Janelle Droessler*[1]*, Laura E. Wolfsberg*[2]*, Xeph Ivankovich*[1]*, Sabine Fuierer*[1]*, Quinn McCulloch*[1]*, George S. Goff*[1]*. (1) Material Physics Applications, Los Alamos National Laboratory, Los Alamos, New Mexico, United States(2) Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Solvent extraction techniques are commonly employed in nuclear chemistry applications to separate actinides from themselves and other impurities among a wide range of liquid systems. These processes necessitate the design of chemical systems consisting of a

targeted extractant dissolved into an organic diluent. Xylenes are often employed as organic diluents in solvent extraction processes with the commercial composition consisting of a varying mixture of four isomers: meta-xylenes, para-xylenes, ortho-xylenes, and ethylbenzene. The variability of this mixture can be of concern for repeatability and consistency of extraction processes.

This research focuses on systematic differences of actinide extraction in acidic and salt-rich chloride systems using individual xylene isomers as diluents for the extractant Aliquat 336® (A336). A336, a quaternary ammonium ionic liquid, relies on anionic exchange and ion association of metal chloride species for extraction.

Benchtop batch extractions were performed to determine distribution ratios (D-values), the final concentration of metal in organic divided by the final concentration in aqueous, of surrogate elements and actinides in a range of HCl and salt compositions. The substitution of each xylene isomer diluent/extractant combination affected D-values to varying degrees. Trends in extraction were analyzed with respect to physical properties data of the individual isomers and A336/isomer combinations.

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NUCL 3927251

Quantifying the morphological and phase changes during the heat treatment of uranium(VI) oxide to produce uranium(V, VI) oxide using in-situ ultra-small-angle X-ray scattering

Anthony Krzysko[1], *Anthony.Krzysko@anl.gov, Derek McLain*[1]*, Jan Ilavsky*[2]*, Ivan Kuzmenko*[2]*, Katherine Hepler*[1]*, Andrew Breshears*[1]*, Kristin DeAngeles*[1]*, Jennifer Steeb*[1]*. (1) Argonne National Laboratory, Lemont, Illinois, United States(2) Argonne National Laboratory Advanced Photon Source, Lemont, Illinois, United States*

Obtaining and quantifying particle morphological features (e.g., size and shape) is important to a few different nuclear forensic applications. For example, particle morphologies can be used as signatures to link an unknown sample to its processing history or place of origin. It has been well established in the literature that the resulting particle size, size distribution, and shape of uranium(V, VI) oxide particles can be used to determine the heating temperature that was used to produce it. Typically, the morphologies are quantified by analysis of images produced by traditional imaging techniques such as scanning electron microscopy (SEM) and visible light imaging. However, there are some challenges associated with the techniques and analysis methods. For example, it has been shown that a large number of particles need to be analyzed in order to distinguish the morphological features between uranium(V, VI) oxides that were produced by heating at temperatures ranging from 600 – 800 °C. This process can be time intensive and cannot be easily performed in situ. In contrast, ultra-small-angle X-ray scattering (USAXS) measurements are fast (< 90 s), representative of the bulk sample, non-destructive, and can be performed during the heating treatment. Moreover, combining USAXS, small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS) provides size and shape information ranging from 6 Å to 10 µm. This research monitored the heat treatment of uranium(VI) oxide to produce uranium(V, VI) oxide at 3 different temperatures (600, 700, and 800 °C) using in-situ USAXS, SAXS, and WAXS. The analysis of the scattering data demonstrated significant morphological differences between the uranium(V, VI) oxides produced at each condition comparable to those produced by traditional imaging. In addition to the primary particle analysis, the µm sized aggregates will be compared for each temperature and possible reaction mechanisms will be discussed.

NUCL 3927408

Exploring actinium chemistry through the lens of biologically-relevant systems

Jennifer Wacker[1]*, jwacker@lbl.gov, Joshua Woods*[1]*, Peter B. Rupert*[2]*, Appie Peterson*[1]*, Alexia G. Cosby*[1]*, Marc Allaire*[1]*, Stefan G. Minasian*[1]*, Wayne W. Lukens*[1]*,* *Roland K. Strong[2], Rebecca J. Abergel[1,3]. (1) E O Lawrence Berkeley National Laboratory, Berkeley, California, United States(2) Fred Hutchinson Cancer Center, Seattle, Washington, United States(3) Department of Nuclear Engineering, University of California Berkeley, Berkeley, California, United States*

Targeted alpha therapy (TAT) strategically delivers alpha-emitting radioisotopes to cancerous cells through biological targeting vectors. In particular, actinium-225 (^{225}Ac; $t_{1/2}$ = 9.92 days) TAT has garnered significant interest with promising clinical studies. Despite these advances, the fundamental coordination chemistry of Ac remains underdeveloped due, in part, to the limited supply of ^{225}Ac and the poorly understood chelation behavior that is further magnified by the spectroscopic silence of the Ac^{III} electronic ground state ($5f^0 6d^0$). To address these challenges, the longest-lived isotope of actinium (^{227}Ac; $t_{1/2}$ = 21.77 years) was used to serve as an analogue to the radiopharmaceutically relevant ^{225}Ac isotope, as the half-life of ^{227}Ac is more amenable to chemical studies that span hours to several days. Furthermore, our group has employed a protein ("siderocalin") to serve as a macromolecular host for ^{227}Ac. Siderocalin binds siderophores and their ferric complexes as part of the mammalian innate immune system, but has also been shown to selectively bind a diverse range of actinide-siderophore complexes. Collectively, we leveraged structural and spectroscopic signatures of both a siderophore chelator and protein host to probe solution thermodynamics and coordination behavior of an Ac^{III} complex. Ac^{III}-chelator-macromolecule complexes will be discussed not only in the context of actinide bonding and periodicity, but also aimed towards broader scopes in radiotherapeutics.

NUCL 3927597

Do I Have Useful Skills? – How to find your fit with the job that is advertised

***Dustin W. Demoin**[1], dustin.demoin@ezag.com, Laetitia H. Delmau[4], **Deborah A. Penchoff**[6], dpenchof@utk.edu, **Vanessa A. Sanders**[5], vsanders@bnl.gov, **June Slaton**[2], June.Slaton@ezag.com, **Henry F. VanBrocklin**[3], henry.vanbrocklin@ucsf.edu, Anthony Degraffenreid[7]. (1) Radiochemistry, Eckert and Ziegler Isotope Products, Valencia, California, United States(2) Human Resources, Eckert and Ziegler Isotope Products, Valencia, California, United States(3) Department of Radiology and Biomedical Imaging, University of California San Francisco, San Francisco, California, United States(4) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States(5) Collider-Accelerator Department, Brookhaven National Laboratory, Upton, New York, United States(6) Innovative Computing Laboratory, The University of Tennessee Knoxville, Knoxville, Tennessee, United States(7) PharmaLogics Holding Corp., Austin, Texas, United States*

During recent decades, nuclear and radiochemistry fields have suffered a workforce shortage. In this panel discussion, individuals involved in hiring for positions across academic and industry positions, who will share information about jobs that are offered and how to tell if you have the skills necessary to be successful in that position. The individuals will each give a short presentation about their own background, what they

are currently working on, any current jobs they have open, and where they see the field of nuclear/radiochemistry going in the future. Individuals will be asked to speak broadly about their experience, to be less particular about their company and more about the broader group they are "representing." There will be ample opportunity for attendees to ask questions of the presenters, and questions can be submitted ahead of time.

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NUCL 3927933

Dissolution of a ^{224}Ra mock pigment sample for future nuclear forensic analyses of a historical ^{226}Ra pigment sample

Jenna R. Garcia[1,2], *jgarc005@tamu.edu, Evelyn M. Bond*[2], *Charles M. Folden*[1]. *(1) Department of Chemistry, Texas A&M University College of Arts & Sciences, College Station, Texas, United States(2) Chemistry- Nuclear and Radiochemical, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Radium paints were used in the early 1900s for the watch dial industry and military instrumentation due to their attractive, self-luminescent properties. These paints are no longer used today as they pose many health hazards; the International Atomic Energy Agency (IAEA) has identified ^{226}Ra, the main radioactive component within Ra paints, as a potential nuclear terrorism material in radiological dispersive devices. To combat nuclear terrorism events, nuclear forensic analytical techniques are used for origin attribution in interdicted samples. Databases of measured nuclear forensic signatures exist in the literature for many nuclear materials; however, forensic signatures for ^{226}Ra radiological samples are nonexistent within the literature. Thus, this work focuses on the development of chemical techniques and procedures for the radiochronometric analysis of a historical ^{226}Ra pigment sample from the early-mid 1900's. This analysis has been proven difficult due to the chemical dissimilarity of the composition of the pigment sample; according to the literature, the components are (ZnS (~99%) and $RaCl_2$ or $RaBr_2$ (~1%)). Multiple pathways to dissolution of the sample have been tested and the efficiency presented for each. This work has studied the dissolution in ultrapure water and also mixed solutions of tetrakis-(hydroxymethyl)-phosphonium chloride (THPC), NH_4Cl, and HCl. Furthermore, the separation of relevant elements is necessary for determination of a radiochronometric age and can be accomplished using chromatographic techniques; the retention factors, *k'* values, will be reported for solutions containing THPC for LN and DGA resins. This talk will discuss results pertaining to the dissolution efficiency of a ^{224}Ra pigment in solutions of THPC/NH_4Cl/HCl and examine the dependency of HCl for a complete dissolution. These results aim to pioneer future nuclear forensic analyses for ^{226}Ra radiological samples and ultimately aim to combat events of nuclear terrorism.

NUCL 3928402

Radioactive Targets: A philosophical consideration

***Etienne Vermeulen**, etienne@lanl.gov, Hye Young Lee. Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

There is a growing need for the production of highly radioactive targets to probe the frontiers of astrophysics, nuclear physics and national security science. At Los Alamos we have demonstrated the basics of what is needed to produce the isotopes for these relatively short-lived targets, purify the material and rebuild it into targets that are useful for secondary irradiation in the neutron beams at the LANSCE accelerator. We will consider here the different aspects that are needed to develop a robust program of producing, characterizing and safely handling highly radioactive, relatively shortlived targets for the user community at large and Los Alamos in particular.

NUCL 3928532

Mechanism of astatine and bismuth sorption on extraction chromatography resins from nitric acid media

***Evgeny Tereshatov**, etereshatov@tamu.edu, Sherry J. Yennello. Texas A&M University, College Station, Texas, United States*

Systematic study of astatine (At) sorption on extraction chromatography resins from nitric acid media has been performed at Texas A&M University. This work covers commercially available resins such as LN, TK400, SR, TRU, and UTEVA. Acquiring an understanding of At behavior in up to 4 M HNO_3 solutions is a key step to develop a rapid and reliable system for At separation and purification. The determined distribution coefficients are greater than 20 for all the resins studied, reaching 400 for TRU and UTEVA resins. For each resin a thermodynamic model has been developed to suggest a possible mechanism of At sorption and corresponding sorption constants have been estimated. Literature data along with new results on bismuth (Bi) sorption by studied resins in nitric acid media have been reviewed and a mathematical model to describe its behavior has been suggested. A ratio of corresponding fit functions of At and Bi assigned to the same resin and acidity has been used to estimate separation factors of these elements. Only the TRU resin is not suitable for efficient At isolation from Bi, while the other four resins demonstrate promising results.

NUCL 3928609

Interested in internships, postdoctoral fellowships, or career jobs at national laboratories? The Seaborg directors have answers. Join them for a presentation/discussion about current and future research opportunities

Mavrik Zavarin[5], *zavarin1@llnl.gov*, ***Rebecca J. Abergel***[1], *rjabergel@lbl.gov*, ***John R. Kennedy***[2], *rory.kennedy@inl.gov*, ***Samantha K. Schrell***[3], *schrellsk@ornl.gov*, ***Franz Freibert***[4], *freibert@lanl.gov*, ***Ping Yang***[4], *pyang@lanl.gov*, ***Annie Kersting***[5], *kersting1@llnl.gov. (1) E O Lawrence Berkeley National Laboratory, Berkeley, California, United States(2) Glenn T. Seaborg Institute, Idaho National Laboratory, Idaho Falls, Idaho, United States(3) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States(4) Los Alamos National Laboratory, Los Alamos, New Mexico, United States(5) Lawrence Livermore National Laboratory, Livermore, California, United States*

Come learn more about actinide research opportunities at the National Laboratories. The Seaborg Institute directors will be hosting a session to discuss research opportunities in actinides chemistry. They will cover their particular research areas and discuss job opportunities for students and postdocs. The session will have ample time for audience members to ask questions.

There are currently 5 Seaborg Institutes (@LLNL, LANL, LBL, INL, and ORNL), all of which conduct collaborative research between the academic community and the national laboratories. They serve as national centers expanding the frontiers of scientific discovery with a focus on training undergraduate students, graduate students, and postdocs in the area of actinide sciences. Come and learn more about their research focus, specialized facilities, and career opportunities.

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NUCL 3929497

Quantification of the enthalpy of Eu(III) and U(VI) complexation to graphene oxide using microcalorimetry

Yu Xie[1]*,* ***Brian A. Powell***[2]*, bpowell@clemson.edu. (1) Environmental Engineering and Earth Sciences, Clemson University, Clemson, South Carolina, United States(2) Chemistry, Clemson University, Clemson, South Carolina, United States*

We used isothermal titration calorimetry (ITC) to measure the enthalpy for the deprotonation of carboxylic functional groups ([≡COOH]) on graphene oxide (GO) as well as the enthalpy of Eu(III) and U(VI) sorption to GO at 25 °C. The GO speciation used for enthalpy calculations was simulated based on an electrostatic double layer model for GO surface protonation/deprotonation and Eu(III)/U(VI) sorption to GO. The enthalpy for the deprotonation of [≡COOH] on GO is calculated to be 14.7 kJ/mol, by fitting the heat release datasets of NaOH titration to GO at variable concentrations (0.1 g/L, 0.5 g/L, and 1 g/L). This endothermic enthalpy for the deprotonation of carboxylic site is consistent with that for bicarbonate. The enthalpy for Eu(III) and U(VI) complexation to GO was calculated to be 16.86 ± 1.83 kJ/mol and 33.8 ± 3.36 kJ/mol,

by fitting multiple bulk heat datasets of $EuCl_3$ or $UO_2(NO_3)_2$ titration to GO. The enthalpies for Eu(III) and U(VI) sorption to GO was extrapolated from batch sorption datasets at variable temperatures based on the van't Hoff relationship in previous study, but these values are not reaction or site specific, while this work presents an alternative method to quantify the enthalpy of reactions for GO associated with the specific functional group.

NUCL 3929733

Thenoyltrifluoroacetone as an extractant for column chromatography: Radiochemical separations from mixed fission and activation product samples

Evan Warzecha*, evan.warzecha@pnnl.gov, Nicolas Uhnak, Ean Arnold, Chelsie L. Beck. National Security Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States*

Radiochemical analysis of short-lived isotopes depends greatly on the ability to separate interferences and the speed at which separations can be performed. New methods and materials are useful in improving separation times, which is particularly important for short-lived isotopes. A new chromatographic resin was created using the extractants 2-thenolyltrifluoroacetone and 1-octanol adhered to an inert support. In high acid concentrations the resin is highly selective for gold, iron, and gallium. This high selectivity allows for the rapid isolation of these analytes from complex matrices. Separations utilizing the new thenolyltrifluoroacetone-based resin have been demonstrated using irradiated uranium with added activation products.

NUCL 3929733

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NUCL 3931422

Isotope harvesting at FRIB: Upcoming opportunities for scientific applications

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When exotic, secondary beams are produced at the Facility for Rare Isotope Beams (FRIB), a majority of the accelerated primary beam remains unused and will be stopped in a water-traversed, spinning drum of Ti64 alloy. The dissipation of such large energy amounts induces the formation of a plethora of valuable radionuclides. The collection of these radionuclides from the aqueous cooling loop through focused 'isotope harvesting' efforts will be an invaluable resource to meet our societal isotope demands.
In the normal operation mode of FRIB, a broad variety of multiple isotopes of each element will be created, and often direct harvesting efforts can only yield samples of moderate radioisotopic purity. An option to increase the spectrum of available pure radioisotopes would be through the implementation of mass separation. At FRIB, a suitable mass analyzer is already part of the existing infrastructure and could be utilized to establish a prototype mass separator. The so-obtained, radioisotopically pure samples will be available for the preparation of targets for neutron reaction measurements and other scientific studies. In addition, the development of a target manufacturing program will also benefit the stand-alone operation of the on-site Re-Accelerator facility and thereby facilitate the parallel operation of multiple facilities at FRIB.
In this talk, I will give an overview of the current target preparation efforts in support of the stand-alone beam program at FRIB. Furthermore, an outlook towards the prospective extension of the existing isotope harvesting program and the future research on radioactive targetry development will be given.

NUCL 3935099

Exploring alternative isotope harvesting techniques through adsorption on metal oxide substrates

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At the Facility for Rare Isotope Beams (FRIB), a primary beam produces secondary beams. The majority of this initial primary beam remains unused and is blocked via a beam blocker. Using a flowing-water system as the blocker will generate a wide variety of different radionuclides that are highly relevant for many scientific fields. The focused collection of the produced radionuclides has been termed 'isotope harvesting'. The common method for extracting the isotopes is based on the employment of ion exchange chromatography resins. To enhance the radioisotopic purity of the harvested isotopes, the addition of a mass-separation step is foreseen in the future. Metal oxides

may prove to be more suitable adsorbent materials. The refractory nature of metal oxides allows a direct introduction into the mass separator and thereby allows for a seamless combination of isotope harvesting and mass separation. A variety of metal oxides were tested in their adsorption towards seven different metals. To simulate the adsorption, solutions of the stable metals were incubated with the metal oxide for several hours. After incubation, the extent of adsorption was quantified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The metal oxides tested so far show near complete adsorption for some elements such as arsenic, but less than 5% adsorption for others such as nickel and manganese. The adsorption of the seven metals onto each metal oxide available will be discussed.

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Characterization of particle edge ambiguity in human segmentation of uranium ore concentrates from scanning electron microscopy images

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Critical goals of nuclear forensics are to support the determination of nuclear material production pathways and sample provenance. Morphology, or the analysis of shape and distribution of material particles, is an emergent approach with the potential of providing signatures of process history. One way of characterizing morphology is by using a human-assisted machine learning material analysis toolkit (MAMA) developed at Los Alamos National Laboratory to segment (outline) nuclear particles from scanning electron microscopic (SEM) imagery. From these segmentations, particle attributes can be quantitatively distinguished and provide the foundation for a signature to identify key processing factors and sample provenance. One fundamental challenge with particle segmentation is when the boundary of the particle is unclear. This introduces uncertainty in the segmentation as well as the downstream results. There are many reasons why this can occur in practice. Consequently, it is a priority to characterize uncertainty for imperfect data such as when particle boundaries are blurry, obscured, or otherwise ambiguous.

This work focuses on the ambiguity of particle segmentation and its impact on quantitative results. We explore the contribution of two types of uncertainty to segmentation: aleatory uncertainty (randomness) and epistemic uncertainty (lack of knowledge). This approach characterizes the inherent uncertainty of the particle edge in the context of the surrounding neighborhood by applying measures from texture analysis to the perimeter of human segmented particles and using these to frame a distribution. From this data, the expression of a particle edge is qualified by upper and lower uncertainty bounds on particle segmentation. These uncertainties can be propagated with the ground truth particle segmentation by the expert to qualify confidence in the quantitative results for particle distribution.

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High performance computing and data science: Advances and challenges in computational modeling for radiochemical applications in 2023

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High-performance computing (HPC) and data science have enabled advances in computational modeling that accelerate the development of solutions in nuclear chemistry and technology applications. This presentation will discuss the state-of-the-art techniques in HPC and artificial intelligence (AI) that have driven significant

improvements in the accuracy, reliability, and efficiency in nuclear and radiochemical applications. The integration of data-driven methods with traditional molecular modeling will be highlighted to provide insights in enhanced predictive capabilities. Multidisciplinary efforts in optimization of radiochemical separations will also be discussed.

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Analysis of chemical interactions from accurate electronic structure calculations

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With modern, powerful computational resources, it is possible to obtain very accurate predictions of the properties of matter. This is done through calculations of the electronic structure for the wavefunctions and density of systems ranging from atoms to clusters to condensed matter. These calculations may be based on a wide range of methods from ab inito Hartree-Fock, HF, coupled with configuration Interaction, CI, to densty functional theory, DFT, for large systems. However, while it is useful to have accurate predictions of the properties of matter, it is necessary to relate these properties to their origin in the character of the chemical interactions and bonding in order to be able to understand the full significance of the properties. In particular, this understanding is necessary to obtain a grasp on the general significance of the predicted properties for related systems. This is most often done with a variant of the population analysis methodology first introduced by Mulliken. However, it is known that these populations have limitations and may lead to incorrect conclusions. The use of several novel methods that characterize the orbitals, the occupations of CI wavefunctions, and the importance of covalent mixing is reviewed. Applications to the electronic structure of PuO_2 is used as an example of the use of these methods.

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Advanced computational strategies for lanthanide & actinide systems

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Accurate simulations of lanthanide and actinide chemistry are crucial for nuclear forensics, separation agent design, and spectroscopic analysis. We present advanced computational protocols incorporating ab initio and density functional theory (DFT) molecular modeling methods to effectively simulate binding interactions in these

systems. Our approach accounts for critical factors such as relativity, spin-orbit coupling, and core correlation effects, thereby improving the prediction accuracy. Furthermore, we explore the potential of artificial intelligence techniques, including machine and deep learning, to provide additional insights into binding selectivity properties. This study demonstrates the efficacy of our computational strategies in understanding and predicting the behavior of lanthanide and actinide systems, paving the way for future advancements in nuclear and radiochemical applications.