NUCL 1

In situ isotope harvesting from the beam dump cooling loop at the Facility for Rare Isotope Beams (FRIB) with hollow fiber supported liquid membrane (HFSLM)

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Currently under construction, the Facility for Rare Isotope Beams (FRIB) will be a new national user facility for nuclear science, producing a wide variety of nuclides by projectile fragmentation. Experiments with beam energies up to 200MeV per nucleon at FRIB will simultaneously produce large quantities of rare isotopes in the beam-dump cooling loop that could be synergistically harvested without interference to the primary user. We have demonstrated that HFSLM is an efficient method for selectively removing isotopes from the cooling loop in situ at the high flow rates and ultra-low concentrations of the system. Feasibility results will be presented for the extraction of ^{48}V.

NUCL 2

Feasibility of harvesting radon and noble gas isotopes from the FRIB Beam Dump

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The Facility for Rare Isotope Beams (FRIB) will produce unprecedented quantities of radioactive nuclei when it comes online in about 5 years. The objective of this study was to assess the feasibility of collecting radon and noble gas isotopes from the cooling water system of the beam dump.
The production of hydrogen gas in the beam dump results in two-phase flow in the section of the cooling system from the beam dump, a spinning titanium drum, to a gas-liquid separator, the head space of which is flushed with nitrogen gas to reduce the hydrogen concentration below 2% in the gas phase. Partitioning of noble gases into the gas phases poses a challenge for harvesting radon and noble gas isotopes of interest.
Membrane contactors will allow radionuclides to be harvested from the

primary cooling flow during FRIB operation by implementation in a secondary bypass stream. Membrane contactors allow constant extraction of gases across a hollow fiber-supported membrane. Depending on the characteristics of the membrane, these devices can be made chemically specific: allowing fine-tuning of the extraction process.

A promising new technology for purification of noble gases of interest is an adsorption-based process at room temperature using selective, solid-state adsorbents called a metal-organic-frameworks (MOF). An important advantage of MOFs is their chemical tunability; one MOFs can be synthesized to be optimally selective for Kr, Xe or Rn at room temperatures. MOFs have higher efficiency, selectivity, and capacity at room temperature over current xenon adsorbents like activated charcoal and Ag-loaded zeolites at cryogenic temperatures. In addition, MOFs require limited pre-treatment of the intake gases and no cryogenic operation.

Based on the design specifications, it appears feasible to harvest selected radon isotopes (^{211}Rn, ^{221}Rn, ^{223}Rn) from the FRIB beam dump cooling system. Harvesting useful quantities of ^{225}Rn appears unrealistic due to its 5 minute half-life. Off-line harvesting from the gas loop is not recommended for shorter-lived radon isotopes (^{221}Rn, ^{223}Rn), due to the total volume of gas, lower radon concentration and time constraint posed on off-line harvesting by decay. Off-line harvesting of longer-lived noble gas isotopes (^{211}Rn, ^{76}Kr) from the gas loop is feasible and will yield useful quantities of these isotopes.

NUCL 3

Evaluation of solid supports for isotope harvesting at Brookhaven Linac isotope producer (BLIP)

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BLIP target cooling water may contain radioactive isotopes which originated from different processes. Among those are proton activation of water (Be-7), recoil form target bodies (V-48) or undesired target leaks (Sr-82). A novel method utilizing solid supports was developed to capture Sr-82, V-48, and Be-7 from 360 gallons of BLIP target cooling water. The approach simultaneously evaluated uptake of metals and radioactive nuclides on solid supports with

different functional groups on the surface, and allowed the determination of the best functional group for optimal uptake. Initial studies were focused on evaluation of different functionalities for capturing Be-7. The results showed that sulfonic acid functionalized solid supports exhibited the highest uptake of Be-7(2.1 mCi of Be-7/solid support). Further the first scale up experiments were conducted where 33 solid supports was used capturing 66 mCi of Be-7.The second scale up experiments conducted in 2016 utilized 139 solid supports and captured 725 mCi of Be-7, along with 733 mCi of Sr-85 and 1036 mCi of Sr-82 which were also present in the cooling water. Acidic conditions were used to release the isotopes from the solid supports and a portion of the solution was used in subsequent ion exchange and/or extraction chromatography to purify Be-7 from Sr-82 to achieve 99% radiochemical purity of both isotopes.
Solid supports were functionalized with the following moieties: Zirconium phosphate, pyridine amine pyridine, quaternary amine, pyridine amide, pyridine acid, pyridine amine acid, pyridine amine, dithioxamide-formaldehyde polymer, thiourea-formaldehyde polymer, Benzo-18-crown-6, 18 crown-6, and benzo-15-crown-5. They were screened in a similar fashion for the retention of V-48. Solid supports with a chelating moiety with two pyridine groups and an amine was found to have the highest V-48 uptake. Purification with subsequent ion exchange chromatography resulted in a 74% recovery of V-48 with 98.9% radiopurity.

NUCL 4

Astatine-211 from harvested radon at the upcoming Facility for Rare Isotope Beams

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The upcoming Facility for Rare Isotope Beams (FRIB) at Michigan State University will use a high-power ^{238}U beam to produce rare isotopes for nuclear physics experiments. When unused portions of the beam are stopped in a water-cooled beam dump, many nuclear reactions will occur, leading to the production of valuable isotopes *in situ*, like ^{211}Rn. Radon-211 is a generator parent of the alpha-emitting medical isotope ^{211}At, and during full power irradiation it is expected to be produced at a rate in excess of 10^{10}atoms/second. However, co-production of other radon and astatine isotopes is unavoidable, meaning that the procedure for harvesting ^{211}Rn and generating ^{211}At must be optimized for achieving maximum radionuclidic

purity. We will present a model of a simple system for generating ^{211}At from harvested radon isotopes at FRIB. The model predicts that more than 50 mCi of ^{211}At can be eluted daily with greater than 99.9% isotopic purity.

NUCL 5

Harvesting ^{48}V at a radioactive ion beam facility

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Many radioisotopes with particular nuclear, physical, and biological properties have been proposed for applications in medicine, stockpile stewardship and fundamental research. Unfortunately, some of these radioisotopes are difficult to produce in the quantity or purity needed for practical applications using traditional production methods at facilities with cyclotrons and nuclear reactors. In particular, the neutron-induced cross sections for many radioisotopes important for nuclear astrophysics and national-security applications remain unmeasured, which leave gaps in the reaction networks. Therefore, developing new routes for obtaining relevant quantities of these rare radioisotopes is necessary in order to fill these gaps. Recently, isotope harvesting from radioactive ion beam (RIB) facilities has been investigated as a potential new pathway to supply these needed radioisotopes.

In order to develop techniques for harvesting isotopes from RIBs, a series of experiments were carried out at the National Superconducting Cyclotron Laboratory. In this work, ^{48}V was collected from an aqueous beam stop and separated from a mixture of secondary-beam ions and unwanted

fragmentation radioisotopes. A cocktail beam of secondary ions created by the spallation reaction of a ^{58}Ni secondary beam was stopped in an aqueous target cell. After collection and sample characterization, ^{48}V was separated from primary beam ions and secondary beam radioisotopes using cation exchange chromatography. The overall extraction efficiency from the aqueous solution was 36.9%, and the isolated ^{48}V had a radiochemical purity of 99.9%.

These data indicate that harvesting large quantities of ^{48}V at the future Facility for Rare Isotope Beams, where isotope production is expected to be several orders of magnitude larger, should be feasible, and may allow the fabrication of radioactive targets that can be used to experimentally determine neutron-induced reaction cross sections. This approach can provide research quantities of isotopes currently unavailable at conventional facilities.

NUCL 6

Production yields of ^{52}Fe from symmetric complete fusion-evaporation reactions

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The development of a heavy-ion method to produce ^{52}Fe that could be harvested radiochemically will be presented. This proton-rich isotope ($t_{1/2}$= 8.3 h) allows the possibility for *in vivo* medical imaging of its distribution, and has been shown to be useful in previous studies. However, current light ion medical cyclotron methods cannot routinely produce ^{52}Fe and reactor methods cannot reach these proton-rich isotopes. Preliminary experiments were performed at the University of Notre Dame’s Nuclear Structure Laboratory using the FN Tandem Van de Graaff accelerator to accelerate heavy ions to create almost symmetric entrance channels to produce ^{52}Fe by fusion-evaporation. For example, an aluminum oxide beam was accelerated just above the Coulomb barrier (E_{beam} = 60 MeV) onto a 1 mm-thick aluminum foil of 99% purity as the target in one reaction. The decays of the irradiated foils were analyzed using a high purity germanium detector over 7 days after irradiation. The production of ^{52}Fe via the ^{27}Al(^{27}Al, 2n) reaction near the Coulomb barrier was compared with other nearly symmetric (p,n),(p, 2n) and (a,2n) reaction channels. The relative production rates of ^{52}Fe and coproduced radioisotopes will be compared using the fusion-evaporation code PACE4, within the LISE++ framework. Preliminary analysis shows good

agreement with predicted isotopes and relative yields and suggests that light ion accelerators and symmetric complete fusion reaction channels near the Coulomb barrier may yield appreciable quantities of ^{52}Fe that could be extracted chemically from the aluminum target relatively easily.

NUCL 7

Isotope harvesting of ^{88}Zr for neutron-capture cross-section measurements

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Understanding the nuclear-reaction network involving Zr isotopes is important for the stockpile-stewardship program. The neutron-capture cross section for the radioactive isotope ^{88}Zr has not been measured and we are working towards filling in this gap in the nuclear data. To produce the ^{88}Zr targets, we collected the ^{88}Zr secondary beam in a water-filled irradiation cell that is part of the aqueous isotope-harvesting end station at the National Superconducting Cyclotron Laboratory at Michigan State University. As the ^{88}Zr samples contained a variety of other products with similar charge-to-mass ratio, separations were developed to isolate the Zr such that it could be used as target material. The separated ^{88}Zr was made into a target and sent for neutron irradiation at a reactor. After irradiation, the production of ^{89}Zr and destruction of ^{88}Zr were monitored via gamma-ray spectroscopy. Details of these experiments and subsequent results will be discussed.

NUCL 8

Use of ^{149}Tb and ^{152}Tb in preclinical and clinical investigations: Its mass separation and subsequent application for imaging and therapy

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Terbium is a unique element, as it provides a quadruplet of radionuclides suited for diagnostics and therapy in nuclear medicine. Much success has been gained from the PSI-ISOLDE collaboration, with the collection and purification of ^{149}Tb (α-emitter, $T_{1/2}$ = 4.1 h), used for preclinical therapy studies and PET imaging, and ^{152}Tb (β^+-emitter, $T_{1/2}$ = 17.5 h), for preclinical and clinical PET imaging, respectively.

Mass-separated beams of ^{149}Tb and ^{152}Tb, respectively, were implanted at ISOLDE-CERN into Zn-coated Au foils. With 1.5 hours of collection and 2 hours decay of co-implanted activities, up to 200 MBq ^{149}Tb could be transported to PSI. Collections of ^{152}Tb lasted 4 to 6 hours and up to 600 MBq ^{152}Tb could be shipped to PSI.

Both the means of collection at ISOLDE/CERN, as well as the chemical separation have been updated over the years, with the most significant upgrades taking place in 2017.

At PSI, the chemical separation system was performed using a new set up and manipulators in a hot cell. The foil containing the Tb nuclide was extracted from the Zn foils by dissolving them in HNO_3/NH_4NO_3. The dissolved nuclides were loaded on to a macroporous strongly acidic cation exchange resin and Tb nuclide eluted using dilute α-hydroxyisobutyric acid (α-HIBA). As an addition, the product eluent was passed through a second resin column, to ensure formulation of the product in chloride form.

^{152}Tb was directly employed for radiolabeling of PSMA-617. PET/CT scans were performed with PC-3 PIP (PSMA-positive) tumor-bearing mice at different time points after injection of ^{152}Tb-PSMA-617.

The successful experimental runs with the updated system have prepared the collaboration well for proposed extended preclinical imaging and therapy experiments in future.

NUCL 9

Quantum and classical approaches to probe the structural, dynamical and hydration properties of tetravalent actinide elements

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For the study of the heaviest elements of the periodic classification, molecular modeling approaches have shown their capacities to be a source of complementary information to experiments that can be carried out, such as those using EXAFS, HEXS or TLRFS ... However, for these elements, especially for actinides, their properties depend largely on their interactions with their environment. As such, a relevant modeling should explicitly take into account the effects of the medium (interaction with the nearest ligands and beyond, effects of temperature, ...). Our group develops and uses numerical tools based on quantum or classical models known as "*ab initio*", that is to say independent of any experimental input data to calibrate them, in order to better understand and better characterize the properties related to dynamic processes and those related to the electronic structure (UV-Vis spectroscopy, magnetism) of ions, molecules, or complexes containing radioelements in liquid medium.

In this presentation, we will discuss specifically the development of classical force fields, to investigate and revisit the behaviours of early tetravalent actinides, Th(IV), Pa(IV), U(IV), Np(IV), Pu(IV) and Bk(IV) in aqueous solution. Our objective is to probe the local structure and explore the trends along the early actinide series in the same bulk conditions with molecular dynamics (MD) simulations.

NUCL 10

Quantum-mechanical studies of actinide complexes: Benchmarking of new methods, novel complexes and novel reactivity

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In this talk, I will discuss our latest results in computational actinide chemistry at the University of Nevada, Reno. We have examined the performance of new accurate and affordable multiconfigurational wavefunction methods for predicting the bond distances, vibrational frequencies, redox potentials, ligand-bond distances and ligand-bond energies of actinide species by comparison with density functional theory, DFT, coupled-cluster, CCSD(T), and complete-active space 2nd order perturbation theory, CASPT2. We describe methods that are particularly suited for developing force field parameters for actinide interactions with environmentally relevant ligands. In addition, we will discuss new results from a combined experimental and theoretical study in which we use DFT methods to characterize novel chemistry of uranium (III) and (IV) complexes. We pay particular attention to the mechanistic pathways involved in these chemistries. Lastly, we discuss how similar reactivities can be facilitated in a trans-uranium element by using ligands to widen the redox-active gap.

NUCL 11

Properties of AnO_2^+ and the pK_a's of aqueous an cations in different oxidation states

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There is substantial interest in understanding the properties and reactivity of actinide containing molecules, including their reactions in aqueous solution. The energetics and structures of the actinyl dioxide cations AnO_2^+ for An = Pa to Lr have been predicted using CCSD(T) with large basis sets and spin orbit corrections. The calculations show that the linear AnO_2^+ with An(V) are the most stable except for CmO_2^+, and beyond EsO_2^+, where the most stable structure has side-on bonded η^2-(O_2), as An(III) peroxides for An = Cm and Lr, and An(II) superoxides for An = Fm, Md and No. It is predicted that the most stable structure of EsO_2^+ is linear $[O{=}Es^V{=}O]^+$, einsteinyl, and that FmO_2^+ and MdO_2^+, like CmO_2^+, also have actinyl(V) structures as local energy minima. The results expand the actinide oxidation state chemistry, the realm of the distinctive actinyl moiety, and the non-periodic character towards the end of the periodic table. The acidities of aqueous An = Th - Cf in different oxidation states have been calculated with multiple solvation shells and show some

interesting trends. These are the first available estimates of the pK_a's for some of these species.

NUCL 12

Topology, stability, solubility, and dynamics of uranyl peroxide cage clusters

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More than a decade ago we synthesized the first uranyl peroxide cage clusters, and since have grown this family of nanomaterials to more than 60 published structures. Uranyl peroxide cage clusters self-assemble in water under ambient conditions, and most are highly soluble in water. This presentation will focus on recent studies that include several new structures, the overall stability of these clusters as detailed by calorimetric measurements, their solubility and properties in water, and the interchange of cluster structures in water triggered by changing pH and counter cations.

NUCL 13

Understanding isomerism in peroxide nanocapsules: Are other isomers possible?

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Since their discovery, uranyl-peroxide nanocapsules have rapidly emerged as a large family of self-assembled capsules. The assembly of different nanocapsules and topologies is highly influenced by the pH and the alkali cations present in solution. In this communication, we have studied all the possible structural isomers of $[(UO_2)_{20}(O_2)_{30}]^{20-}$ (U_{20}) using density functional theory calculations and explored if different alkali counterions could tune the most stable isomer. This is the first step towards the study of the stability of different isomers in endohedral uranyl-peroxide nanocapsules.

NUCL 14

Broad look at the energy landscape of nanoclusters and their transformations

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Polyoxometallate nanoclusters (molecular aggregates containing 2-100 metal ions, displaying bonding within the cluster through oxide, hydroxide, peroxide and other anions, and charge balancing by alkali or other cations) have been found in a number of systems containing actinides and also in other systems containing aluminum, niobium and other metals. These clusters are viewed as intermediates in the reaction pathways linking dissolved ions and solid phases but, until recently, little has been known about the thermodynamics of these transformations. Here I summarize recent experimental thermochemical data which show definitively that the clusters are intermediate in enthalpy and probably free energy between isolated ions and nanophase precipitates. I suggest that further calorimetric study, perhaps by *in situ* calorimetry of formation, ageing and transformation reactions related to the aggregation of such clusters, leading to larger moieties which eventually precipitate as nanophases of different possible structures, is a logical and feasible next step in characterizing this energy landscape. Earlier calorimetric studies of zeolite formation and the ageing of hydroxyapatite suggest possible experimental methodologies.

NUCL 15

Aging of actinide solid sources during multi-year exposure to environmental conditions

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Exposure of actinide bearing solid phases to environmental conditions may result in a myriad of chemical or physical modifications including dissolution/precipitation, oxidation/reduction, and/or recrystallization/amorphization. Each of these reactions may have an impact on the fate and transport of the actinides in the envionment. To better understand such processes, a series of field lysimeter experiments have been used to monitor the changes in chemical and physical properties of a variety of U, Np, and Pu bearing solid phases including $Pu(V)NH_4CO_3(s)$, $Pu(IV)(C_2O_4)_2(s)$, $Pu(III)_2(C_2O_4)_3(s)$, $Pu(IV)O_2(s)$, $Np(IV)O_2(s)$ and $Np(V)O_2NO_3(s)$. Formation of dissordered PuO_2 type phases from reduction of $Pu(V)NH_4CO_3$ was observed under both field and laboratory conditions but accelerated under field conditions. Similarly, the oxidation of $Np(IV)O_2(s)$ under field conditions leads to formation of a much more disordered solid

phase with a significantly altered morphology than the initial Np(IV)O_2(s). Migration of Np and Pu from initially NpO_2(s) and PuO_2(s) was significantly retarded relative the to migration of oxidized sources. However, a small fraction of Np and Pu released from the source is proposed to be due to transport of colloidal species thought to be NpO_2(s) and PuO_2(s) type nanoparticles. The results of these experiments will be discussed in terms of evaluating the history of the sample through analysis of the microcrystalline structure and the influences of aging under various environments.

NUCL 16

Tetravalent actinides – from polymeric complexes to nanoparticles

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Tetravalent actinides show a strong tendency towards hydrolysis. This forces the formation of polynuclear species. However, the polynuclear species undergo further polymerization and form colloids. One way to isolate polynuclear species is to introduce terminating groups which hinder further polymerization. We found that carboxylates are well suited for this task. Larger clusters can form either highly ordered nanoparticles, complete amorphous structures, or transitions between them. Nanoparticles with an ordered structure can be stabilized by the introduction of termination functions, whereas amorphous nanoparticles can be potentially stabilized by introducing ions that modify the surface charge. These modifications support the structure analysis of the species. The nanoparticles of tetravalent actinides can form colloid suspensions which are stable over years. Due to their low solubility, tetravalent actinides are considered as nearly immobile in the nature. The surface charge may significantly enhance their migration.

NUCL 17

Hydration of uranyl fluoride and a novel chemical pathway to uranyl peroxide

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Uranyl fluoride exists both as a hexagonally-coordinated anhydrous crystal (UO_2F_2) and as a pentagonally-coordinated crystal hydrate ($[(UO_2F_2)(H_2O)]_7(H_2O)_4$). In-situ Raman spectroscopy with temperature and relative humidity control was used to further characterize the transition between these two phases. Assignment of the phases based on Raman signature is possible because the symmetric uranyl stretching frequency of each phase is distinct.

Further hydration of $[(UO_2F_2)(H_2O)]_7(H_2O)_4$ was also investigated using micro-Raman spectroscopy and scanning electron microscopy with energy-dispersive x-ray spectroscopy to analyze particles equilibrated at different water vapor pressures. Although $[(UO_2F_2)(H_2O)]_7(H_2O)_4$ is relatively stable at ambient conditions, elevated water vapor pressure induces a loss of fluorine within the crystal structure, producing uranyl hydroxide and peroxide species. The formation of uranyl peroxide species is especially interesting because of the absence of hydrogen peroxide in the system, which has generally been assumed to be necessary for the formation of these species.

NUCL 18

Actinide oxide and peroxide nanoclusters: Structure and environmental stability

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Uranyl peroxide nanoclusters play a potential role in the fate and transport of uranium in the subsurface environment. Understanding the interactions of these nanoclusters with abundant subsurface minerals and the mechanisms by which they interact is crucial for public and environmental safety. The first part of this talk will discuss interactions of the well-studied uranyl peroxide nanocluster U_{60} with the iron oxide mineral hematite (α-Fe_2O_3). A particular focus of the discussion will be on the role of counterions in surface complex formation.

The aqueous chemistry of Pu(IV) is complex due to its propensity to hydrolyze under all but very acidic solutions and readily form colloids. The structure and assembly of these colloids is highly debated, but is generally believed to be a complex mixture of hydroxides and hydrous oxides. This is unfortunate given the importance of the Pu colloid with respect to plutonium solubility, nuclear waste reprocessing, and environmental fate and transport. The second part of

this presentation will discuss the synthesis and structure of a family of plutonium oxide clusters and high-temperature calorimetric measurements of these novel structures. Further study of these clusters is expected to shed light on mechanisms of formation and expand our understanding of aqueous plutonium chemistry.

NUCL 19

Probing the bonding in dimers of tetravalent cerium and actinide homologues

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Cerium can be stabilized in solution in a tetravalent form in the presence of nitrates, predominantly as ceric ammonium nitrate (CAN) assigned as a monomeric hexanitrate cerium structure. However, recent synchrotron X-rays and Raman spectroscopy have challenged this picture, and propose instead an unusual Ce−O−Ce dimeric linkage observed when CAN is dissolved in water.[1] Conversely, tetravalent thorium and plutonium form dimers with a double μ_2-OH bridge.
To rationalize the formation of this dimeric species, we will scrutinize the structure, spectroscopy (Raman, infrared) and the bonding of this peculiar dimeric species, in particular with respect to f/d metal participation to the bridging interactions.

The structures and vibrational spectra of various isomers of the cerium, thorium and plutonium dimer have been density functional theory methods. Natural bond orbital (NBO) and quantum theory of atoms-in-molecules (QTAIM) approaches have been used to analyze the nature of the μ_2-O and μ_2-OH bridging chemical bonds. The theoretical results will shed light on the relative preference of μ_2-O single bridge with respect to μ_2-OH double bridges.

NUCL 20

Coordination polymer (CP) networks and molecular complexes of tetravalent actinides (Th, U, Np) with aromatic polycarboxylate ligands or polyoxometalate (POM) species

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Coordination polymers are built up from the association of metallic centers with organic (e.g. O- or N-donor) ligands. In the particular case of actinides (An), precedent studies have reported mainly the synthesis of such solid networks bearing U(VI) or Th(IV), while trans-uranium elements have been much less studied due to their high radiotoxicity and limited amount of the material source. Among the possible oxidation states of An, the tetravalent state has been investigated most actively and large polyoxo clusters have been isolated for U or Pu. In contrast, there are very few data concerning Np(IV) compounds. The knowledge of the formation of such polynuclear An(IV) species could be of significant importance for the fate of An in contaminated soils containing O-donor ligands, such as humic acids, or other organic pollutants (e.g. phthalates).

In the present communication, we firstly present the formation of several series of uranyl-organic frameworks associated to poly-carboxylate linkers, by following the pH variation parameter of the reaction medium, related to the hydrolysis rate. This strategy was then applied to actinides(IV), which are known to exhibit a strong affinity for hydrolysis reaction in order to form inorganic entities with high nuclearities. In a first approach, the control of water content in reaction media containing organic solvent will be investigated in different chemical systems with Th(IV) and U(IV) in the presence of dicarboxylic acids molecules (typically terephthalic acid), and was then extended to Np(IV) for some cases. The structural descriptions of the different coordination polymers will point out the nuclearity variation of the inorganic bricks from mononuclear $[AnO_9]$ up to hexanuclear entities $[An_6O_8]$. The particular case of the poly-oxo cluster $[An_{38}]$ will be discussed, and its formation will be described with U(IV) and Np(IV) in different solvents. The crystallization of U(IV) and Np(IV) compounds with various aromatic polycarboxylate ligands was then considered in water medium and crystal structures of coordination networks with phtalate and mellitate have been analyzed. The last point deals with the isolation and crystallization of polynuclear clusters of actinides (Th(IV)/U(IV)) embedded within large anionic polytungstate moieties ($[SiW_9O_{34}]$, $[AsW_9O_{33}]$). Trinuclear, tetranuclear and hexanuclear motifs bearing actinides(IV) have thus been identified in these systems.

NUCL 21

Commissioning the EMMA spectrometer at TRIUMF

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The ElectroMagnetic Mass Analyser (EMMA) is a new experimental facility at TRIUMF. Located after the ISAC-II accelerator, EMMA is a symmetric QQEDEQQ-type mass spectrometer capable of separating the recoiling nuclear reaction products from the beam. With the low emittance radioactive beams delivered from ISAC-II at energies up to at least 6.5 A MeV, EMMA is designed for fusion evaporation and transfer reactions of interest in nuclear structure and astrophysics studies. A vacuum mode separator, EMMA disperses ions according to mass/charge in the focal plane. During successful commissioning runs over the last year, the dispersion was measured and found to agree with ion optical calculations. Further, the angular, energy, and mass / charge acceptances were characterized and the first successful fusion evaporation reaction was performed. EMMA is currently being coupled with the TIGRESS γ-ray detector array, to perform detailed in-beam spectroscopy. Today, we present the current status of the EMMA mass spectrometer as it begins its experimental life.

NUCL 22

Separation of Pb, Bi and Po by cation exchange resin

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A separation of 209Po, 207Bi and 212Pb using AG 50Wx8 and AG MP 50 cation exchange resins in an HCl medium was developed. A procedure in which Po(IV) elutes first in 0.2 M HCl, followed by Bi(III) in 0.4 M HCl and finally Pb(II) in 2 M HCl was established. The separation using AG 50Wx8 provides a much better elution profile than that of AG MP 50 with no overlap between the elution bands. This separation has the potential to be used as an isotope generator for producing 210Po from 210Pb.

NUCL 23

Thermal analysis of lanthanide chelates for nuclear forensics

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In an effort to meet the growing demand for more rapid separation methods, this work reports the development and thermodynamic characterizations of organometallic species as a vehicle for the rapid separation of volatile nuclear fission products. Volatile organometallic complexes can be rapidly separated from each other via gas phase chromatographic separations due to differences in adsorption enthalpy. Because adsorption and sublimation thermodynamics are linearly correlated, there is considerable motivation to determine sublimation enthalpies to improve the ability to predict separations effectiveness. A method of using thermogravimetric analysis (TGA) is employed in this study on complexes of fourteen lanthanides, and up to four different chelating ligands. 1,1,1,5,5,5-hexafluoroacetylacetone (hfac), 1,1,1-trifluoro-2,4-pentanedione (tfac), 2,2,6,6-tetramethyl-3,5-heptanedione (dpm or thd), and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (fod) are all used to synthesize homoleptic complexes of the lanthanides. These 56 complexes are characterized with melting point, ICP-MS, FT-IR and elemental analysis. Sublimation enthalpies are determined using the Langmuir method involving isothermal jump heating. An empirical correlation is used to estimate adsorption enthalpies of lanthanide complexes on a quartz column from the sublimation data. TGA-MS and melting point are also used to confirm sublimation and the stability of the chelate through the sublimation region.

NUCL 24

Recovering barium from strontium resin using chelating agents

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Cs-137 is of special interest to nuclear forensics investigators. Due to its 30-year half-life and emission of gamma radiation at certain known energy levels, the isotope is commonly used in industrial, research, and medical facilities. The relative abundance of commercial-grade Cs-137 suggests that investigators are more likely to encounter lost or stolen sources containing Cs-

137 than any other radioactive isotope. An important part of identifying the origin of an unknown radioactive source consists of determining the age of the source. This can be accomplished by separating the Cs-137 from its daughter, Ba-137, and determining the ratio of the two. Current age-dating accuracy and precision are highly dependent on the recovery of the parent and daughter isotopes after separation. Separation of Cs-137 and Ba-137 is typically accomplished using extraction chromatography with Sr resin, after which mass spectrometry is utilized to determine the atom ratio of the two isotopes. Recovery of Ba-137 for analysis has been found to be problematic due to inconsistent chemical recoveries and the prevalence of natural Ba in laboratories. Previous work done on the age-dating of Cs-137 ceramics at ANL suggested that using a solution of 0.05 M ethylenediaminetetracetic acid (EDTA) at pH 6 promoted recovery of Ba-137 from chromatography resin, however further studies were still needed. This presentation will cover the results of a comparative study to test the effectiveness of different chelating agents, at various pH levels and concentrations, in recovering barium from Sr resin.

NUCL 25

Exploring the effect of the diluent on trivalent *f*-element extraction by the di-alkyl acidic organophosphorus extractant HEH[EHP]

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The extraction of trivalent *f*-elements by 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) is at the core of lanthanide hydrometallurgy for recovery from minerals and in the Advanced TALSPEAK and the ALSEP processes for lanthanide/actinide separations. To broaden the state of knowledge of the basic features of HEH[EHP] interactions, the role of the organic diluent in *f*-elements separations has been investigated. This study presents the results of an investigation of the trivalent *f*-element separations by HEH[EHP] in 22 different diluents from dilute nitric acid solutions. The study used the basic techniques of liquid-liquid extraction slope analysis of selected lanthanide radiotracers (obtained by neutron activation at the WSU Nuclear Science Center) to characterize the apparent metal:extractant stoichiometry. The results demonstrate that the coefficient of extractions are impacted by the diluent effect, with a log K_{ex} ranging from -0.29 ± 0.02 in *iso*-octane to -6.05 ± 0.02 in chloroform. The apparent stoichiometries of the extracted metal complex is also seen to vary over the range of $LnA_3(HA)_2$ in *n*-

decane to $LnA_3(HA)_4$ in methyl isobutyl ketone. This solvent effect on the K_{ex} and the stoichiometries will be discussed.

NUCL 26

Comparison the solvent extraction behavior of Re(VII) with Tc(VII)

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Heptavalent rhenium, Re(VII), is often considered an acceptable analog for Tc(VII); use of stable Re instead of radioactive Tc would simplify experimental work. This study investigates the validity of the analogy for solvent extraction systems. Dual radioisotope-labelled liquid-liquid extraction (LLE) experiments were carried out incorporating both Tc-99m(VII) (with Tc-99(VII) carrier) and Re-186,188(VII) tracers (with stable Re carrier) in order to quantify the suitability of Re(VII) to act as an analog for Tc(VII). Extraction of each metal by tetraphenylphosphonium chloride in chloroform from a 1 M ionic strength aqueous solution was quantified. The distribution coefficient, D, of each metal was determined using gamma spectrometry and as a function of the extractant concentration (0.00 to 1.00 mM) and pH (0, 2, 4, 6, 8). The extraction equilibrium constant, K_{ex}, was quantified for each metal. Results show that, while extraction of TcO_4^- was characterized by a greater K_{ex} value than for Re(VII) extraction across the pH range, the trend of K_{ex} as a function of pH was virtually identical for both metals. Additional LLE experiments using Re(VII) and Tc(VII) individually were carried out under identical conditions that were employed for the dual radioisotope-labelled samples. These results are in good agreement with the dual-metal LLE experiments. The extraction behavior of Tc(VII) and Re(VII) were also studied in perchlorate and nitrate media. Extractions in nitrate media showed a decrease in efficiency from chloride media, while extraction was essentially suppressed in perchlorate media.

NUCL 27

Spectroscopic speciation studies and kinetic investigations on the actinide lanthanide SEParation process (ALSEP)

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Separation of the minor actinides is a critical component to the management and storage of used nuclear fuel. Once uranium, plutonium, and neptunium are removed from the used nuclear fuel, the minor actinide americium is the most significant contributor to the radiotoxicity of the resultant waste after 300 years. Due to chemical similarities between the actinides and lanthanides, separating americium from the fission product lanthanides is challenging. Liquid-liquid separation processes that exploit the electronic structure differences between the lanthanides and actinides separate these ions by employing hard base/soft base modalities to selectively bind the lanthanides and actinides, respectively. The Actinide Lanthanide SEParation (ALSEP) process, a three step liquid-liquid extraction system which combines the extractant ligands 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) in one organic phase, has shown great efficiency and promise for selective recovery of trivalent actinides such as americium, although the stripping step of ALSEP suffers from slow kinetics. In this work, we begin the process of piecing together the chemical mechanisms of ALSEP, first by investigating metal-complex speciation, and then by gathering kinetic information.

Using visible spectrophotometry of neodymium, we examined both the bulk phase equilibrium species and the mixed extraction system in real time. Initial studies of mixed systems reveal that Nd is extracted into the ALSEP solvent from nitric acid solutions as a mixed HEH[EHP]-T2EHDGA complex without detectable intermediate species. Analysis of the series of in-situ time-resolved spectra also reveals the presence of three different organic phase Nd complexes in the scrub step as Nd is transferred from the mixed HEH[EHP]-T2EHDGA complex to the expected Nd-HEH[EHP] complex at an aqueous pH of 3.5. Transient Nd-containing species are also observed in the spectra of the stripping step when Nd partitions between the ALSEP organic phase and a DTPA containing aqueous phase.

Using a microfluidics setup, kinetic studies were also carried out on the system. The complexity of the ALSEP system necessitates beginning these investigations with a simplified system where the individual constituents were eventually each added sequentially to illuminate the impact of each component on the stripping kinetics.

NUCL 28

Sodium bismuthate solubility in nitric acid

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The prospect of nuclear power as a viable alternative energy source would be considerably improved by closing the nuclear fuel cycle. The recovery of actinides, particularly Am, from spent nuclear fuel reduces the amount of radioactive waste requiring long-term storage and, in addition, has potential as a fuel source in current and advanced reactors. However, the chemical similarity of Am(III) to the other trivalent actinides and lanthanides makes for a complicated separation process. It's been shown that the oxidation of Am(III) by sodium bismuthate in nitric acid solution generates Am(VI), and this hexavalent americium can subsequently be readily separated from nitric acid solutions through solvent extraction techniques. However, the limited solubility of sodium bismuthate quickly becomes rate limiting in the americium oxidation, and the dissolved Bi(V) quickly reduces to Bi(III). Therefore, to maximize the yield of Am(VI), a sustained, high, sodium bismuthate concentration in nitric acid is desired. Unfortunately, quantitative solubility limits have not yet been determined for sodium bismuthate in nitric acid, especially at non-ambient temperatures. Establishing these solubility parameters, especially in the presence of other anticipated extraction process chemicals, could provide a more effective, optimal, technique for separating americium from lanthanides and other actinides.

NUCL 29

Investigating formation and competitive exchange kinetics for DTPA complexed Eu ions in aqueous solution

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Obtaining absolute ligand complexation kinetics for metal ions in both the aqueous and organic phases is essential for a quantitative understanding of large-scale nuclear waste reprocessing efforts involving solvent extraction. In this work we have focused on quantifying the complex formation kinetics for

the ligand DTPA reacting with lanthanide ions in acidic aqueous media. Previously, these rate constants were measured using metal-dye complex displacement techniques, but we have found this approach to significantly underestimate rate constants due to the slow kinetics of dye decomplexation. However, by using the change in europium luminescence upon its binding to DTPA, an exact, absolute, rate constant can be measured. Establishing this value allowed determination of the formation constants for other lanthanides by observing competitive complexation. We have also determined the exchange rate between different complexed lanthanide ions. The combination of exchange rates and competitive complexation were determined in three separate experiments; pre-loaded luminescent, competitive and pre-loaded non-luminescent. Exchange rates depended strongly on temperature, pH, and buffer concentrations. The order of loading of the complexing ligand was also important, giving insight into the preferential nature of the complexation of these lanthanide ions.

NUCL 30

Expanding the structural toolkit to characterize heavy actinide complexes

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Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, it significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques as well as transmission electron microscopy to investigate specific heavy actinide coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. We will discuss some innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron

microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5*f*-element sequence.

NUCL 31

Synthesis and reactivity of multimetallic uranium nitrides

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Uranium nitrides are attractive candidates for stoichiometric and catalytic N-transfer reactions, small molecule transformation, and for advanced nuclear fuels. However, the reactivity of molecular nitride compounds remains basically unexplored. Recently we identified synthetic routes to molecular polymetallic nitride complexes containing uranium in low oxidation state. We will present the remarkable reactivity of the nitride bridged diuranium(IV) complex $Cs\{(N)[U(OSi(OtBu)_3)_3]_2\}$, with CO_2, CS_2 and CO, leading to the formation of new N-C bonds. Furthermore, we will show that the reduction of the metal centers leads to a multimetallic K_3UNU nitride bridged diuranium(III) complex, which is able to effect the cleavage and functionalization of dinitrogen.

NUCL 32

Development of UF_6 research at ICCF: Purification, corrosion and novel compounds

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During nuclear fuel production, one of the most notable compounds is uranium hexafluoride which is used for the enrichment process of uranium. The industrial synthesis of UF_6 is the hydrofluorination of uranium mining concentrates through a process called conversion. The first stage aims at obtaining UF_4 from the mining concentrate, then converting this UF_4 to UF_6, and finally storing UF_6 before its use in the enrichment process. Depending on the source, this uranium is susceptible to contain impurities that can lead to the formation of secondary mixed phases and any addition of oxygen in the process will lead to the presence of diverse uranium oxyfluoride. Additionally during the industrial stages, the uranium compounds will interact with different metal linings of the fluorination ovens, the piping in the industrial site and the walls of the containers. All these factors lead to the need for research on the purification, corrosion and novel compounds linked to UF_6 in industrial conditions. This research is undertaken at the Institut de Chimie de Clermont-Ferrand, and in part at AREVA, the leading French uranium company, and this presentation will outline the achievements on such a particular chemical compound.

NUCL 33

Hexavalent uranium, neptunium and plutonium nitrate complexes

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The hexavalent actinides, U, Np, Pu provide a convenient periodic series to explore the chemistry of the early actinide ions. As an entry into this chemistry we have studied the chemistry of the actinyl(VI) ions in nitrate media, focusing primarily on the understudied transuranium NpO_2^{2+} and PuO_2^{2+} systems. Our approach combines the chemical synthesis of actinyl(VI) nitrate complexes from solution and their characterization using single crystal X-ray diffraction and spectroscopic methods including UV-Vis-NIR, Raman, and fluorescence spectroscopy in attempts to correlate the observed solid state structures with the solution speciation. We have extended these studies from aqueous to organic solutions to investigate the speciation of the actinyl nitrate complexes of relevance to separations processes such as those encountered with the Aliquat series of quarternary amines. Here we are interested in the formation of ion-pairs between the anionic actinyl complexes and the cationic quarternary amines. We demonstrate the effects of ion-pair formation on the solution speciation and extraction efficacy.

NUCL 34

Supramolecular assembly and tuning of actinyl cations

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Assembly of molecular actinyl species (particularly uranyl) may be achieved through judicious choice of coordinating ligands that bear appropriate peripheral functionality, or ‘synthons,’ to promote non-covalent interactions in

the second coordination sphere. In particular, combining N-donor ligands such as phenanthroline (phen) and terpyridine (tpy) with halogen functionalized carboxylic acids creates a platform for directing halogen bonded interactions. Beyond assembly, ligands may also manipulate structural features and electronic properties. Two systems that highlight this potential are UO_2-phen-2,4,6-trihalobenzoates where the uranyl cation may be bent significantly away from linearity, and UO_2-tpy-*p*(or *m*)-halobenzoates where the degree of electron donation from equatorial ligands influences Raman and luminescence spectra and facilitates oxo interactions. Presented will be am overview of these systems as well as some general 'rules' for supramolecular assembly of actinyl species.

NUCL 35

Exploring actinyl oxo reactivity: Macrocyclic neptunyl inclusion compounds

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Pentavalent and hexavalent actinides, $An^{V,VI}$, have the ability to form a trans-dioxo entity, $[O=An^{V,VI}=O]^{n+}$, the actinyl cation. The $[An^{V,VI}O_2]^{n+}$ building block features two strongly bound axial oxygens which are generally considered to be chemically inert. However, actinyl complexes that exhibit oxo reactivity do exist, where the oxo atom of one actinyl cation bonds to the equatorial plane of a second actinyl cation. This bonding motif between two $[O=An=O]^{n+}$ units is commonly referred to as a cation-cation interaction (CCI) and is more frequently observed in pentavalent actinyl species, notably $[Np^VO_2]^+$. Additionally, weaker bonding interactions between neptunyl oxo groups and low-valent metal cations can occur. The current study explores neptunyl, $[Np^VO_2]^+$, oxo reactivity through the systematic investigation of neptunyl inclusion compounds with the 18-crown-6 ligand. To further evaluate the role of neptunyl-neptunyl and neptunyl-cation interactions on the crystal chemistry and vibrational frequencies of neptunyl compounds, interactions with a series of low-valent metal cations, M^{n+} (n = 1, 2, 3), were examined. Single crystal X-ray analysis provided structural characterization of the solid phase, with specific focus on the position of either the neptunyl cation or the low-valent metal cation within the crown ether molecule. This information was paired with solution and solid-state vibrational spectroscopy to elucidate the strength of the neptunyl bonds within this system.

NUCL 36

Complexation of dioxoactinide ions by aqueous-soluble Schiff bases – Effects on solvent extraction

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Several of the actinides have higher oxidations states (*e.g.*, V and VI) available under conditions in which they exist as linear dioxo cations, distinguishing their coordination environments from trivalent cations. While the stability of these oxidation states can be a challenge for some of the transuranic actinides under acidic conditions, reports suggest that these oxidation states may be stabilized by coordination of ligands to the equatorial plane of the actinyl ion. For example, studies indicate that Schiff bases have been able to stabilize U(V). As an alternative strategy, we are exploring water soluble Schiff bases as pre-organized chelators of actinide(V/VI) ions. Results of the extraction of An(III, V/VI) and Eu(III) cations from aqueous nitrate solutions containing tetradentate or pentadentate water-soluble Schiff bases *N,N*'-*bis*(5-sulfonatosalicylidene)-diaminoethane (H_2salen-SO_3) and *N*,*N*'-*bis*(5-sulfonatosalicylidene)-triaminoethane (H_2saldien-SO_3) by *bis*(2-ethylhexyl)phosphoric acid in toluene demonstrate significant holdback of U, Np and Pu. Under the same conditions, the trivalent Eu and Cm experience quantitative extraction. Combined with spectroscopic results indicating strong complexation of U(VI), Np(V) and Pu(V/VI) by salenSO_3 and saldienSO_3, and weak interaction with Ln(III) ions, these studies illustrate that similar ligand frameworks may be useful as selective holdback reagents in the separation of actinyl and trivalent lanthanide/actinide cations from aqueous media. Refined measurements of metal ion complexation and extraction will be discussed, with support from Np and Pu spectroscopic studies that interrogate their speciation under conditions similar to the extraction. The results of these studies can inform us about An and Ln complexation chemistry in solution, and may afford the design of separation systems under conditions not commonly considered.

NUCL 37

Complexation of technetium(IV) with selected halides

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Technetium-99 represents 6.1% of the fission product yield of U-235. It exists in nature in two main oxidation states; Tc(VII) species are mobile in the environment and the less mobile Tc(IV) species occur in reducing environments, such as soils or underground repositories. Tc(IV) has a solubility of approximately 10^{-7} M in water, but the addition of complexing ligands increases Tc solubility and environmental mobility. It is important to investigate the interactions of Tc(IV) with environmentally relevant ligands. The stability constants of Tc(IV) complexes with several ligands that can be found in the soil (citrate, acetate, oxalate, EDTA and several other polyamino-polycarboxylates) have been quantified. Smaller and weaker complexing monodentate ligands, such as the halides, are also expected to be present in ground waters surrounding waste repository sites. These ligands can also play a role in increasing the solubility of Tc(IV) as previously seen with larger ligands, but no data is currently available on halide complex stability constants with Tc(IV). This study focuses on Tc(IV) complexation with halide ligands. The stability constants for the Tc(IV)-halide complexes were determined using a solvent extraction method.

NUCL 38

Interrogating the role of water in metal ion extraction into room temperature ionic liquids

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The fission product ^{90}Sr has a number of important practical applications, however, its release to the environment poses substantial risks to human health. Accordingly, there has long been interest in methods for its separation and preconcentration from biological and environmental samples for subsequent determination. Classical approaches to accomplish this involve

complex and tedious sample treatment steps, resulting in low sample throughput. Although extraction chromatography has reduced the time and tedium associated with this separation, certain aspects of the method remain problematic.

Ionic liquids (ILs) have shown promise as the basis of new systems for the separation and preconcentration of ^{90}Sr, displaying unique selectivity for strontium over other metal ions inherent to biological samples. The mechanisms by which metal ions partition between an aqueous and IL phase are more complex than those observed in molecular solvents, however, and the equilibria remain incompletely understood. This can render an IL-based separation difficult to control. In an effort to better define the equilibrium processes involved in Sr(II) extraction by a crown ether (*e.g.*, dicyclohexano-18-crown-6; DCH18C6) into hydrophobic ILs, we have been evaluating a three-pathway model that is dependent on, among other factors, the aqueous acidity. In a recent study, we observed a linear correlation between the extent of extraction of Sr(II) and the equilibrium concentration of water in the ionic liquid phase. Under the conditions of extraction, metal ion transfer is thought to be limited to two of the three pathways, through which the hydration of co-extracted nitrate ions and the exchange *via* a hydronium ion-DCH18C6 complex would predominate. Our goal has been to verify and quantify these mechanisms.

To this end, two hydrophobic imidazolium-based ILs, one of them containing an alcohol functionality to encourage water dissolution, have been synthesized as their *bis*[(trifluoro- methyl)sulfonyl]imide salts. Vibrational and NMR spectroscopy have been employed to interrogate the states of water in these ILs and to explore the competition between acid, water, and metal ions for DCH18C6 dissolved in them. By quantifying the partitioning of various species in the titration of acid and metal ion, it is expected that a more complete, thermodynamics-based understanding of these systems will emerge.

NUCL 39

Effect of matrix constituents on the separation of plutonium and americium from bone samples

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There are numerous methods available in the literature for separating and analyzing radionuclides of interest from an array of environmental matrices.

The quality of these methods is however impeded by the elemental constituents that are commonly found in many of these samples. The presence of interfering constituents can result in incomplete separation of the radioisotopes of interest as well as a reduced rate of recovery. This is especially the case when analyzing complex matrices such as samples of bone and bone ash. Alpha-emitting isotopes of plutonium and americium are bone seekers. This means they have an affinity to accumulate in actively metabolizing portions of bones of many mammals including humans. It is therefore extremely important to study and evaluate the uptake of these radionuclides in human bone samples. Nevertheless, in agreement with literature, high concentrations of calcium present in the hydroxyapatite that constitutes the bone as well as sodium and potassium also present have the potential to strongly affect radiochemical separation methods. The objective of this research is to investigate the influence of the major and minor constituents present in bone on the radioanalytical determination of plutonium and americium using extraction chromatographic resins.

NUCL 40

Sequential extraction techniques to investigate movement and bioavailability of soil contaminants

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The nuclear reactor accident at the Fukushima Daiichi power plant resulted in the release of large quantities of various radionuclides into the environment. While airborne releases mainly consisted of volatile elements such as iodine, cesium and tellurium, elements such as plutonium and other actinides were also released through aquatic pathways. Actinides were also introduced into the environment through debris scattered by the explosions in three of the reactors. The surroundings of the Fukushima nuclear power plant provide therefore an involuntary, but nonetheless unique opportunity to investigate the behavior of plutonium and cesium in an eco-system. Several areas in the vicinity of the power plant are still considered an exclusion zone and have not been cleared for human resettlement. While these areas are not suitable for permanent habitation, they are accessible for field work. The purpose of this research is to analyze the movement and bioavailability of radiocesium and plutonium in the ecosystems contaminated by the Fukushima Daiichi nuclear reactor accident. This will be done by collecting and analyzing soil, sediment, water, and vegetation samples from within the inclusion zone. Most of the

existing studies have focused on determining the total amount of cesium and plutonium in soil. While this provides important data on the distribution of these radionuclides in the environment, it yields limited information on the bioavailability of these elements. Therefore, in this work the samples will be analyzed using sequential extraction techniques. By treating the samples with increasingly aggressive chemicals, it is possible to discover the geological host phase to which the radionuclides are bound. In addition to further the overall understanding of cesium and plutonium transport pathways in natural ecosystems, this research will also provide an opportunity to validate the sequential extraction procedures developed using real-world samples.

NUCL 41

Radiolytic degradation of tributyl phosphate in the presence of uranium

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Understanding and characterizing the radiolytic degradation of TBP has been an ongoing topic of research. In the work presented here, degradation constants for the radiolysis of tributyl phosphate as a function of various process variables, such as the inclusion of nitric acid as well as metal uptake, were determined. Degradation constants were found for both high LET and low LET (gamma) radiation exposure. Results indicate that susceptibility to gamma radiolysis is roughly twice that of high LET and that acid uptake by TBP has little effect on the overall degradation for both high and low LET irradiations. The inclusion of metal uptake affects the degradation of TBP by forming complexes that absorb a portion of the energy deposited by radiation. These TBP-metal complexes break down during irradiation and degradation. constants for the complex were determined for both high and low LET radiation. Similar to pure TBP, gamma radiation affects metal complexes greater than high LET radiation.

NUCL 42

Separation of actinium from thorium using polyoxometalates

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Actinium-225 (t1/2: 9.92 d) is an alpha-emitting radionuclide with nuclear properties well suited for alpha therapy of malignant tumors. The present global supply of ^{225}Ac is 1.7 Ci per year yet the global demand is 50-100 Ci. Currently, the production of ^{225}Ac from proton irradiation of ^{232}Th metal targets is being investigated at BNL. One proposed method for separation of Ac-225 from bulk Th targets involves the use of Polyoxometales (POMs). POMs are large metal oxide clusters, which have been used to chelate high-valent actinides and lanthanides. The modified Wells-Dawson POM ($[P_2W_{17}O_{61}]^{6-}$) has a very high affinity for thorium. This study seeks to take advantage of the affinity of POMs for Th to separate Ac-225 from bulk thorium for Ac-225 production. The separation is carried out by adding the POM to aqueous solutions of thorium, lanthanum and, actinium as individual metals and as mix metal solutions and contacting those solutions with 3% octylamine in chloroform. The extractions are quantified using ICP-OES. This study has shown that the POM completely extracts the Th from the aqueous solution and preferentially extracts the Th over the La and Ac

NUCL 43

Development of a radiotherapeutic nanoparticle for infection

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Metal chalcogenide nanoparticles labeled with ^{35}S are being developed to treat drug-resistant tuberculosis. Initially copper sulfide was investigated. Surprisingly the nanoparticles exhibited poor radiochemical stability in water and rapidly leeched activity. The nanoparticles were stable for months under argon. Copper indium sulfide nanoparticles were then investigated. These exhibited poor stability as well, but their stability could be enhanced by shelling with zinc sulfide. The resulting stability of the core/shell particles was proportional to the amount of shell precursor solution added. Small amounts resulted in nanoparticles of interim stability that rapidly degraded after a week. In contrast larger amounts created a core/shell structure stable for months.

The synthesis and stability studies of the nanomaterials will be presented.

NUCL 44

^{72}As a candidate for PET imaging: From production to *in vivo* imaging

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Advanced gastric cancer is the third leading cause of cancer related deaths worldwide. A host of monoclonal antibodies (mAbs), which are highly selective, are now approved for cancer therapy. However, there is a need to determine whether these therapeutic mAbs are effective. In order to evaluate their efficacy mAbs are labeled with radioisotopes and used as imaging agents. The labeled mAbs are then tested against patient specific organoids and tumor models, which are personalized cancer models, to visually observe drug sensitivity, uptake, and effectiveness. Due to the slow distribution kinetics of these antibodies, typically on the order of days, potential candidates for radiolabeling must possess comparable physical half-lives.^{72}As, a potential positron emission tomography (PET) radionuclide, is well suited due to its appropriate half-life, 26 hours, and ease of accessibility through the use of a portable generator. This portable ^{72}Se/^{72}As generator can be milked every 3-5 days to produce material for over one month. In this study ^{72}As was produced using a metal arsenic target at the Brookhaven LINAC Isotope Producer (BLIP). ^{72}Se was separated from co-produced material and loaded onto the generator. The potential generator was optimized and evaluated for breakthrough of the parent isotope. Monoclonal antibodies were labeled with ^{72}As through the use of a trithiol chelating ligand. Initial *in vivo* images in patient-derived tumor xenografted mice show that non-specific antibodies do not have uptake at the tumor location. Further studies will be completed with tumor specific antibodies to determine tumor uptake and to assess mAb therapies.

NUCL 45

Synthesis and *in vitro* evaluation of ^{99m}Tc/^{186}Re-cyclized somatostatin receptor-targeting peptides for the diagnosis/therapy of neuroendocrine tumors

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In this work we utilized the integrated labeling approach for the design of novel radiometal-cyclized somatostatin receptor (SSTR) antagonists with potential applications in imaging (^{99m}Tc) or therapy (^{186}Re) of neuroendocrine tumors (NETs). In particular, we report the synthesis and *in vitro* evaluation of ^{99m}Tc/^{186}Re-cyclized peptides, employing the potent SSTR2 antagonist sequence X-4-NO_2-Phe-DCys-Tyr-DTrp-Lys-Thr-Cys-DTyr-NH_2, where X = Ac (peptide **1**) or DOTA (peptide **2**). The ^{99m}Tc-cyclized analogues were prepared by reacting ^{99m}Tc-glucoheptonate with 40 μM linear (SH) **1** or **2**, promoting ligand exchange on the $^{99m}TcO^{3+}$ core and affording ^{99m}Tc-**1** and ^{99m}Tc-**2** in quantitative radiochemical yields (RCY >95%). The ^{186}Re-**1** analogue was synthesized by reacting $^{186}ReOCl_3(PPh_3)_2$ with 130 μM linear **1** in moderate RCY (>50%). Radiotracers consisted of isomeric products, two isomers for ^{99m}Tc/^{186}Re-**1** and three isomers for ^{99m}Tc-**2**. Comparative HPLC studies revealed similar elution patterns to the previously-characterized non-radioactive Re-**1** and Re-**2** analogues of known nanomolar SSTR affinity. Lipophilicity was measured via the “shake-flask” method (PBS/n-octanol) and $\log D_{7.4}$ values were 0.81 for ^{99m}Tc-**1**, 0.76 for ^{186}Re-**1** and -1.46 for ^{99m}Tc-**2**. *In vitro* stability studies were performed at 37 °C in PBS (pH 7.4), against 1 mM L-cysteine and in rat serum, and percent stability was determined with radioTLC and HPLC analyses. The ^{99m}Tc-tracers were sufficiently stable *in vitro* at 4 h in PBS (82% for ^{99m}Tc-**1** and 99% for ^{99m}Tc-**2**), in L-cysteine (71% for ^{99m}Tc-**1** and 65% for ^{99m}Tc-**2**) and in rat serum (77% for ^{99m}Tc-**1** and 99% for ^{99m}Tc-**2**, with low non-specific protein binding of 18% for ^{99m}Tc-**1** and 21% for ^{99m}Tc-**2**). The ^{186}Re-**1** tracer exhibited moderate *in vitro* stability (>57% in PBS at 1 h); efforts are underway to prepare and evaluate the ^{186}Re-**2** tracer. These findings indicate that direct ^{99m}Tc/^{186}Re-cyclization of SSTR-targeting peptide antagonists is feasible and may be further applied as an alternative approach (to the traditional use of bifunctional chelates) in the design

of ^{99m}Tc/^{186}Re-radiolabeled biomolecules for targeting SSTR-expressing NETs.

NUCL 46

Metal-ion speciation in non-polar solvents: A chemical-separations study

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Solvent extraction (SX), a widely used chemical separations process, is driven by very small differences in the free energies of a targeted metal-ion (M^{n+}) in two immiscible phases. The challenge for predicting extraction efficacies centers on a detailed knowledge of the M^{n+} speciation in these two phases, such that the relative energetics can be computed with the accuracies necessary to inform process design. Whereas there are literature reports describing distances, numbers, and identities of species coordinating to metal solutes under a variety of solvent conditions, this work directly focuses on the change of speciation that occurs as an M^{n+} ion is transferred from an aqueous solution into a non-polar solvent. Examples will include tetravalent Ce and Th ions in acidic nitrate aqueous phases and how their coordination environments change when they are transferred into an octane solution using tributyl phosphate (TBP) as an organic phase complexant (extractant). We use high-energy X-ray scattering (HEXS) data, in conjunction with standard laboratory and separations techniques, to ascertain solution species and relate them to separations efficacies. In addition to implications in SX processes, the importance of changing solvent polarity will also be discussed from the perspective of synthetic strategies for consideration when designing new materials for energy-relevant technologies.

NUCL 47

Structral and spectroscopic studies of U(VI), Np(VI), and Pu(VI) hydrolysis chemistry

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The hydrolysis of actinyl(VI) ions was intensively studied in order to understand the solution behavior of the actinide cations. Prior studies including Raman and IR vibrational spectroscopy, potentiometric titration, EXAFS and ^{17}O NMR for uranyl species suggested that several monomeric and polymeric species are successively generated in solutions until the predominance of monomers $UO_2(OH)_4^{2-}$ and/or $UO_2(OH)_5^{3-}$. Unlike their uranium analogue, few studies were performed on neptunyl and plutonyl cations. In these studies, essentially monomeric species were characterized although dimeric and other polymeric plutonium compounds were revealed or suggested. Previous attempts to model the chemical behavior of Np(VI) and Pu(VI) relied on extrapolation of the thermodynamic constants of the uranyl analogue. Prior results on Pu(VI) hydrolysis shown the weakness of this approach. In order to clearly identify the various species involved, a study including Raman spectroscopy, UV-Vis spectrophotometry and single-crystal XRD were started. Our studies revealed a series of monomeric and polynuclear hydrolysis species of U(VI), Np(VI), and Pu(VI) that have been characterized in both the solution and solid state using the aforementioned methods. In this study we correlate the solid state spectra to the species observed in solution to better understand the behavior of these cations in alkaline aqueous solution.

NUCL 48

Counter-cation control of tetravalent actinide hydrolysis and condensation

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In aqueous solutions, the chemistry of tetravalent actinides (An^{IV}) is dominated by hydrolysis and condensation. For decades, this chemistry has been well-recognized, but poorly understood, due to the tendency for these reactions to yield ill-defined amorphous precipitates. However, recent efforts exploiting anionic ligands and careful pH control have resulted in the isolation and structural characterization of discrete An^{IV} polynuclear clusters. Notable examples include the octahedrally-arranged oxo-/hydroxo-bridged Th^{IV}, U^{IV}, and Pu^{IV} hexanuclear clusters and the oxo-bridged 38-member Pu^{IV} cluster – all of which contain structural motifs resembling the atomic arrangement observed in the thermodynamically stable fluorite-lattice AnO_2 compounds.

Structural differences between these polynuclear clusters are predominantly limited to the number and identity of decorating anionic ligands on the cluster surfaces, suggesting that, although such anionic ligands have a clear influence on the ability to isolate An^{IV} hydrolysis products, these ligands, with exceptions, do not impact the overall tendency of An^{IV} toward hydrolysis and condensation. In contrast, we demonstrate here that counter-cations, specifically Rb^+ or quaternary ammonium (R_4N^+) cations, can drive enhanced coordination of nitrate to Pu^{IV} in crystalline solids, effectively out-competing the formation of Pu^{IV} hydrolysis and condensation products, namely the dihydroxo-bridged Pu^{IV} dinuclear cluster, which forms in the absence of these counter-cations. On the basis of our previous Th-nitrate study, which demonstrated a clear correlation between counter-cation hydration enthalpies and observed compositions of Th^{IV}-nitrato monomeric complexes, our findings indicate that electrostatic interactions between counter-cations and Pu^{IV}-nitrato monomeric complexes strongly influence reaction outcomes and should be considered an additional variable in controlling An^{IV} hydrolysis and condensation.

NUCL 49

Complexation of neptunium with small organic ligands using NMR spectroscopy

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With over 60 structures available in the literature, uranyl clusters have been created with many different linkages. While simple oxygen linkages are the most prevalent in these clusters, small organic ligands have also been successfully incorporated. Isolating clusters of the higher actinides has not been as successful as with the uranyl system. However, observing the complexation reactions of the ligands used in the uranyl cases with the higher actinides may provide insight into why the transuranic clusters are so hard to make. With that in mind, we have studied the complexation of ^{237}Np (V) and Np(VI) with small organic ligands using Nuclear Magnetic Resonance (NMR) spectroscopy. Following our variable-pressure study on the rate of self-exchange of carbonate around $[NpO_2(CO_3)_3]^{4-}$, 1-hydroxyethylidenediphosphonic acid (HEDPA) and oxalate were used as ligands of interest, due to their previous incorporation into uranyl clusters. One-dimensional NMR measurements were used to follow the complexation

that occurs throughout various pH ranges, while variable-temperature NMR was used to probe the kinetics of the complexation.

NUCL 50

Influence of counter-cations on neptunyl speciation and its redox behavior in chloride media

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Counter-ions are widely used in actinide chemistry as relatively innocent charge-balancing species, which provide control of ionic strength, solubility of ionic complexes, and structure packing in solids. However, the interplay between actinide-ligand/solvent complexes and counter-ions are often overlooked because of the expected relatively weak electrostatic interactions among them. One exception is in the field of actinide separations where counter-ions such as quaternary ammonium cations (R_4N^+) are critical for selectively driving the formation and transfer of metal-ligand complexes between two phases by perturbing the equilibria of metal-ligand/solvent complexation. The question remains whether a similar phenomenon of counter-ion directed metal-ligand complexation exists in the formation of molecular actinide complexes in solution. To understand the bonding interactions between counter-ions and actinide complexes, we systematically studied the influence of a series of monovalent counter-cations on the formation of molecular neptunyl-chloride complexes from aqueous solutions. By comparing neptunyl(V/VI) speciation in solution and in solids formed from evaporation in the presence of counter-cations, we demonstrated that counter-cations can affect neptunyl ligand complexation and shift the $Np^{V/VI}$ electrode potential of the resulting complexes. These results open a new avenue for using counter-cations to direct the formation of actinide-ligand complexes and to control the redox chemistry of actinides.

NUCL 51

Advances in radiopharmaceutical chemistry at the BNL Hot Laboratory

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The Hot Laboratory at Brookhaven National Laboratory has been the site of several developments crucial to the future of the field of Nuclear Medicine and particularly to the future of ^{99m}Tc as the core radionuclide in nuclear medicine. The most fundamental of these was the development of the ^{99}Mo/^{99m}Tc generator by Jim Richards and Walter Tucker in the late 1950s.
The ^{99}Mo/^{99m}Tc generator is, chemically, an amazingly simple system that to this day provides high-specific-activity ^{99m}Tc on an as-needed basis to nuclear medicine clinics throughout the world. However, despite the ready availability of ^{99m}Tc from the ^{99}Mo/^{99m}Tc generator, the development of ^{99m}Tc radiopharmaceuticals initially lagged because of the chemical challenge of producing useful radiopharmaceuticals from the TcO_4^- that is eluted from the generator. This situation changed dramatically in 1970 when Bill Eckelman, working with Jim Richards, developed the “instant kit” method for preparing ^{99m}Tc radiopharmaceuticals using Sn(II) as a reducing agent, a discovery that facilitated the development of new ^{99m}Tc radiopharmaceuticals for imaging the kidneys, bone, heart, and brain, among other organ systems.

A significant concern in the development of ^{99m}Tc instant kits was the biological fate of the Sn(II) used in the kits. The person who led this area of research at BNL was Suresh Srivastava. While early investigations focused on elucidating the biological fate of the tin, these studies led to the realization that there were interesting aspects of the biological chemistry of tin to be explored. One example of this was development of a method to prelabel red cells with Sn(II) in vivo, such that they essentially label themselves with ^{99m}Tc, an approach that circumvents many of the challenges of labeling red cells ex vivo. A second example was the use of ^{117m}Sn to track the biological fate of tin from the instant kits. These studies led to the observation that ^{117m}Sn-DTPA accumulated in the bone; a somewhat surprising result, since metal-DTPA complexes are more typically found in the kidneys. This observation, in combination with the fact that the decay of ^{11}Sn produces a large number of conversion electrons that deposit their radiation dose in very close proximity to the decay site, led to the development of ^{117m}Sn-DTPA, one of the very first theranostic agents for bone pain and osseous metastases.

These and other BNL contributions to radiopharmaceutical chemistry will be discussed.

NUCL 52

Radiometals in diagnostic and therapeutic radiopharmaceutical applications

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The University of Missouri Research Reactor (MURR) houses both a 10 MW research reactor and a 16.5 MeV PETtrace cyclotron. The reactor is a source for making neutron-rich radionuclides, which tend to be beta emitters, while the cyclotron tends to produce proton-rich radionuclides, which tend to be positron emitters. We have focused on theranostic radionuclides and matched pair radionuclides, including $^{72/77}$As, ^{186}Re and ^{105}Rh, for potential medical applications. The production and separation chemistry, chelate and metal chemistry, radiotracer chemistry, specific activity and biological factors that have been addressed or need to be considered for radiometals will be discussed with the ultimate goal of specific tumor targeting in mind.

NUCL 53

Characterization and *in vivo* evaluation of ^{99m}Tc and ^{188}Re peptides as potential SPECT imaging and radioimmunotherapy agents

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Several ^{99m}Tc and ^{188}Re pentapeptide-tetrazine constructs were prepared by reaction of peptide metal complexes with tetrazine constructs in DMSO. For all constructs, the stable macroscopic rhenium standard was synthesized and characterized for structural determination of the radiolabeled constructs. Stability studies in PBS and serum, logD studies to assess hydrophilicity and charges of the chelate and the appended peptides will be coordinated with biodistribution studies in healthy mice to determine a suitable candidate for *in vivo* pretargeting studies. In the pretargeting studies, mice bearing the A33 antigen-expressing SW1222 colorectal cancer xenografts were injected with A33-TCO and the corresponding radiolabeled-tetrazine construct were imaged via SPECT. The radiolabeled tetrazine constructs have been fully characterized by mass spectrometry and NMR spectroscopy of their macroscopic rhenium analogs and co-elution of the macroscopic and tracer analogs. The ^{99m}Tc pentapeptide-tetrazine constructs exhibit the highest overall stability in both PBS and serum. The physical characteristics of the ^{99m}Tc and ^{188}Re pentapeptide-tetrazine constructs are encouraging for increased tumor uptake and reduced non-target organ uptake. New ^{99m}Tc and ^{188}Re pentapeptide-tetrazine constructs were prepared and characterized. These constructs, with hydrophilic, charged residues and PEG groups, are stable, which is encouraging for pretargeting imaging and radioimmunotherapy (RIT).

NUCL 54

New approach for the isolation of ^{225}Ac isotope from proton irradiated Th target

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Alpha particle-emitting isotopes are being investigated for use in radioimmunotherapeutic applications for treating cancer. Of the prospective α-emitters, ^{225}Ac isotope with a short 10 day half-life is of major interest. ^{225}Ac is being investigated mainly to produce ^{213}Bi in a reusable generator and alone as a potential radionuclide for attachment to vectors for targeted treatment of cancer. The main source of ^{225}Ac is from the long-lived parent ^{229}Th (half-life= 7340 years). However, this provides limited quantities of ^{225}Ac that are insufficient for the current pre-clinical and clinical research demand. Therefore, an alternative method for the production of ^{225}Ac based on ^{229}Th spallation is being evaluated. The Medical Isotope Research and Production (MIRP) facility at Brookhaven National Laboratory is investigating high energy proton irradiation of thorium targets to produce ^{225}Ac. Thorium targets irradiated with proton energies at 90 to 200 MeV produces 400 isotopes resulting from thorium fission. The conventional method for ^{225}Ac purification is very time consuming and generates a large amount of waste. The aim of this work is to evaluate new methods for the separation of Ac from Th.
We investigated the use of polyoxometalates (POMs) and 3,4,3-Li(1,2-

HOPO), for the selective separation of Th from ^{225}Ac using liquid-liquid extraction methods. Several parameters were studied (extracting agents, organic solvent, extracting agent dilution) using batch studies for defining the best conditions.
While octylamine has no extraction behavior for Th, our results show that, POMs form an ion pair complex with octylamine. The latter extracts Th to organic phase with 100% ^{225}Ac remaining in the aqueous phase. A second extraction method was studied utilizing lanthanum as a surrogate for ^{225}Ac. 3,4,3-Li(1,2-HOPO) was used for the selective complexation of Th in HNO_3 aqueous phase leading to La extraction by 10% HDEHP in xylene. Then, La is back-extracted from HDEHP by using 7M HCl. This process provided 78% recovery of La. The optimized processes leads to the selective separation of Th from ^{225}Ac/La using POMs and 3,4,3-Li(1,2-HOPO) with a global recovery yield of 78-100 %.

NUCL 55

History of the BNL radioisotope research program: Contributions of Suresh C. Srivastava

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I collaborated with Dr. Suresh C. Srivastava for 36 years. During that time we developed over 25 radioisotopes, mostly for nuclear medicine applications, using the Brookhaven Linac Isotope Producer (BLIP) and the High Flux Beam Reactor at Brookhaven. The first isotope that was successfully used clinically was Xe-127 ($t_{1/2}$ 36.4d) for diagnosis of lung function problems. In recent years both Sr-82 ($t_{1/2}$ 36.4d) and Ge-68 ($t_{1/2}$ 271d) have been routinely provided from BNL to support the Sr-82/Rb-82 generator for cardiac imaging in hundreds of thousands of patients per year and the Ge-68/Ga-68 generator for a variety of diagnostic imaging studies. In addition to these successes, the BNL research program actually concentrated a great deal of effort on the development of radioisotopes for therapeutic applications in cancer, reflecting Dr. Srivastava's interest in expanding the use and benefits of isotopes in nuclear medicine. The first such therapeutic isotope development from BNL was Sn-117m ($t_{1/2}$ 14.0d), followed by Cu-67 ($t_{1/2}$ 2.58d), Au-199 ($t_{1/2}$3.17d) and most recently Sc-47 ($t_{1/2}$ 3.35d) and Ac-225 ($t_{1/2}$ 10.0d). Dr. Srivastava was an early proponent of isotopes with both imageable photon and particle emissions (alphas and betas) for combined imaging and therapy with the same agent, a concept now called theranostics. Selected highlights of these developments during Sr. Srivastava's career will be presented.

NUCL 56

MU Research Reactor: A valuable resource for medical radioisotopes

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The University of Missouri Research Reactor Center (MURR) began operation over 50 years ago and was recently relicensed by the Nuclear Regulatory Commission for another 20 years of operation. In addition to many other research and service endeavors, one focus area of MURR's Research & Development efforts is on the production and supply of radioisotopes of interest for medical applications. With a 10 MW research reactor and a 16.5 MeV GE PETtrace cyclotron, MURR produces dozens of radioisotopes. Beta-emitting neutron-rich radioisotopes, formed in the reactor by neutron capture of the target nuclei, are useful to therapeutic applications. Medical cyclotron production leads to a complementary and neutron-poor suite of radioisotopes that often decay by positron emission, making them suitable for diagnostic applications. MURR, as a unique resource to the nuclear medicine community, will be discussed and examples of past and current projects involving medical radioisotopes will be highlighted.

NUCL 57

Manufacturing and applications of Sn-117m in nuclear medicine

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Sn-117m has unique characteristics that make it ideal for a variety of nuclear medicine applications. The isotope emits a primary 159 keV imaging photon that is easily detectable with any SPECT camera system. The accompanying mono-energetic conversion electrons have a therapeutic effect limited to a range of ~300 μm which also minimizes any shipping and handling issues. Together these characteristics make this theranostic isotope a prime candidate for several personalized nuclear medicine applications.

This isotope can be produced in large quantities as a low specific activity (< 21 Ci/g) product in reactors via the Sn-116(n,γ) or Sn-117(n,n'γ) reactions. A carrier-free, high specific activity (up to 20,000 Ci/g) isotope can be manufactured with ~50 MeV cyclotrons employing either Sb(p,x) or Cd-116(α,3n). Methods for extracting and purifying the Sn-117m from Sb or Cd

have been developed.

Sn-117m has been used to label a wide variety of targets including proteins, anti-bodies and small molecules. In recent animal and human Phase I/II cardiovascular trials to detect and treat vulnerable plaque, the Sn-117m was chelated to aminobenzyl DOTA before being conjugated to annexin V. Results demonstrated the ability of this molecule to both target and image the plaques. Additionally, a remarkable therapeutic effect was observed at very low doses (~10 cGy).

In oncology, Sn-117m (chelated to DTPA) has been successfully used in over 120 humans for bone pain palliation in a Phase I/II trial. Labeling of neuroendocrine cancer targeting molecules has also been demonstrated. The isotope, in low specific activity form, has been electroplated onto stents and implanted into several animal models to demonstrate the efficacy and finite range of the conversion electrons.

Rheumatological applications include a homogeneous Sn-117m colloid that is being used to treat canine osteoarthritis (OA). Future veterinary applications include treating equine OA and human rheumatoid arthritis (RA). Labeled compounds are also being developed to image and treat RA systemically.

Additional future applications take advantage of the limited irradiation of normal tissue in immune and inflammatory CNS conditions that could provide new therapies for this immunologically privileged system. In conclusion, the novel isotope Sn-117m is successfully finding application in several aspects of human nuclear medicine and is now also creating new opportunities in the emerging field of veterinary nuclear medicine.

NUCL 58

Speciation of technetium in ionic liquids

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Technetium-99 (^{99}Tc $t_{1/2}$: 2.1x 10^5 years; β_{max}: 293.7 keV) is a high-yield (6%) fission product in light-water reactors, which presents major challenges in separations and containment technologies. The use of ionic liquids (IL) as a possible alternative media for separations is being explored. In order to access the potential use of ILs for separations, a fundamental understanding of the interactions of technetium and ILs must be understood. We are investigating speciation of technetium in neat ILs as well acid-IL mixtures. One system studied is the speciation of TcO_4^- in the IL Trimethylbutylammonium Bistriflimide (N_{1114} NTf_2) and Bistriflimidic acid ($HNTf_2$). $HNTf_2$ is a known super acid and recently been shown to be an even stronger acid when dissolved in (IL) bearing the NTf_2 anion. N-alkylammonium pertechnetate (TcO_4^-) salts were combined with varying concentrations of $HNTf_2$ in an IL with the corresponding cation as the Tc salt. The speciation was studied using UV-VIS, ^{1}H and ^{99}Tc NMR, and XANES. Preliminary results suggest that the TcO_4^- anion is protonated in the IL to form $HTcO_4$ (pertechnic acid). Pertechnic acid is typically generated using large amounts of a non-coordinating acid i.e Sulfuric acid (>9M) in aqueous media. The species formed in acid-IL solution is observed using far less acid (<100mM). The reactivity of the pertechnic acid species in the ionic liquid is also investigated. In another study, the speciation of technetium as Tc(V) oxo or Tc(VI) nitrido incorporated into a polyoxometalate is investigated electrochemically in IL and in acetonitrile. The IL extends the viable electrochemical range and Tc (IV), Tc(V), Tc(VI) and Tc(VII) species are identified

NUCL 59

Development of novel theranostics

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Significant advances have been made in identifying vectors for targeted therapy applications. The aim being to treat the right patient with the right drug at the right time at the right dose. As each patient disease is unique and thus the treatment, accurate patient selection and response monitoring is essential enhancing the need for theranostics. As vectors have advanced in their size, shape and complexity, so to must the radionuclides be that are used to radiolabel these vectors. The radionuclides are incorporated or attached to the drug molecule for diagnostic imaging and targeted radiotherapy, particularly for metastatic cancer. These diagnostic tools aid not only in diagnosing disease, but in quantitating expression and assessing normal tissue uptake, enabling the calculation of the appropriate dose to minimize normal tissue toxicity and maximize efficacy. Advances have been made in the production facilities and processes that are now available for radionuclide production

allowing for the development of improved radionuclides which can allow choosing the right radionuclide with the appropriate nuclear properties to be attached to a given vector. This presentation will highlight the development and evaluation of novel radionuclides for theranostics.

NUCL 60

Award Address (Glenn T. Seaborg Award for Nuclear Chemistry sponsored by the ACS Division of Nuclear Chemistry and Technology). What it was like to hit upon the “theragnostics” paradigm: “A personal journey” at BNL

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A number of new modalities involving radiopharmaceutical therapies have given great impetus for research on therapeutic radionuclides tailored for specific applications. Certain of these dual-purpose *(“"theragnostic”)* radionuclides are showing the exciting potential of pre-therapy low-dose imaging, followed by higher-dose treatment in the same patient, thus possibly bringing us a major step closer to *personalized medicine.* This presentation will re-introduce and re-inforce this relatively novel paradigm, conceived, developed, and promoted at Brookhaven National Laboratory (BNL). This involves use of theragnostic radionuclides, which have imaging photon emissions suitable for necessary pre-clinical information, and therapeutic electron emissions for targeted therapy, in the same patient. Beginning since the mid-1980’s, our work with Sn-117m convinced us that it is arguably one of the most promising theragnostic radionuclides with unique nuclear, physical, and chemical properties. Results with this radionuclide will therefore be covered in greater detail. In contrast to most therapeutic alpha/beta emitters, Sn-117m (t½, 14.0 days; γ 159 keV, 86%) decays via isomeric transition, with the emission of mono-energetic conversion electrons. These emissions have a very high LET for therapeutic effectiveness. Also, with the 159 keV γ-photon emission, Sn-117m is perfect for pre-therapy SPECT imaging. When selectively targeted, various Sn-117m radiopharmaceuticals are beginning to show great promise for imaging plus therapy for a number of inflammatory conditions, including cancer, atherosclerotic disease, and other disorders, causing much reduced myelosuppression and greatly reduced dose to normal organs.

NUCL 61

Chelator-free radiolabeling of nanoparticles

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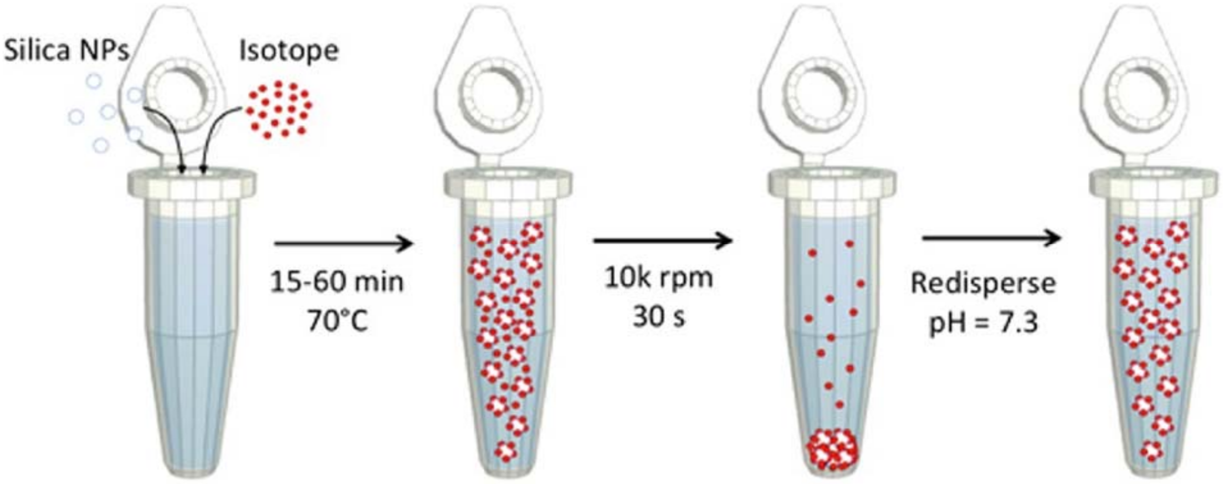
Chelator-free nanoparticles for intrinsic radiolabeling can be used for whole-body imaging and therapeutic applications. Several reports have demonstrated the principle of intrinsic radiolabeling. However, the work done to date has suffered from much of the same specificity issues as conventional molecular chelators, insofar as there is no singular nanoparticle substrate that has proven effective in binding a library of radiosotopes. We demonstrate that amorphous silica nanoparticles serve as general substrates for chelator-free radiolabeling and demonstrate their ability to bind six medically relevant isotopes of various oxidation states with high radiochemical yield. The stability of the binding to the silica correlates well with the hardness of the radioisotope, which validates our postulate that oxophylic radiometal ions bind to the oxygens on the surface. Thus hard, oxophilic ions, such as the positron emitters zirconium-89 and gallium-68, are remarkably estable in vivo stability. Though chelating agents are commonly used to radiolabel biomolecules, nanoparticles offer the advantage of attaching a radiometal directly to the nanoparticle itself without the need of such agents. However, softer radiometals, such as the widely employed copper-64, do not stably bind to the silica matrix and quickly dissociate under physiological conditions. This limitation is overcome via the use of silica nanoparticles functionalized with a soft electron-donating thiol group to allow stable attachment of copper-64. This approach significantly improves the stability of copper-64 labeled thiolfunctionalized silica nanoparticles relative to native silica nanoparticles, thereby enabling in vivo PET imaging, and may be translated to other softer radiometals with affinity for sulfur. The presented approach expands the application of silica nanoparticles as a platform for facile radiolabeling with both hard and soft radiometal ions.



NUCL 62

EDTA-inspired chelating poly-hydroxamate ligands for lanthanide and actinide coordination chemistry and applications

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Despite the paramount historical importance of chelating polyhydroxamate ligands in coordination chemistry, such as the iron-binding ferrichrome siderophores, development of chelating polyhydroxamate ligands for f-element coordination chemistry has greatly lagged behind that of the d-elements. Hydroxamates such as benzohydroxamates and natural siderophores have played key critical roles in illuminating the coordination and environmental chemistry of the actinides, respectively. Furthermore, complex ligand topologies, primarily for the lanthanides, have employed hydroxamates (often in the form of hydroxypyridinones) for applications as potential MRI contrast agents, lanthanide luminescent agents, and radiopharmaceuticals. We hereby report the synthesis of EDTA-inspired decadentate polyhydroxamate ligands with variable arm lengths, as well as insights into their coordination of lanthanides and the early actinides.

NUCL 63

Is ^{210}Po a good indicator for anthropogenic radioactivity?

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Anthropogenic radioactivity generated by nuclear or chemical events results in the liberation of a quadrillion of Becquerel and tons of materials to the environment. These events include nuclear accidents, nuclear weapon experiments, and high levels of generated radioactive and chemical wastes. ^{210}Po is a high-energy alpha emitter that presents in the environment at extremely low concentration. It is considered as one of the highly toxic elements and is estimated to contribute about 7% of the total effective dose equivalent to human from ingested natural internal radiation. The assessment of ^{210}Po in nature could be used as an indicator of anthropogenic radioactivity. The ^{210}Po concentration activity present in the most frequently sold cigarette produced in Lebanon was assayed employing alpha spectrometry after a radiochemical separation and spontaneous deposition of Po on a copper disk. Although the geographical nature of Lebanese land is an extension of the Syrian territory, the polonium activity concentration obtained is 8.8 times higher attributed to the use of phosphate fertilizers in agriculture. The individual committed effective dose was estimated to be equal to 219 ± 17 μSv/year of cigarette smoking.

NUCL 64

Luminescent determination of aqueous complexation and extractant kinetics for lanthanide ions

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To completely understand the chemistry of metal-loaded ligand species used in the extraction and separation of lanthanides and actinides from used nuclear fuel requires that the complexation kinetics of the different ligands with metals be quantitatively evaluated. In this study, the absolute complexation kinetics of the europium ion by the aminopolycarboxylic acid DTPA (diethylenetriaminepentaacetic acid) were directly measured using the change in luminescence for europium. Data have also been obtained for other lanthanide ions through competitive complexation, with exchange rates for these different metal ions elucidated. Applying the same luminescence-based technique in the organic phase has also allowed for the bulk phase rate constants of the complexation kinetics for the organic extractants CMPO and TODGA for europium and terbium. This approach aims to fully understand the

kinetics occurring within the solvent extraction based metal separation method for lanthanide/actinide separations by applying the established rate constants for the individual phases together with extraction experiments to better determine the interfacial kinetic properties, thereby allowing the complete modelling of extraction systems.

NUCL 65

Application of inelastic neutron scattering for uranium oxyfluorides

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Neutron spectroscopy and diffraction offers a unique tool for investigating uranium compounds. In particular, we have been interested in phase transitions in uranyl fluoride hydrate ($UO_2F_2 + x(H_2O)$), whose combination of high and low Z elements pose challenges for traditional analysis techniques such as X-ray diffraction or electron microscopy. Here, we present inelastic neutron scattering (INS) measurements collected at the Spallation Neutron Source at Oak Ridge National Laboratory of $UO_2F_2 + x(H_2O)$, and demonstrate both the qualitative and quantitative utility of this technique. With neutrons' exceptional sensitivity to hydrogen, we show that specific water librational bands can be assigned based on isotopic substitution, and identify two populations of exchangeable and non-exchangeable waters. In the low-energy regime, we use quasielastic neutron scattering to demonstrate and model the diffusive motion of these two populations of water. Quasielastic neutron scattering data suggest that one type of water motion is strictly localized, executing a slow rotational diffusion about the O-H bond, whereas the other type of water demonstrates a degree of translational freedom.

NUCL 66

Structural analysis, complexation, and binding selectivity of lanthanides and actinides: A theoretical investigation

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Knowledge-based design of selective agents for binding to lanthanides and actinides is essential to optimize separations, stock-pile stewardship, environmental remediation, nuclear fuel disposal, and extraction of fission products, amongst others. In particular, design of efficient ligands for separations of rare earth elements is critical to accelerate separation processes for nuclear forensics, and to guarantee availability of critical materials.

Predicted structural properties, electron withdrawing effects, and Gibbs free energies of reaction of lanthanide-, and actinide-containing compounds will be discussed, with focus on cyclic imide dioximes, carboxylic acids, and beta diketones.

NUCL 67

Studies of flerovium homologs with thiacrown ethers

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Recent studies of the chemical behavior of copernicium (Cn, element 112) and flerovium (Fl, element 114) together with the discovery of isotopes of these elements with half-lives suitable for chemical studies have spurred a renewed interest in the development of rapid systems designed to study the chemical properties of elements with $Z \geq 114$. Due to the short half-lives of the transactinide elements, fast and efficient separations are necessary to evaluate their properties, such as ionic radii and chemical speciation, by comparing to their lighter homologs. Separations based on macrocyclic extractants show promise for achieving short separation times, large extraction yields, and high separation factors required for transactinide studies.

In this study the potential of different macrocyclic extractants for suitability to a Fl chemical system has been investigated. Previous studies showed the promise of crown ethers for the extraction of Fl homologs (Pb, Sn and Hg);

however, the kinetics of the extractions were very slow. Thiacrown ethers, which replace the oxygen atoms with sulfur, act as softer Lewis bases compared to traditional crown ethers. Initial studies using the sulfur analog of 18-crown-6, hexathia-18-crown-6 showed vastly increased kinetics in comparison to the traditional crown ether, though only extracted Hg. The extraction of Pb with 18-crown-6 is believed to be based solely on the cavity. With a simple thiacrown the negative charge density is oriented to the outside of the ring, and therefore, this cavity stabilization of a Pb complex does not form. In this study a novel thiacrown ether, dibenzohexathia-18-crown-6 was synthesized and characterized for its affinity toward Hg, Pb and Sn. The benzene substituents will force orientation of at least four sulfur atoms such that a negatively charged cavity (analogous to the typical crown ether) is formed.
Liquid-liquid extraction studies were performed with the homologs and pseudo-homologs of Fl using dibenzohexathia-18-crown-6 in benzene. Kinetics of these extractions were also investigated.

NUCL 68

Transport properties of binary and ternary asymmetric warm dense plasma mixtures modeled by orbital-free DFT molecular dynamics

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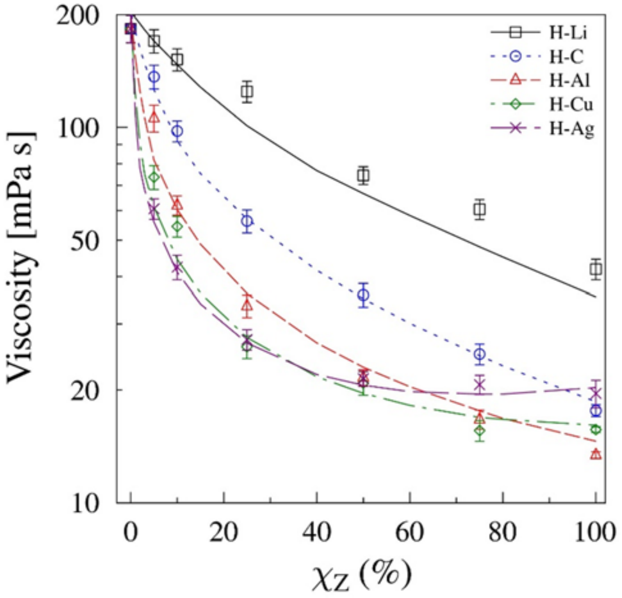
We calculate concentration dependent transport properties of assymetric warm dense plasma mixtures at pressure-temperature equilibrium. Orbital-free density functional theory based molecular dynamics (OFMD) simulations are used to accurately determine these transport properties from first principles. We compare our results to a more approximate pseudo-ion in jellium model. Results demonstrate that small concentrations of heavy elements have a drastic effect on light element transport. Crossover behavior from kinetic to correlated regimes is also shown. Hydrogen over-correlation, due to the heavy element, translates into a strong enhancement of nuclear reactions which is evidenced by the calculation of the H factor using the Widom expansion. Additionally, results from simulations of ternary mixtures will be presented.



NUCL 69

Ab initio study of the mechanisms and energetics of chlorination on Zr(0001)

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The United States produces a large amount of cladding material from used nuclear fuel, which could approach 1,000 MT/year in the next 50 years. In nuclear fuel recycling, spent nuclear fuel assemblies are disassembled and the cladding hulls are separated from the U oxide spent fuel. Zr can be recovered from Zr cladding using the chlorination method. Zirconium alloys, including Zircaloy-4, Zircaloy-2 and Zr-Nb alloys are the most common fuel cladding materials in nuclear light water reactors due to their favorable mechanical properties, corrosion resistance, low thermal-neutron capture cross section and criticality. However, the presence of impurities in the recovered $ZrCl_4$ was reported, including Sn, Cr and Fe. Thus, further efforts are necessary to improve the purification process significantly. As part of an effort to gain fundamental understanding of chlorination processes occurring in fuel cladding materials, we have investigated the adsorption of atomic and gaseous chlorine on Zr (0001) surface, using density functional theory (DFT).

Our finding shows that chlorination of Zr(0001) is exothermic for dissociative adsorption of a single chlorine molecule, and that further chlorination to 1 ML can also occur exothermically under Cl-rich conditions. Dissolution of Zr compounds has been investigated in this study including three possible exfoliation processes. It is found that exfoliation of the top Cl−Zr−Cl sandwich layers is among the most energetically favorable degradation pathways leading to Zr(0001) surface dissolution. Further investigation to understand how the formation of $ZrCl_4$ occurs experimentally is ongoing.

NUCL 70

Effect of North Korea’s nuclear test in September 2017 for air radiation dose rates inside cabin flights from Singapore to Narita, Japan

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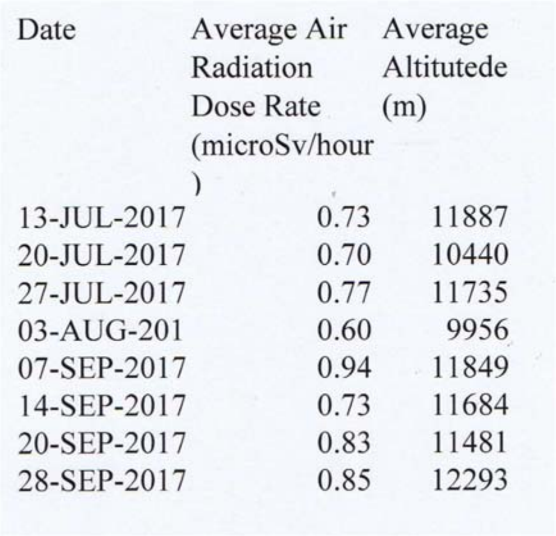
The results of the observations of average air radiation dose rates inside cabin on scheduled passengers flights All Nippon Airways (ANA) NH804 (Operated by Boeing 787) from Singapore to Narita (Suburbs of Tokyo), Japan in July, August and September 2017 are as follows. The average altitude of observations is 11415 m. North Korea conducted its sixth nuclear test on 03-SEP-017 and after the test average air radiation dose rates are higher than before the test.



Date	Average Air Radiation Dose Rate (microSv/hour)	Average Altitutede (m)
13-JUL-2017	0.73	11887
20-JUL-2017	0.70	10440
27-JUL-2017	0.77	11735
03-AUG-201	0.60	9956
07-SEP-2017	0.94	11849
14-SEP-2017	0.73	11684
20-SEP-2017	0.83	11481
28-SEP-2017	0.85	12293

NUCL 71

Development of a microinjection system form high efficiency addition of dopants to the inner surface of National Ignition Facility capsules: ANDARIST

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To perform measurements of nuclear cross sections using National Ignition Facility (NIF) DT capsules, a new method of adding dopant materials to the capsule has been developed, called ANDARIST (Apparatus for NIF Doping Automated Robotic Injection System for Targets) Previous attempts to sputter materials into the capsule ablator shell resulted in large outer surface deformations, poor capsule performance, and was limited to nuclides with very long half-lives. To consider using shorter-lived nuclides, such as ^{88}Y, dopant materials must be added to a NIF capsule after production by injecting material through the fill tube hole.
A microinjection system has been developed. High precision robotics, digital microscopy and In Vitro Fertilization (IVF) manipulation and injection technologies are used to lower a < 1 μm microinjection capillary through both the 10 μm fill hole and its smaller 5 μm counter bore. Once the needle is on the inner surface of the capsule a microinjector is used to add the dopant materials into the capsule. The capsule is then spun under low heat to evaporate solvent leaving behind a thin layer ($10^{13\sim16}$ atoms) of dopant material on the inner surface.

NUCL 72

Technetium incorporation in scheelite: Insights from first-principles

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Atomistic investigations of crystalline scheelite, CaWO4, and 99Tc-bearing scheelite, CaWO4:Tc, have been carried out using density functional theory.

The lattice constants, bulk modulus, and volume compression data of CaWO4 have been calculated and compared with experimental data, with a focus on predictive understanding of 99Tc incorporation in CaWO4. Defect formation energies have been computed for several possible interstitial (I) and substitutional (S) sites of 99Tc in CaWO4. Both I(Oh) and S(W) sites were found to be energetically favourable for Tc doping. X-ray diffraction (XRD) spectra for each 99Tc defect type have been simulated to help interpret the complex experimental XRD patterns. This work on CaWO4:Tc provides insights into materials generated during nuclear weapons testing and useful spectral signatures for nuclear forensics.

NUCL 73

Predicting vibrational spectra of uranyl hydrates

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Actinide hydrates are incredibly complex systems to deal with computationally because of the presence of f-electrons, van der Waals interactions, and dynamic water. Density functional perturbation theory has been used successfully in the past to predict vibrational properties of static actinide solids with high symmetry. However, this method is less effective for more dynamic systems, such as hydrates with hydrogen-bonded water molecules that can rotate or translate through layers or pores. These mobile water molecules can affect various vibrational modes, especially in cases of strong hydrogen-bonding.

For these complex hydrates, vibrational spectra can instead be predicted using Born-Oppenheimer ab initio molecular dynamic simulations. The system is evolved in time by performing a DFT calculation at each time step and then updating the atom positions based on the calculated forces. Once a trajectory has been calculated, the power spectrum showing all vibrational frequencies is obtained by the fast Fourier transform of the velocity autocorrelation function. Infrared and Raman spectra can then also be calculated by transforming the calculated electron density at each step from diffuse Bloch orbitals to maximally localized Wannier functions. The center position and spread of these localized functions can be used to track changes in the dipole moment and polarizability, allowing the infrared and Raman spectra to be obtained from the relevant autocorrelation functions.

The utility of this methodology for complex systems has been demonstrated by predicting infrared and Raman spectra of multiple uranyl crystal hydrates of relevance to the uranium fuel cycle. Computational prediction of these spectra complements experimental work by informing band assignments and modeling how spectra may be expected to change various structural perturbations.

NUCL 74

Coupled cluster studies of intermolecular interactions involving actinide dioxide cations: Cation-cation interactions (CCIs) and complexes with small molecules (CO and N_2)

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Actinyl cations are particularly important in actinide chemistry, e.g., the actinyl(V) cations NpO_2^+, PuO_2^+, and AmO_2^+ in aqueous media, as well as of course the U(VI) uranyl cation, UO_2^{2+}. Gas phase actinide dioxide cations, AnO_2^+, have also been previously observed experimentally for An = Pa – Cm. The present work reports coupled cluster studies of two distinctly different intermolecular interactions involving actinide dioxide molecules and cations - (a) cation-cation complexes involving two actinyls with An=U – Cm and (b) the interaction of UO_2^{q+} and NpO_2^{q+} with either CO or N_2. In each case new all-electron correlation consistent basis sets are used with the DKH3 scalar relativistic Hamiltonian at the CCSD(T) level of theory. Spin-orbit coupling is included at the 4-component Dirac-Hartree-Fock level.

In actinyl CCI complexes the oxo-oxygen on one actinyl is weakly bonded to the central An of the other. The overall stability is the result of a competition between charge transfer stabilization and Coulombic repulsion, which is more subtle than the previously accepted Lewis acid-base explanation. All CCIs in the gas phase are characterized by strong coulombic repulsions upon approach of the two monomer cations, but in many cases a kinetically stable CCI results, with calculated local minima having well depths as large as ~15 kcal/mol, which is accompanied by an overall ~0.6e (NPA) charge transfer. The present gas phase results agree qualitatively with the CCI stabilities observed experimentally in condensed phases.

Small molecule bonding and activation with actinides have been previously studied by experiment in the gas phase. In particular, actinide-containing molecules/cations have been shown to form thermodynamically stable bonds with small molecules and sometimes even activate them. In the present work

$UO_2^{0/1+/2+}$ and $NpO_2^{0/1+/2+/3+}$ were chosen to interact with CO and N_2. Accurate structures and bonding enthalpies will be reported with stabilities ranging from ~15 to 40 kcal/mol. C-O and N-N bond lengths in the complexes are lengthened relative to the separated molecules by up to ~0.06 Å, which can be regarded as a weak activation.

NUCL 75

Properties and covalency of high oxidation state AnF_x complexes

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There is intense interest in compounds with metals in formal high oxidation states, for example the properties of actinide fluorides for molten salt reactors. Computational chemistry electronic structure approaches are being used to predict the structures and the vibrational frequencies of neutral, anionic, and cationic actinide fluorides AnF_x where An = Th - Cf to determine the maximum formal oxidation state of the actinide. The different oxidation states of these actinide fluorides together with varying spin states of each complex were studied using DFT (density functional theory) with the B3LYP exchange-correlation functional. The TZVP basis set was used for F and the Stuttgart basis sets with effective core potentials were used for the actinides. A NBO and electron configuration analysis was performed on each of the complexes. Various energetics were calculated for each complex including the electron affinity, ionization energy, bond dissociation energy, fluoride affinity, and fluorocation affinity to provide information on redox properties and Lewis acidities. The energetics were plotted as a function of increasing Z as well as a function of oxidation state to provide insight into the covalency of the actinide fluorides.

NUCL 76

Active thermochemical tables: A novel approach to understanding actinide chemistry

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Accurate knowledge of thermodynamic properties is essential to the understanding of a chemical process across a wide range of applications. The Active Thermochemical Tables (ATcT) provide a unique approach to the determination of these quantities more accurately and reliably than other methods. As opposed to traditional approaches that sequentially evolve the thermochemistry, ATcT is based on constructing a thermochemical network (TN), statistically adjusting it to self-consistency using a "worst offender" approach, and then solving simultaneously for all species. In instances where an experimental determination proves to be insufficient or inconclusive, ATcT has the capability of improving the accuracy and reliability of the available data both by augmenting a result with high accuracy theory and by comparing all current experimental determinations, thus finding a possible consensus among published results. ATcT currently includes ~1600 chemical species comprised primarily of main group species related to combustion. The present work begins to extend ATcT to include actinide-containing molecules. Numerous actinide molecules are well understood, such as those used in the nuclear fuel cycle, but there is a dearth of accurate thermochemistry for most actinide species, especially those involving transuranium elements. A crucial ingredient limiting the accuracy of available thermochemistry is the derivation of partition functions. The accurate determination of low-lying electronic states is particularly important for actinide containing molecules due to their abundance. A controversy currently exists over the partition functions of $UO_{(g)}$, $UO_{2(g)}$, and $UO_{3(g)}$, stemming from the assignment of low lying excited electronic states. Through the use of ATcT, and by utilizing high accuracy quantum calculations with the FPD composite thermochemistry approach, the correct partition functions and resulting thermodynamic constants have been determined. This provides an integral link between gas phase theory/experiment and condensed phase experimental results.

NUCL 77

Continued advancements in the radiochemistry program at the University of Iowa

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Advancing research and developing technical expertise in radiochemistry is a matter of profound importance given the aging radiochemistry workforce and current needs in the area of national security, nuclear waste management, environmental monitoring, and medicine. The University of Iowa is making a concerted effort to invest in radiochemistry research and education, resulting in the formation of a rapidly growing undergraduate and graduate training program in this area. This poster will highlight faculty research, achievement of our undergraduate and graduate students, and current curriculum development in the areas of radiochemistry and actinide chemistry at the University of Iowa. In addition, I will discuss future efforts to expand our current offering and research capabilities to build a sustainable and nationally renowned program in radiochemistry and radiation sciences at the University of Iowa.

NUCL 78

New ligands for the selective binding and extraction of light lanthanides

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The focus of this work is the design and testing of a new generation of polydentate ligands for the selective extraction of trivalent lanthanides from hydrochloric and nitric acid. This work exploits the differences in ionic radii across the series to selectively extract light lanthanides and studies the effects of counter-ions on extraction strength and efficiency.

NUCL 79

Iodine saturated absorption spectrometer for laser frequency calibration

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Saturated absorption spectroscopy was used to measure well-known hyperfine spectra of molecular iodine, providing frequency calibration of a narrow-linewidth continuous-wave dye laser. This dye laser system is used as probe laser used for laser spectroscopy for nuclear structure studies at the BEam COoling and LAser spectroscopy (BECOLA) facility at the National Superconducting Cyclotron Laboratory at Michigan State University. An iodine-vapor cell was used as a sample, and pump and probe laser beams were split from a common laser beam using polarization optics. The two beams were counter-propagated in the cell. The pump beam was modulated with an optical chopper, and a lock-in amplifier was used to demodulate the

probe-laser-light signal at the chopping frequency to eliminate Doppler-broadened background. Complete hyperfine spectra were observed for a variety of rotational, vibrational, and electronic transitions around 600 nm. Characterization of systematic error as well as improving resolution of the hyperfine spectra are ongoing. This newly-built system will be used to calibrate and stabilize lasers used for continuous wave lasers used for collinear laser spectroscopy of rare isotopes at the BECOLA facility at NSCL and later at the Facility for Rare Isotope Beams.

NUCL 80

Actinide science at the University of Notre Dame

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The actinide science program at the University of Notre Dame is an informal, graduate-only academic program within the Department of Civil & Environmental Engineering & Earth Sciences (CEEES). The program focuses on several aspects of the nuclear fuel cycle including mineralogy, environmental chemistry, nuclear waste disposal, materials science, and nuclear forensics. This poster will highlight the University's analytical research facilities, major funded research projects, and the benefits of being a graduate student or postdoctoral scholar within the actinide science program.

NUCL 81

Synthesis and optical/scintillating properties of transparent ceramics

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One main component of radioactivity detectors is a scintillation material. In photometric analysis, accurate resolution of incident wavelengths is vital to the integrity of the process and results. However, especially at high energy where photons tend to have high penetration values, the sensitivity and resolving power is severely limited. In order to detect at these high-energy frequencies, detectors utilize scintillator materials to absorb high energy photons and emit a larger number of lower energy photons to which the detector is more

sensitive. Apart from large and inflexible single crystals which are notoriously finicky and expensive to produce with limited resolution, new-generation scintillators can be made of nanocomposites and ceramics. However, traditional methods for composite synthesis yield large aggregates and inhomogeneities, while retaining a high polymer fraction, rendering them unsuitable for device manufacture. Solving this problem is an active area of research. A promising method for this includes the creation of transparent ceramics from nanoparticles. In this study, we are synthesizing scintillating nanocrystals, which will be formed into free standing transparent ceramic pellets by sintering after cold press for use as a scintillator. The lanthanum zirconate nanoparticles are synthesized via ammonium co-precipitation or an alternative urea co-precipitation method both of which lead to the same precipitate precursor. The precursor is then calcinated via a facile molten salt method, then pressed into a pellet, and finally undergo sintering to achieve transparency. The optical and scintillating properties of these nanoparticles and ceramics will be tested and proven to be beneficial in detecting radiation.

NUCL 82

Determination of radioactive krypton (Kr-85) in air

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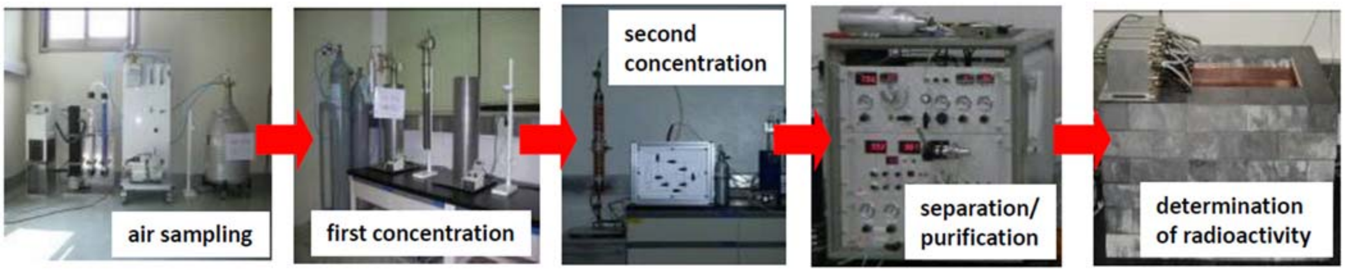
Kr-85 is the radioactive noble gas which is a beta emitter with a half-life of 10.76 years. Kr-85 is produced by three major pathways of nuclear reaction by cosmic radiation in the upper atmosphere, spontaneous fission of heavy elements in the Earth's crust and anthropogenic activities such as nuclear weapons tests, nuclear-fuel reprocessing plants and nuclear reactors. Recently, the major source of atmospheric Kr-85 is the release from the nuclear fuel reprocessing plants. The determination of Kr-85 in air is carried out owing to two major purposes of the environmental radioactivity monitoring and the detection of nuclear activities of neighboring countries. Our method based on a Germany BfS-IAR system was used for the determination of Kr-85 in air in this study. The analysis system consists of steps of air sampling, first concentration, second concentration, separation/purification and determination of radioactivity. The obtained activity concentration of Kr-85 is ca. 1.53 Bq/m^3 at the west of South Korea. To determine the low concentration of Kr-85 rapidly, the adsorption and desorption system is very important. In this presentation, we will review and compare various

adsorbents for the efficient adsorption/desorption of Kr-85. In addition, we will talk about the automation of the Kr-85 analysis system which is our present work. The method for the determination of Kr-85 has not matured yet. It needs more advanced techniques. We expect our presentation will be a stepping stone to develop the automated analysis system for Kr-85 in air.



NUCL 83

Determination of radioactivity of uranium and thorium in environmental samples by using fusion and sequential separation method, and its evaluation using key validation parameters

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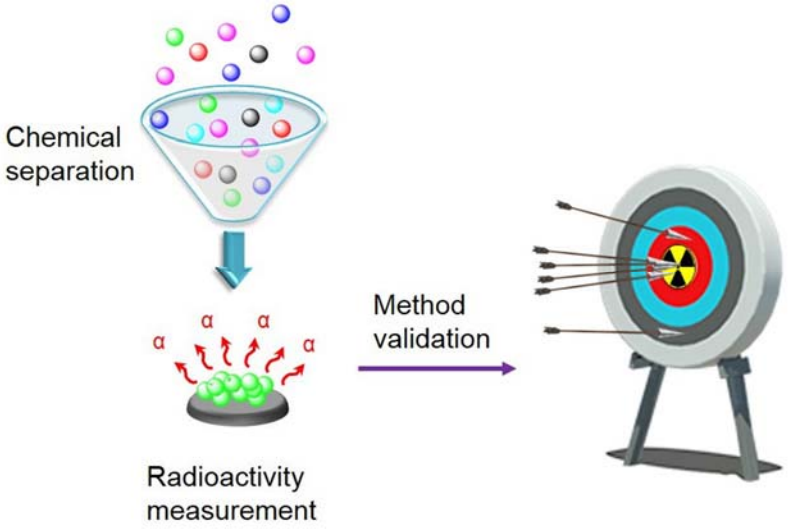
Monitoring of radioactivity of nuclides in soil is important to reduce hazardous effects to the human health by the uptake and accumulation of the radionuclides because water-soluble radionuclides compounds in the soil migrate into vegetables, which are eaten almost every day, by complex process such as leaching, capillary rise, runoff, sorption, root uptake, and re-suspension. Generally, the radioactivity concentration in environmental samples is low, and many samples should be analyzed for the monitoring of radionuclides in the environment. Therefore, the development of a rapid and precise method for the determination of radioactivity in environmental samples is very important. The fusion method is a very effective way for a rapid and complete sample dissolution, and the sequential separation method helps speed up separation times for the separation of two or more nuclides in samples. In this study, the fusion technique was used to dissolve a soil sample completely, and uranium and thorium were separated by the sequential method. The separated uranium and thorium were analyzed using alpha-particle spectrometry. The developed method was evaluated by assessing the key validation parameters, and demonstrated a satisfactory quality level of the selected criteria of the performance. The developed method is expected to apply to the measurement of the low-level activity concentration of radionuclides in various solid samples with a high level of accuracy.



NUCL 84

Investigating the impact of gamma radiation on rare-earth hafnate nanocrystals

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Improved methods for nuclear waste disposal are crucial for the long term storage and safety of high level radioactive waste (HLW) products. To withstand the harsh effects of gamma irradiation, a material must be able to accommodate numerous radiation damage effects. A proposed method to treating that waste is to encapsulate it in a matrix made of complex oxide materials, such as pyrochlores with a general forumula of $A_2B_2O_7$. The rare-earth hafnate pyrochlores have the potential to advance the current methods of HLW disposal due to their robust chemical stability in radioactive environments, their high thermal stability, and their natural structural compatibility with radionuclide species. In this study, based on a combined co-precipitation and molten-salt synthesis method: nanoparticles of yttrium,

lanthanum, praseodymium, gadolinium, erbium and lutetium hafnates were synthesized at 650°C. Of the compositions irradiated with different doses of γ-rays, yttrium, praseodymium, gadolinium and erbium hafnates proved to be the most chemically stable samples, maintaing their initial crystal structure throughout the irradiation process even to the highest expsoure, i.e. 12800 Gy. While further investigation is still undergoing, e.g. on the particle size effects, these rare-earth hafnate nanocrystals have shown the potential to advance the current methods of HLW disposal due to their robust chemical stability in radioactive environments, their high thermal stability, and their natural structural compatibility with radionuclide species.

NUCL 85

Radiochemistry at Colorado State University

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Radiochemistry has a long tradition at Colorado State University going back to the first classes in radiochemistry and radiation chemistry taught in 1964. In 2002, Radiochemistry was established by Dr. Ibrahim as its own formal specialty within the Radiation Protection and Measurements Section in the Department of Environmental & Radiological Health Sciences. In the past CSU's radiochemistry faculty and students have participated in a variety of research efforts, such as the monitoring of fallout from nuclear weapons testing in soil, water, plants and animals and the radiochemical analysis of mill tailings and effluents associated with uranium mining. One of the largest and most interesting radiochemistry projects initiated by CSU was the determination of off-site plutonium concentrations in soils from the Rocky Flats site.

Current radiochemistry research efforts focus on environmental monitoring, nuclear forensics, emergency response as well as the nuclear fuel cycle. In addition, faculty and students from CSU have been collaborating very closely with scientists from the Institute for Environmental Radioactivity at Fukushima University to study the environmental impact of the Fukushima nuclear accident.

This presentation will provide an overview of the Radiochemistry Program at Colorado State University and its laboratory facilities. It will also give examples of current research areas.

NUCL 86

Eliminating basis-set incompleteness error in relativistic chemical computations

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MADNESS (Multiresolution Adaptive Numerical Environment for Scientific Simulation) is a general purpose numerical framework for fast computation with guaranteed precision in many dimensions. Initially motivated by applications in chemistry (molecular electronic structure) it has been successfully applied in nuclear physics, molecular and atomic physics, and other fields. We review the basic elements of this computational approach and contrast it with the mainstream approach that employs atom-centered Gaussian basis sets. The errors and computational costs are also compared and, for the non-relativistic models initially tested, MADNESS proves both faster and more accurate. Finally, we discuss the initial application of this approach to both quasi-relativistic (Douglass-Kroll) and relativisitic (Dirac-Fock-Coulomb) approaches for which it provides the first fully-numerical results for general polyatomic systems.

NUCL 87

Characterization of Es, Fm, Cf separations: A comparison of experimental and computational efforts

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The separation of Cf, Es, and Fm is important to the field of nuclear science as Cf is used in reactors as a start-up method, examination of welds in high tolerance sitations, and in other areas. This project involved performing two separate experiments. The first experiment involved understanding the capability of performing large stand-off measurements with high purity germanium (HPGe) gamma-ray measurements in an effort to understand methods by which diversion could be detected. This work was performed using a GeGi detector to determine if the Es and Fm streams could be

observed while being diverted from the separations column. The second information set that was observed was understanding the ability of these elements to be separated using alpha-hydroxybutyric acid. This separation data was compared to computational methods of the same experiment and results will be discussed.

NUCL 88

Composite *ab initio* thermochemistry for f-block elements: Is kcal/mol accuracy achievable?

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Using accurate composite ab initio thermochemistry approaches such as the Feller-Peterson-Dixon (FPD) methodology, kcal/mol or even kJ/mol accuracy in thermochemical properties can be readily achieved for molecules composed of elements from the first few rows of the periodic table when coupled cluster approaches are reliable. This is made possible by the use of systematically convergent, correlation consistent basis sets and the systematic recovery of all major contributions to the property of interest, e.g., valence and outer-core electron correlation, relativistic effects, diagonal Born-Oppenheimer corrections, etc. In this work, extension of the FPD approach to the f-block elements is presented, including the development of new all-electron correlation consistent basis sets for the lanthanide and actinide elements. Applications involving various actinide halides and oxides will be presented using the CCSD(T) method with either the DKH3 or X2C scalar relativistic Hamiltonians. After extrapolation to the complete basis set (CBS) limit with inclusion of outer-core correlation (5s5p5d electrons of the actinide elements), spin-orbit coupling, Lamb shift, and a correction involving non-HF orbitals, accuracies within 3 kcal/mol are obtained for properties such as bond enthalpies, ionization potentials, and heats of formation. Results in the 1 kcal/mol range were obtained in the few cases where electron correlation beyond CCSD(T) were possible. In addition to the usual importance of accurately recovering electron correlation effects, the calculation of spin-orbit coupling is one of the most challenging aspects. A major limitation in the assessment of this approach is the lack of sufficiently accurate experimental results for comparison.

NUCL 89

Relativistic *ab initio* accurate minimal basis sets for the lanthanides

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Valence virtual orbitals (VVOs) are a quantitative and basis set independent method for extracting chemically meaningful lowest unoccupied molecular orbitals (LUMOs). The VVOs are formed based on a singular value decomposition (SVD) with respect to pre-computed and internally stored *ab initio* accurate minimal basis sets (AAMBS) for the atoms. The occupied molecular orbitals and VVOs together form a minimal basis set that can be transformed into orthogonal oriented quasi-atomic orbitals (OQUAOs) that provide a quantitative description of the bonding in a molecular environment. In the present work, full valence relativistic AAMBS are developed for the lanthanides. The bonding characteristics of lanthanides in molecular environments are then characterized based on the OQUAOs to quantify the roles of the 4*f*, 5*d*, and 6*s* orbitals.

NUCL 90

Combining minimal basis set localizations with strong correlation approaches towards *ab initio* lanthanide chemistry

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Lanthanides present a great challenge to quantum chemistry. Often, reasonably accurate energies are achieved through a variety of approximations, but accurate *ab initio* energies remain out of reach. Difficulties stem largely from 1) the lack of well-defined minimal basis set type initial guess orbitals and 2) the fact that many Lanthanide containing compounds not only typically have an open shell reference but also require a strong correlation approach. In recent work *(J. Phys. Chem. A.* **2017***, 121,* 3588*)*, quantitative localized orbitals that span a full-valence orbital space have become available for transition metals at a reduced computational cost

through calculations of inexpensive orbital overlaps. This work has now been extended to Lanthanides. Furthermore, various methods have been developed to treat strong correlation at reduced computational cost (e.g. the density matrix renormalized group approach). In this work, alternative solutions to the strong correlation method that augment existing approaches are considered. This alternative approach stems from the use of split-localized orbitals in a statistical manner.

NUCL 91

Understanding structural and thermochemical properties of actinide-containing compounds

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Computational methodologies including *ab initio* methods with relativistic Hamiltonians, as well as Density Functional Theory (DFT) are utilized to predict thermochemical and structural properties of actinide-containing compounds. These properties are crucial to understand binding preferences and separations of actinides. Systematic evaluations of the performance of computational methods are essential to enhance predictive capabilities to better understand the behavior of the actinide elements. Gibbs free energies of reaction, dissociation energies of actinide halides calculated at various levels of theory will be presented.

NUCL 92

Ab initio thermochemistry of transuranium molecules: Halides of U, Np, and Pu

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The chemistry of actinides plays an important role in the nuclear fuel cycle. Limited experimental data exists, however, for transuranium molecules arising from the difficulty in production and safe handling of these species. This is particularly true for those in the gas phase. For instance, the only gaseous actinide molecule with an experimental heat of formation with an uncertainty within 1 kcal/mol is UF_6. Accurate gas phase thermochemistry, however, can be essential to understanding the stability of actinide species in more complex environments. High level quantum chemical calculations are now capable of

filling these gaps, but like all actinides, transuranium species can be very challenging to investigate with ab initio methods due to the large number of electrons, strong relativistic effects, and partially filled 6d and 5f shells, leading to a large range of available oxidation states.
In the present work, the Feller-Peterson-Dixon composite approach is employed to calculate the atomization energies, heats of formation, and bond dissociation energies for a series of actinide (An) halides, AnX_m (X=F, Cl, Br, m=4-6), with An=U, Np, and Pu. The largest component to the total energies is from a complete basis set (CBS) extrapolation using recently developed eXact 2-component (X2C) relativistic correlation consistent basis sets (cc-pV*n*Z-X2C) for U, Np, and Pu at the CCSD(T) level of theory. Corrections are then included for contributions from correlation effects from the outer-core (5s, 5p, 5d) electrons, the Lamb shift, zero-point vibrational effects, and spin-orbit coupling. Scalar relativistic effects are included from the onset by utilizing the X2C Hamiltonian. Spin-orbit calculations used the full 4-component(4c) Dirac-Coulomb-Gaunt Hamiltonian.

NUCL 93

Understanding the electronic structure and chemical bonding of f-element coordination compounds

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Electronic structure and metal-ligand bonding interactions of actinide and lanthanide complexes are of fundamental importance in actinide chemistry and actinide materials related to nuclear fuels, waste management, and environmental problems in dealing with contaminated sites and cleanup. However, due to the inherit relativistic and electron correlation effects and complicated multireference character of electronic states involving valence f, d and s orbitals, the understanding of electronic structure and chemical bonding of f-element compounds are rather difficult to decipher. Great progress has been in the recent years by joining together the theoretical and experimental efforts. In this talk, we will report how theoretical work has helped us in better understanding the electronic structure and metal-ligand bonding interaction of f-element coordination compounds and resulting in good agreement with experimental vibrational and optical spectroscopic measurements. The employed computational methods include both density functional theory and post Hartree-Fock wave function theory, and the nature of metal-ligand bonding interaction is analyzed and discussed.

NUCL 94

Local configuration of excess oxygen in UO_{2+x} from the first-principles molecular dynamics

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Determination of the local configuration of interacting defects in a crystalline, periodic solid is problematic because defects typically do not have a long-range periodicity. Uranium dioxide, the primary fuel for fission reactors, exists in hyperstoichiometric form, UO_{2+x}. Those excess oxygen atoms occur as interstitial defects, and these defects are not random but rather partially ordered. The widely-accepted model to date, the Willis cluster based on neutron diffraction, cannot be reconciled with the first-principles molecular dynamics simulations present here. We demonstrate that the Willis cluster is a fair representation of the numerical ratio of different interstitial O atoms; however, the model does not represent the actual local configuration. The simulations show that the average structure of UO_{2+x} involves a combination of defect structures including split di-interstitial, di-interstitial, mono-interstitial, and the Willis cluster, and the latter is a transition state that provides for the fast diffusion of the defect cluster. The results provide new insights in differentiating the average structure from the local configuration of defects in a solid and the transport properties of UO_{2+x}.

NUCL 95

Crystal structure prediction: Using genetic algorithms and DFT to search for novel stable and metastable uranium oxides

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The existence of non-stoichiometric uranium oxides is well known. However, many of these possible structures are not well-characterized experimentally because traditional analysis tools fail to easily characterize the structure of systems with low or no translational symmetry. Even stoichiometric uranium oxides such as U_3O_8, U_4O_9, and UO_3 exhibit complex crystal phases when varying temperature and pressure. Using a combination of genetic algorithms and Density Functional Theory (DFT) calculations, stable or metastable

UO_x crystals can be identified. Several structure prediction codes already exist that use genetic/evolutionary algorithms to successfully predict novel crystal phases, such as the Genetic Algorithm for Structure Prediction (GASP) and the Universal Structure Predictor: Evolutionary Xtallography (USPEX) codes. USPEX can do additional searches for metastable states using an evolutionary metadynamics algorithm.

We have used these structure prediction codes, combined with the Vienna *ab initio* Simulation Package (VASP) to search the uranium-oxygen system for novel stable and metastable states. By further calculating experimental observables such as the vibrational spectra of low-energy predicted structures, direct comparisons to experimentally obtained data of unknown compounds can be made and unknown experimental samples can potentially be assigned to one of the predicted crystal structures.

NUCL 96

Mechanistic models for uranium sorption on iron minerals: Comparing their parametrization and surface species

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The migration of contaminants though the environment can be retarded by various processes – one of them being sorption onto mineral phases along the flow paths. This process is itself a variable combination of surface complexation, ion exchange, surface precipitation, diffusion and others. However, the data accuracy is currently still limited due to a restricted understanding of molecular events decisive for the binding onto and incorporation into solid phases. In particular, underlying surface speciation is often inconsistent and range from assumed unrealistic postulations up to spectroscopically evident species with great impact on the corresponding thermodynamic data. Respective mechanistic models required for prognostics based on reactive transport are often lacking an evaluated, consistent set of species and thermodynamic parameters. This work provides answers to these problems.

Recently, surface-sensitive spectroscopic methods developed significantly, permitting the derivation of thermodynamically consistent sorption data sets. In combination with binding site densities (including ones from crystallographic measurements), surface complexation models are deduced that describe the sorption of radionuclides accurately and with less surface species then assumed in a vast number of literature references published in the past. Due

to the realistic surface speciation and the internal consistency, these models are more robust to varying chemical and environmental conditions (pH, pe, composition of the aqueous phase).
This work aims on a re-evaluation of already published protolysis and sorption raw data. As examples, the sorption of uranium(VI) onto various iron(III) and iron (II) containing mineral phases (ferrihydrite, goethite, hematite, magnetite), ubiquitous in nature and also being corrosion products of waste containers, will be presented. There, the use of the spectroscopically verified, bidentate bound uranyl surface complex is sufficient to fully describe the radionuclides sorption. Even with simple models like the diffuse double-layer model only one surface species is necessary for the sorption calculation. In most cases also the CO_2 containing ternary system does not call for additional species. Eventually, a full integration with the thermodynamic reference database THEREDA (http://www.thereda.de) is envisaged to provide a comprehensive database for a holistic geochemical modeling.

NUCL 97

Electronic structure of uranium arene interactions

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Uranium-arene interactions are being explored by synthetic chemists at an increased rate as they provide the opportunity to understand the role electrostatic and covalent interactions play in tuning the nature of the uranium-ligand bond, and in turn the oxidation state on the metal. For complexes with uranium in oxidation states (III) and (IV), our group is interested in using a combination of density functional theory and complete active space SCF methods (CASSCF/CASPT2) to further understand the bonding in a spectrum of complexes. Cases where the arene bridges can act as reservoirs to accommodate charge in order to avoiding inter-electronic repulsion and allowing for varying oxidation states at the uranium center are of particular interest. The role of the other ligands in the complex as well as the symmetry at the uranium center will also be discussed.

NUCL 98

Hydrolysis reactions of actinide oxides and actinide oxides nitrates

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Hydrolysis reactions of actinide oxides play an important role in the initial steps of the conversion of actinide oxides to compounds containing OH groups. These reactions are important in the design of new nuclear fuels as well as environmental cleanup. Experimentally, these type of reactions are being studied in the gas phase at Lawrence Berkeley National Laboratory where the actinide cations and anions are identified using a mass spectrometer. Although the experimental work determines reaction products, it does not determine their structures or the overall energetics. Our results using electronic structure calculations provide a structural and energetic background which explains the experimental results providing us with unique insights into the chemistry of the +III/+IV/+V oxidation state of the actinides, especially the transuranics about which little is known because of their radioactivity and the cost to synthesize these atoms. The potential energy surfaces for the reactions of H_2O with actinide dioxides with the An in the +IV oxidation states for all the actinides and $AnO(NO_3)_3^-$ with H_2O and HNO_2 for An = Th, - Bk have been predicted at the DFT and CCSD(T) levels. The energetic results are correlated with oxidation states and electronic populations.

NUCL 99

Computational study of a novel Schiff-base ligand–uranyl complex: Characterization of physical and chemical properties

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In the present work, Computational studies were applied to investigate a novel Schiff-base ligand–uranyl complex, $UO_2(SaldienSO_3)^{2-}$, in aqueous solution. In particular, DFT geometry optimization calculations demonstrated that the complex could adopt two different conformers, endo- and exo-conformer with respect to the secondary amine nitrogen, resulting in different binding character at the coordination site. Electronic structure calculations were conducted to calculate the UV-visible and NMR spectrum for the complex in both vacuum and aqueous solvent. Frequency calculations were used to obtain the vibrational spectrum of the complex, as well as the thermodynamic quantities, such as free energies that were used to determine (1) the relative

thermal stability between the two conformers; and (2) the binding affinity between uranyl and the ligand. The calculated results could provide physical insights for understanding the driving force for the ligand and uranium binding process, which is important for developing a novel extraction method for reprocessing spent nuclear fuel.

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Structure and bonding of lanthanide hydroxides Ln—OH (Ln=La-Lu)

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Density functional theory calculations are reported for the complete series of lanthanide hydroxides. The calculations have been used to explore the structure and bonding of this series and to determine if any periodic trends should be expected. Interestingly, the calculations predict that all structures of this series will be linear. Moreover, the metal-hydroxide bond is best characterized as a covalent triple bond. The results also suggest the bond is not purely covalent and does exhibit a degree of ionic character. The metal-oxygen bonds include contributions from Ln 5d orbitals and O 2p orbitals, while 4f orbitals do not directly contribute to the formation of these bonds.