NUCL 1

Radiation effects in molten salts

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The next generation molten salt nuclear reactors will operate under extreme conditions of temperature and radiation that have not been well characterized. Radiolysis of the proposed chloride salts is expected to produce reactive electrons and chloride radicals that can react with added solutes or the interfaces of reactor components. Stable chloride dimers and trimers may also initiate chemistry. The Molten Salts in Extreme Environments EFRC has a team of radiation experts working to understand the fundamental species produced in the radiolysis of molten salts and their reactivity with interfaces and solutes. This presentation will present our plans for identification of the stable products in the radiolysis of molten salts. Radiation produced species are expected to react with available interfaces and radiation is expected to modify interfaces so that they are more susceptible to corrosion processes driven by the molten salts. An outline of our experimental capabilities and preliminary results will be presented.

NUCL 2

Liquid fueled molten salt reactor fuel salt composition evolution and implications for operations and performance

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In liquid-fueled molten salt reactors, fuel (e.g., uranium, plutonium, or thorium salts) is dissolved within a carrier salt, which flows through the core, piping, pumps, and heat exchangers. During operation, this fuel salt is continuously changing due to irradiation (i.e., fission and transmutation), fueling, and passive and active elemental removal processes. Reactor physics tools designed and validated for predicting the isotopic change in light water reactor solid fuel have been extended to account for fueling and elemental removal processes and to track and decay isotopes that are removed from the fuel salt. Predicting fueling rates, removal rates, and waste storage burdens with these tools is critical for reactor system and fuel cycle design. In addition, changes in the elemental composition of the fuel salt drives changes in its thermophysical properties and corrosion potential. Predicting these changes provides for ensuring safe system operations and designing mitigation mechanisms to maintain acceptable fuel salt conditions. The thermophysical and chemical properties of the changing fuel salt

help define the behavior of fuel salt constituent elements during a reactor event; the mobility and volatility of these elements directly impact the source term quantification included in a reactor licensing case. Leading fluoride and chloride molten salt reactor concepts target different fuel cycle outcomes, with fluoride concepts generally having a maximum burnup (e.g., fissions per initial uranium atom) similar to that of current light water reactor fuel at discharge. Leading chloride concepts target greater fuel cycle benefits that require a much higher burnup, resulting in the buildup of significantly more fission product elements within the fuel salt. The expected operating lifetime of these systems is over 7 years; ensuring the longevity and reliability of components and piping exposed to the fuel salt environment is crucial for the economic viability of the technology.

NUCL 3

Fundamental study of electrochemically separated uranium in the presence of cerium in molten LiCl-KCl electrolyte

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This study investigates the effects of varying the overpotential (25 mV, 50 mV, 100 mV, 200 mV) of the electrochemical cell and weight percent ratio of uranium to cerium (1:0, 2:1, 1:1, 1:2, 1:0) in the molten LiCl-KCl electrolyte in order to understand the fundamentals of uranium electrodeposition as well as causes for salt occlusion and lanthanide co-deposition. Electrochemical techniques will be used to study electrochemical phenomena of the system affected by varying the overpotential of the electrochemical cell and uranium-cerium weight percent ratio. Information such as ion mobility and adsorption/desorption to electrode surfaces via electron emission spectroscopy and redox potentials of the system via cyclic voltammetry and square-wave-voltammetry have the potential to provide a better understanding as to why salt occlusion and lanthanide co-deposition occur. To investigate any contaminant carry-over, the electrochemically separated uranium samples are harvested and analyzed using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) capabilities for morphological and elemental surface composition analysis. The crystallography of these samples is studied using x-ray diffraction (XRD) to determine if any uranium-cerium alloy is present, which would lead to the assumption of co-deposition. Finally, the elemental volumetric composition is analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

NUCL 4

Measuring the structure of bulk KCl/MgCl$_2$ molten salts using X-ray and neutron scattering

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Molten salts are complex materials whose unique properties make them ideal for a number of applications including concentrated solar power and advanced nuclear reactors. Understanding the local structure, intermediate-range order and their dynamics is critically important because these properties can impact the behavior of the molten salt including its thermal and transport properties and its ability to solvate metal ions such as dissolved fuels or fission products. In this work, we explore the bulk molten salt structure of a series of binary $KCl/MgCl_2$ molten salts with varying relative composition. Total X-ray and neutron scattering of the molten salts was measured in order to obtain the pair distribution functions as a means to understand the dynamics of molten salt structure. We also investigated the effect of added chromium on the structural order of the molten salts.

NUCL 5

Investigating structure and speciation of metals in molten salt system using X-ray absorption fine structure

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Molten Salt Reactors (MSRs) are the leading candidates out of the six Gen IV advanced nuclear power reactor designs chosen for deployment for nuclear energy in the US. MSR technology is particularly attractive due to better passive safety, operation at atmospheric pressure, high thermal efficiency, lower spent fuel per unit energy and increased solubility of fission products in molten salts. To facilitate robust and economical design of such systems, accurate knowledge of fundamental understanding of the structure and speciation of salts and metals in and near molten salt – cladding interfaces is necessary. Speciation of solutes is important because it determines chemical behavior in solution and the complex speciation from fission and corrosion products impact kinetic, thermodynamic, and transport properties of the molten salt systems.

Molten Salts in Extreme Environments (MSEE) EFRC aims to investigate speciation of metals in molten salt systems by utilizing in situ synchrotron based XAS methods. In our work, Extended X-ray Absorption Fine Structure (EXAFS) and X-Ray Absorption Near Edge Structure (XANES) are used to investigate local coordination environment and chemical structure of metal species such as Nickel in Zinc Chloride based molten salt systems. A combination of XANES, EXAFS and theoretical spectroscopy modeling reveal changes in the local structure around Ni towards distorted $NiCl_2$ phase as the weight loading of Ni the exceeds solubility limit. In addition, the effect of metal concentration and temperature on changes in local and chemical structure of metal is investigated. XAS studies are complemented by spectroelectrochemical studies of molten salts, enabling a direct correspondence between UV-Vis peak shape and coordination geometry and number, determined by EXAFS. Such knowledge of changes in chemical structure of salts and speciation of metals in molten salt environments will provide critical understanding needed to predict and control the physical and chemical properties of molten salts and corrosion mechanisms in molten salt systems.

NUCL 6

Spectroscopic and electrochemical investigation of f-elements and optical materials in molten salt

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Molten salt reactors are a rapidly growing field of interest for applications in nuclear energy. This leads to a growing need to understand the fundamental chemistry of molten salt systems. However, the tools for monitoring and characterization are currently unavailable. Current approaches for characterizing molten salts are limited to grab samples or small crucibles. These methods are not ideal for in situ characterization of molten salts systems, resulting in a gap in quantifying the evolution of molten salt chemistry. Spectroscopic monitoring paired with electrochemical modulation can provide fundamental information to determine speciation, concentration, and oxidation state of optically active species within the molten salt environment. Select f-elements within molten salt media have distinct spectral fingerprints that can be used as the basis for quantitative measurement. These analytes can be electrochemically modulated to accurately track the spectroscopic signature in a harsh complex environment, like that of molten salts. This work combines electrochemical modulation and spectroscopic detection to characterize target analytes within a molten salt media. This technique will provide fundamental information to help fill in literature gaps regarding redox chemistry, diffusion coefficients, speciation and interaction behavior. Studies will include experimental design, molten salt composition, and analytical technique. Preliminary studies have demonstrated the absorption based spectroelectrochemical modulation of uranium within a molten chloride media using cyclic voltammetry. This work is being expanded on to further characterize U and other f-elements in within the molten salt environment, including adequate optical materials for interrogation of the molten salt system.

NUCL 7

Application of electrochemical and laser spectroscopic methods for composition measurements of UCl_3-$MgCl_2$-$GdCl_3$ in LiCl-KCl molten salt

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This study aims to estimate the concentration of multiple species in LiCl-KCl molten salt via the combined implementation of two methods. The first method for time efficient composition analysis utilizes laser-induced breakdown spectroscopy (LIBS). LIBS involves focusing a pulsed high energy laser onto a sample, creating a plasma plume from the sample's ablated surface. As this plasma cools down, an elemental spectrum is generated from the elements returning to their ground state. This spectrum can be collected via fiber optics and analyzed to determine the composition of the sample. The second method of salt composition analysis utilizes a variation in the working electrode depth in the electrochemical cell. By changing the immersion depth of the electrode, the characteristic cathodic peak current density of the salt species is measured. The cathodic peak current density is directly related to the salt concentration through the Berzins-Delahay Equation. For this study a matrix of UCl_3-$MgCl_2$-$GdCl_3$-LiCl-KCl salt concentrations will be tested with UCl_3 ranging from 0.5 – 10.0 wt%, $MgCl_2$ ranging from 1.0 – 5.0 wt%, and $GdCl_3$ ranging from 1.0 – 5.0 wt%. $MgCl_2$ was chosen as a surrogate for Pu in the electrorefiner due to their similar standard potential and $GdCl_3$ was chosen to be representative of the active rare earth salt species which accumulate in the salt. The goal of this study is to show that a combined electrochemical and laser system is capable of monitoring UCl_3 concentration in the presence of other species. All samples will undergo electrochemical and LIBS testing; then, a portion of these samples will be tested via ICP-MS to verify each elemental concentration.

NUCL 8

Modeling Cr dissolution in molten KCl-$MgCl_2$

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A complete thermodynamic description is the basis for understanding molten salt compatibility. The behavior with Cr is important as Cr is a constituent of many structural alloys being considered for applications utilizing Cl bearing salts. Prior modeling work has extended the Calculation of Phase Diagrams (CALPHAD) assessment of the KCl-$MgCl_2$ pseudobinary to the integral K-Mg-Cl true ternary by allowing for excess K or Mg via F-centers. This lays the foundation for including other excess metallic additions for multicomponent thermodynamic assessments that can more accurately represent corrosion behavior. Using this approach the inclusion of excess Cr as well as $CrCl_2$ and $CrCl_3$ species in the Modified Quasichemical (MQC) model for the melt will be

discussed. Phase diagram illustrations and thermochemical calculations using the MQC will be presented and compared with experimental corrosion results where appropriate.

NUCL 9

Surface segregation behavior in molten salt facing Ni-Cr alloys: First principles investigation

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Corrosion of metal surfaces and interfaces in molten salt systems stands as one of the largest remaining obstacles that must be overcome before a viable molten salt reactor can be realized. In Cr containing Ni-based superalloys, envisioned for use in the structural and piping components of these systems, the dominant form of corrosion is the depletion of Cr atoms near the surface and along grain boundaries. At this moment, the mechanisms underlying Cr depletion are not fully understood, and the challenges associated with studying molten salts make it unlikely an answer will be found experimentally without considerable time, effort, and cost. Carefully devised computational modelling may lessen this burden by providing acumen and insight that could help narrow the range of possible reaction pathways. In this work, density functional theory (DFT) is employed to model the effect adsorbed salts atoms have on the surface segregation of a Cr atom in an fcc Ni matrix. Surface segregation energies describe the energetics associated with the location of a solute atom near a surface (i.e. the relative energy of an atom when its located in the bulk versus at the surface). Calculations show that under a clean surface (i.e. no adsorbed salt atoms) it is energetically favorable for the Cr atom to inhabit the 3rd or 2nd surface layer, but largely unfavorable for it to sit in the outermost 1st layer. When a Cl or F atom is adsorbed to the surface the segregation energy to the 1st layer decreases considerably, suggesting the adsorption of salt atoms increases the likelihood of a Cr atom segregating to the surface. Comparison of these effects with other potential adsorbates, such as O or OH may help to unriddle the mystery underlying Cr depletion. This talk will report new insights into material-salt interfaces through atomistic modeling.

NUCL 10

Measurement of molten KCl-$MgCl_2$ salt penetration depth in nickel alloys using LIBS

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Molten Salt Reactors (MSRs) are an advanced reactor design of interest to the nuclear power industry, as their design allows for operation at lower pressures and higher temperatures compared to Light Water Reactors (LWRs). MSRs also have passive safety features such as large negative reactivity coefficients. Moreover, there is potential to produce less waste with shorter lifetimes than current reactor designs, in addition to breeding of fuel for better utilization of uranium and thorium resources. However, MSR designs currently face challenges associated with the corrosion of structural materials, limiting the possibility of MSR viability. The mechanisms corrosion behavior in these systems are not well understood and require study.

The objective of this work is to study mechanisms of salt infiltration and de-alloying in structural materials. Laser-induced breakdown spectroscopy (LIBS) was used to investigate alloy surfaces after exposure to molten salt. A binary nickel – chromium alloy with a 16 % weight percent Cr composition was tested, as Ni-Cr alloys and their derivatives are of primary interest for structural use in molten salt systems. Samples were exposed to a KCl-$MgCl_2$ eutectic salt at a temperature of 700°C for 1000, 2000, and 2500 hours. These static tests were conducted in molybdenum capsules to control external impact on the corrosion. Salt preparation along with test conditions were tightly controlled to limit impurities in the salt and inhibit any additional corrosion processes that could cause fluctuation or high error in results. A commercially available LIBS instrument outfitted with a high-resolution echelle spectrometer was used to collect the optical emission spectra of the LIBS plasmas.

This talk will report new insights into the behavior of nickel alloy interfaces in contact with molten chloride salts. LIBS data will be used to show how salt infiltrates into the alloys and interacts with alloy constituents.

NUCL 11

Analysis and modeling of the equilibrium behaviors of U and Pu in molten LiCl-KCl/Cd system at 500°C

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In the field of pyroprocessing of used nuclear fuels, liquid cadmium is applied in different ways to recover transuranics from molten salt, while effecting some degree of separations between transuranics and lanthanides. A model of the separation performance between uranium and plutonium across the phase boundary between molten salt and liquid cadmium is presented. The salt is the LiCl-KCl eutectic with solute concentrations of UCl_3 and $PuCl_3$. The cadmium is the liquid cadmium phase field from the Cd-U-Pu ternary alloy system. The model used to describe the behavior of uranium and plutonium in the salt/cadmium system is applied to describe the behavior of plutonium and lanthanide in the salt/cadmium system.

NUCL 12

Measurement and analysis of equilibrium potentials of Ag/AgCl reference with respect to Cl_2/Cl^- in LiCl-KCl eutectic salt

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In this study, Cl_2/Cl^- reference system was established with a special designed quartz cell where Cl_2 gas was trapped on a glassy carbon electrode surface allowing the thermodynamic equilibrium between Cl_2 and Cl^- ions. Based on the Cl_2/Cl^- reference, effects of temperature (ranging from 723 K to 823 K in an increment of 25 K) and AgCl concentration (0.00039, 0.0043, 0.01, 0.022, 0.050, 0.10, and 1.0 – all in mole fraction) on equilibrium potential of Ag/AgCl reference electrode were being explored. Here, the glassy carbon was used as the working electrode whereas the Ag wire, directly exposed to the bulk salt, was used as both the reference and counter electrodes. Open circuit potential (OCP) of the working electrode was first read using the potentiostat. Then, Cl_2 gas was flowed through the quartz tubing at slow flow rate. OCP was further observed to evaluate the equilibrium potential of Ag/AgCl versus Cl_2/Cl^- electrode. Preliminary results indicated that the measured values ranged from -0.877 V to -1.361 V and followed linear correlations against temperature and concentration. However, pure AgCl showed slight upward in comparison to other observed linear trends. Compared to the previously published data sets, this study provided a full spectrum of data yielding consistent data conversion for Ag/AgCl reference, applicable for different experimental conditions. In addition, the activity coefficients of AgCl in LiCl-KCl salt were calculated using ideal Gibbs free energy at supercooled liquid standard state. The activity coefficients ranged from 0.0012 to 1.19, which did not conform to a linear relationship to AgCl concentration. Further results will be presented and discussed.

NUCL 13

Thermophysical properties of $CaCl_2$-KCl-$MgCl_2$ eutectic salt

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This study explored the important thermophysical properties (e.g., specific thermal capacity, heat conductivity, etc.) of $CaCl_2$-KCl-$MgCl_2$ ternary salt system as it could be applied to thermal energy storage systems as a high-temperature phase change material—including melting point and thermal stability. Differential scanning calorimetry was performed with different compositions of $CaCl_2$, KCl, and $MgCl_2$ to determine the eutectic composition. Then, thermal stability of the eutectic was studied by thermally cycling the eutectic and evaluating the change of melting temperature and latent heat. This study would provide a feasibility for the consideration of $CaCl_2$-KCl-$MgCl_2$ as a thermal energy storage material.

NUCL 14

First principles molecular dynamics simulations of U(III) and U(IV) in molten chlorides

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Molten chloride salts are one of the two main choices to dissolve nuclear fuels for fast-spectrum molten-salt reactors, as a generation IV reactor design. In this talk, we discuss our work of using first-principles molecular dynamics simulations based on density functional theory to investigate the structure of UCl_n (n = 3, 4) in molten NaCl and $MgCl_2$ at various mole fractions. Coordination, structure, and dynamics of the first solvation shell will be analyzed in detail as a function of increasing uranium concentration. More important, network formation will be examined in detail to compare the difference between UCl_3 and UCl_4 as well as that between NaCl and $MgCl_2$. These findings will help fill the knowledge gap in understanding the fuel behavior of UCl_n (n = 3, 4) in molten chlorides.

NUCL 15

Zn-doped, graphene-like carbon nitride for uranium extraction with high capacity

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The development of functional materials for the highly efficient capture of radionuclides, such as uranium from nuclear waste water, is a trending research nowadays. Here, few-layered Zn doped graphene-like carbon nanosheets (Zn-GLCs) that are fabricated in the solvent of molten salt and applied as sorbents to remove U(VI) ions from aqueous solutions are presented. The Zn-GLCs exhibit a large capacity, wide pH suitability, an ultrafast removal rate, stability at high ionic strengths, and excellent selectivity for U(VI) as compared to classical graphene-like carbon nitride. The nanosheet structure of Zn-GLCs with average diameter of 10 nm not only assures the rapid mass diffusion, but also exposes a sufficient active site for the adsorption. Strong covalent bonds such as Zn-O-U are generated between the heteroatom with UO22+ according to X-ray photoelectron spectroscopy analysis and X-Ray Powder Diffraction. This work highlights the interaction mechanism of metal ions with UO22+, thereby shedding light on the material design of uranium immobilization in the pollution cleanup of radionuclides.

NUCL 16

Synthesis, radiolabeling, and characterization of phenoxypheny acetamide or pyrazolopyrimidine derivatives for imaging the TSPO kDa with PET

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Neuroinflamation plays a vital role in many diseases affecting in the brain, including Alzheimer's disease, Perkinson's disease, multiple sclerosis and stroke. Ligands of TSPO (translocator protein), a marker for activated microglia have been used as PET tracer to reflect neuroinflamation in patients. TSPO can be found throughout the body and expressed in very low concentration in normal brain. The increase in TSPO expression is correlated to microglial activation following brain injury. Accordingly, TSPO are potential targets for evaluate neuroinflammatory changes in variety of CNS disorders and development of radioligands for PET imaging. In addition TSPO is also overexpressed in different types of cancer. Developing selective probes for TSPO specific binding is challenging due to the several drawbacks such as high plasma protein binding, low brain uptake, highly variable kinetic behavior and high lipophilicity. In the present study, to improve the structural correlation of DPA-714 and PBR28 to devise a structure having a higher binding affinity and low lipophilicity. We synthesized a series of phenoxyphenyl acetamide (PBR28) and pyrazolopyrimidine derivatives, evaluated their TSPO binding affinity against [^{3}H]PK11195 and successfully radio-labeled most active compound that representing the highest binding affinity with fluorine-18.

NUCL 17

Morphological and chemical evolution of Ni and Ni-20Cr microwires in molten KCl:MgCl$_2$

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Molten salts are a promising high temperature heat transfer fluid in part due to their high specific heat, and ability to operate at close to ambient pressure. This has incited interest for their use in molten salt nuclear reactors and solar thermal power plants. Molten salt reactor (MSR) feasibility was demonstrated in the Molten Salt Reactor Experiment at Oak Ridge in the 1970's. Since then, corrosivity has been identified as a key remaining hurdle to widespread adoption of MSRs. In response, numerous corrosion-resistant, Ni-based alloys such as the Hastelloy series have been developed, but these alloys are prohibitively expensive and lacking in high temperature strength. It has been shown in complex Ni-based alloys, Cr depletion is a main observation of corrosion. However, the precise mechanism of this corrosion is not fully understood. Here we explore Ni and Ni-Cr alloy corrosion in pure KCl:MgCl$_2$, with a focus on the metal-salt interface. The three-dimensional morphological structure and chemical

constitution of Ni and Ni-Cr microwires has been probed using X-ray nanotomography and transmission electron microscopy with energy dispersive X-ray spectroscopy and electron energy loss spectroscopy.. With Ni-only the system seems to be dominated by corrosion along interfaces and defects such as grain boundaries, contrasted with the Ni-Cr system where differing diffusivities lead to porosity potentially created by Kirkendall effects, and surface rearrangements occur. Both systems ended with a shell only structure. These results further the fundamental understanding of Ni and Ni-Cr interactions with molten salts. This will help build a foundation for the development of more complex alloy systems for containment of molten salts.

NUCL 18

Molten salt reactor off-gas monitoring using laser induced breakdown spectroscopy

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Molten Salt Reactors (MSRs) are one category of advanced nuclear reactor designs receiving increased attention, which is evidenced by significant investments from both government and private industry into MSR technology development. The attractiveness of MSR technology predominately stems from inherent safety features including low pressure operation, passive decay heat cooling, and large negative temperature coefficient of reactivity. A key component of any nuclear reactor is the off-gas system. MSR designs present a unique set of off-gas related challenges due to the fuel being in liquid form. A generalized MSR concept involves the flowing of an inert cover-gas, such as argon or helium, over the molten salt fuel. Volatile species and aerosols can be caught within the cover-gas under both normal and off-normal operating conditions. It is therefore required that off-gas treatment technologies be developed to ensure that radioactive species are not released under any condition. A key aspect of developing and deploying these off-gas treatment technologies is instrumentation for monitoring the concentrations of species in the off-gas before and after treatment. Laser Induced Breakdown Spectroscopy (LIBS) is one of several promising analytical techniques for MSR off-gas monitoring. LIBS has been used to detect hydrogen through curium. Typical limits of detection of in the low tens of parts-per-million and can be lowered further with optimal system design and advanced LIBS set-ups (double-pulse LIBS, hyphenated techniques, etc.). In addition to elemental concentrations, extremely high-resolution spectrometers may be used to obtain isotopic information. This contribution will give an overview of MSR off-gas monitoring requirements, potential approaches to using LIBS for off-gas monitoring, as well as recent progress on the design and testing of a LIBS off-gas monitoring system for MSRs.

NUCL 19

Iodide in fluoride salts: Its behaviors and iodine ion separation

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Iodine is the major halogen, and it is a fission product or a decay product of its precursors, for example, Te. Iodine will form some iodide with other fission products (e.g. CsI) which can dissolve into the primary salt. Therefore, nearly all iodine isotopes remain in the salt in the form of I^- instead of validation. ^{131}I and ^{133}I were found in MSRE exiting gas which came as a result of volatilization of Te precursors. Since element iodine is a vaporized material, it is one of the major radioactive source term concerns for other types of reactor such as Na-cooled reactor. However, iodine is in the form iodides that can remain in the salt for MSRs, therefore, the salt has a high retention capability of iodine. The iodides in the salt may have some impacts on the salt properties including physical and thermochemical properties. However, such data are very scarce and impacts on the salt properties are not well understood. The iodide in the salt may also lead to corrosion.

The present study investigated iodide electrochemical behaviors in molten fluoride salts and iodine ion separation from the salt. The study tested two type of working electrode: Tungsten and graphite. Based on the thermodynamic calculations experimental measurments, the oxidation potential of W is more negative than that of iodine ion, therefore, W electrode cannot be applied as the anode for iodine separation, and then graphite electrode was selected. The electrochemical measurements using graphite working electrode indicates that there is a passive layer which complicates the behaviors of iodide ion by the blocking effect of the layer at the graphite working electrode. The blocking effects made the redox potential shift to a sufficiently positive value. In this case, the oxidation current actually decreases as the potential moves positive, and the process of the iodide ions penetrating through this film becomes rate-limiting. An increase in the concentration of iodide relieved the ‘blocking effect’ and yielded a higher current. The reason for this might be the little amount of replacement of passivation layer by the addition of sodium iodide. Moreover, both cyclic voltammetry and chronoamperometry test were employed to identify the characteristic of the separation of iodide ions. Finally, two pathways, the formation of either I_2 gas or KI_3 gas, were proposed for the separation mechanism of iodide ions from the system from both thermodynamic calculations and experimental demonstrations.

NUCL 20

Fission product volatility in molten salt reactors

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Molten salt reactors (MSRs) represent a completely different paradigm of fission and activation product volatility in comparison to ceramic-fueled reactors. In the latter, fission gases are contained during reactor operation. Safety systems in containment are designed to handle rare, high pressure releases under severe accident conditions. For a salt-fueled MSR, gases evolve continuously during normal operation and are treated and confined within a dedicated off-gas system that operates at pressures only slightly above ambient. The chemical and physical phenomena that affect fission product volatility include: the redox state of the salt; bubble formation and release, or void fraction; metal precipitation and relocation in the primary circuit; generation of mists, airborne particles, and aerosols in the pump bowl headspace; decay of noble gas fission products; headspace purging with inert gas; and radiolysis. This talk will review historical data on fission product release from MSRs that operated at Oak Ridge National Laboratory, including the Molten Salt Reactor Experiment (MSRE). Recent developments on salt redox chemistry will be discussed including preparation of a thermodynamic database for chemical species relevant to MSRs. The database includes binary and ternary systems of actinides, lanthanides, fission products, and transition elements, the latter primarily coming from corrosion of reactor materials. The effect of redox chemistry on speciation and volatility of fission products will be presented, along with preliminary experiments investigating salt volatility using a dedicated thermogravimetric analysis instrument equipped with a differentially pumped quadruple mass spectrometer. These experimental results can be analyzed to provide missing thermodynamic data on salt species that are missing from the fore-mentioned database. They will be compared with alternative methods to determine thermodynamic properties in molten salts, including electrochemical methods.

NUCL 21

Electrochemical study in molten salts: Assembly and characterization of micro-reference electrodes

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Molten salts have many uses in the energy sector including molten salt reactor coolants and fuel recycling. The behavior of analytes within these systems, however, is not well understood. Of particular interest are the actinides, fission products, and corrosion products. The extreme temperatures and corrosive nature of the salts makes the study of these analytes difficult. The ability to study redox behavior *in-situ* is needed to maintain safe operation and control corrosion rates. A key element of electrochemical

characterization of molten salts is in the choice of reference electrode because most commercially available reference electrodes are not well suited for molten salts. Here we show the assembly and characterization of several micro-reference electrodes designed for use in molten salts. Each electrode was characterized in molten salts and were tested for long-term stability as well as the accurate measurement of analytes such as europium. Here we discuss our recent work on this project.

NUCL 22

In-situ spectroelectrochemistry of transition metal and lanthanide chlorides in molten chloride salts

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Molten salts are proposed for use as a heat transfer fluid in a number of advanced nuclear reactor designs, as well as for the electrolyte for pyormetallurgical reprocessing of used nuclear fuel due to their high temperature stability, electrochemical properties, and heat transfer characteristics. To facilitate robust and economical design of such systems, accurate knowledge of fundamental properties is necessary. To investigate the molecular and electronic structure of molten salt systems, we have developed a versatile high-temperature apparatus for *in-situ* spectroelectrochemical studies of molten salts. UV-Vis-NIR spectra of various transition metal and lanthanide chlorides dissolved in molten chloride salts have been coupled with electrochemical measurements to provide a more complete picture of the molecular and electronic structure of molten salts. UV-Vis absorption measurements were performed *in-situ* in Ar gloveboxes at INL using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer coupled via fiber optics to a custom built furnace located inside the glovebox.

NUCL 23

Computational protocol for binding selectivity of lanthanide and actinide systems

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Understanding the of binding selectivity of lanthanides and actinides system is crucial for nuclear forensics, designing separation agents, and understanding spectra. Theoretical predications predictions and computational protocols often are determined that include that include effects from relativity, spin-orbit coupling, and core correlation are shown. Various computational methodologies ranging from ab initio and DFT including single- and multi-reference and relativistic effects in lanthanide- and actinide-containing compounds will be presented with focus on level of theory dependence and

computational cost are used to understand the dependence of the predicated results along with effects do to basis set choice.

NUCL 24

Predicting the properties of actinide complexes in the gas phase and in solution

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There is a need to develop new approaches for separations for the actinides for the development of new nuclear reactors for efficient energy generation and for cleaning up the environment at nuclear weapons production sites. In addition, the actinides present a relatively less well-understood domain of chemistry and the presence of *5f* electrons can make the chemistry significantly different from that in other parts of the Periodic Table. Thus, there is substantial interest in understanding the properties and reactivity of molecules containing actinides, including their reactions in aqueous solution. We will describe how computational electronic structure theory can play a role in helping us to understand the actinides and the difficulties in employing such methods for the reliable prediction of the properties of the actinides, for example, the role of relativistic effects. Hydrolysis reactions are important in transformations of actinide ions and oxides into hydroxides. These processes impact environmental transport, nuclear fuel processing, and waste treatment and disposition, We will describe applications to the hydrolysis chemistry of actinyl dioxide cations AnO_2^+ for An = Pa to Lr, including how their behavior changes with the number of *5f* electrons. The impact of anionic ligands on AnO_2^{2+} will also be discussed. The acidities of aqueous An = Th - Cf in different oxidation states have been calculated with multiple solvation shells and exhibit some interesting trends. These are the first available estimates of the pK_a's for some of these species. Issues in the design of new organic separation agents such as frustrated Lewis basic complexants will be discussed including the potential for separating actinides from lanthanides and issues in the design and synthesis of new complexants, for example solubility.

NUCL 25

De novo design of ligands for selective trivalent f-elements complexation

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Current technologies used for separation of trivalent lanthanides and actinides are based on multistage extraction cascade with relatively low efficiency at each stage. Difficulties of separation process arises from similarity of trivalent lanthanides and actinides properties and liquid-liquid extraction is used either as a basic separation

technique or as a model experiment for more complicated system.
Significant improvement can be reached by development selective and effective extractants, that could form a stable complex with a single ion (or at least with a single group of ions) in presence of competing ones. Now we know several groups of such ligands with satisfactory selectivity and other properties (as solubility in target diluent, nitric acid resistance, etc) and a process of development is usually devoted to modifications of these basic frameworks.
On the other hand, a process of selective ligand development is very similar to drug design process, where we try to find a molecule with the best affinity to the biological target. In the case of drug design, using computational models, especially based on machine learning is an essential part of development process.
Here we would like to present an example of adopting drug design approaches to lanthanides and actinides complexation problem. We have collected databases containing complex stability constants for trivalent f-elements. For each element we built models based on neural network architectures predicting target constants (R^2~0.8, RMSE~2[*logK*]). We also ‘unboxed’ these models to determine key fragments of molecule with the most significant influence on stability constant value. This approach can ‘offer’ molecular fragments increasing or decreasing constant value.
Finally, we combined models with genetic algorithm available not only to predict values of a drawn molecule, but to construct new molecules with increasing target property.

NUCL 26

How calculations unite with synthesis to tackle novel actinide chemistry

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Uranium chemistry has undergone a renaissance due to both its utility in the nuclear power industry as well as for potential catalysis. In both cases, new ligands must be developed for binding of uranium in multiple oxidation states and coordination geometries. These binding motifs as well as the binding strength of the ligands can be understood through both experimental (spectroscopic and X-ray diffraction) as well as theoretical calculations. In this presentation, two case studies will be examined. First, the binding of uranyl with amidoxime type ligands for extraction of uranium from water or detection will be discussed. Second, organometallic uranium chemistry in lower oxidation states with *N*-heterocyclic carbenes will be presented. In both cases, small variations in ligand sterics and electronics allow for distinct geometries about the uranium center which is observed in both the experimental data and calculations.

NUCL 27

First principles molecular dynamics simulations of UCl_n–NaCl (n=3, 4) molten salts

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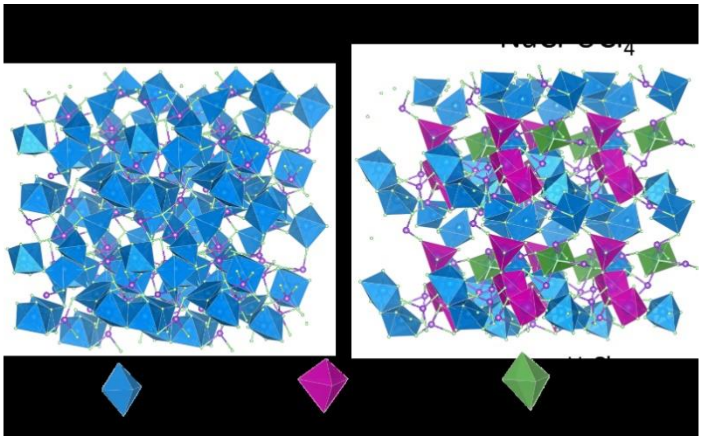
Molten chloride salts are one of the two main choices to dissolve nuclear fuels for fast-spectrum molten-salt reactors, as a Generation IV reactor design. Both U^{3+} and U^{4+} can stably exist in molten chlorides, but the differences in their structure and chemical properties in molten NaCl are not thoroughly understood. In this work we use first principles molecular dynamics simulations based on density functional theory to investigate the structure of UCl_n (n=3, 4) in molten NaCl at various mole fractions. We find that 7-fold and 8-fold-coordinate structures of Cl around U become more populous in UCl_3-NaCl when UCl_3 concentration is higher than 25 mol%, while in UCl_4-NaCl the 6-fold-coordinate structure is the leading species when the UCl_4 concentration is higher than 33 mol%. Moreover, we find that the first solvation of Cl around U is more dynamic in UCl_3-NaCl than UCl_4-NaCl, evidenced by weaker U-Cl bonds and faster U-Cl dissociation in the former. Further analysis reveals that a network structure with sharing Cl^- between U cations starts forming at the low U^{3+} concentrations, whereas the U^{4+}-Cl^--U^{4+} linkages become noticeable only after U^{4+} concentration is larger than 33 mol%. This work sheds new light on the difference between U^{3+} and U^{4+} in molten NaCl.



NUCL 28

Modeling highly assymetric mixtures in the warm dense plasma regime: From enhancement factors to transport

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Warm dense plasmas composed of highly asymmetric, by atomic mass and charge, mixtures are found in planetary systems, stars, internal confinement fusion capsules and nuclear applications. We utilize a variety of methods to simulate the dynamics of these mixtures at high temperatures, including orbital-free density functional theory, Yukawa potentials, effective-one component plasma theories and jellium models. On one side, the effect of heavy species on light element fusion reactions, through a change in the local thermodynamic conditions, will be discussed. One the other, we will discuss the complex transport dynamics for binary and ternary mixtures, where the timescales related to varying ion types are significantly different. Additionally, we will address the unique numerical challenges which accompany such systems, especially ternary mixtures.

NUCL 29

Probing the electronic structure and chemical bonding of actinide organometallic compounds

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Actinide organometallic complexes exhibit diverse coordination geometries and novel chemical properties such as rich redox chemistry and high reactivity in molecular systems, due to the additional 5f valence shell compared to d-block elements. The availability of 5f orbital participation in chemical bonding promotes unusual electronic structures and a greater variety of metal-ligand bonding possibilities. Understanding electronic structure and chemical bonding of actinide organometallic complexes is of fundamental importance for establishing a more perspective and though interpretation of basis bonding principles, trends, and electronic structure changes across the actinide series that were mainly built upon the actinide inorganic complexes. These new insights could impact on the research areas related to the 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 5f, 6d and 7s orbitals, the understanding of electronic structure and chemical bonding of actinide organometallic compounds is rather difficult to decipher. Great progress has been made recently 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 chemical bonding of actinide organometallic compounds and resulting in good agreement with experimental optical spectroscopic measurements. Calculation results

show that the actinide 5f and 6d molecular orbitals play an important role in shaping electronic absorption spectral features in actinide organometallic compounds.

NUCL 30

Examination of the sensitivity of computational models to hyperparameter selection

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The ability to isotopically enrich (and measure the enrichment of) hexafluoride compounds of Molybdenum and Uranium has applications in space travel, nuclear security, and medical isotope production. Because of the large overhead costs of standing up enrichment programs for these compounds, a reliable, fast, and accurate computational model is desirable. Appropriate selection of model complexity and hyperparameters may reduce the computational time required to obtain accurate results. To better understand these tradeoffs, a statistical analysis was performed on sets of simulated structural, spectroscopic, and thermochemical data for hexafluoride compounds (MoF6, UF6) to measure the deviation introduced by simpler models, and if these deviations could be mitigated with appropriate selection of model parameters.

NUCL 31

Marking the 80th anniversary of the discovery of nuclear fission by chemists

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The report by O. Hahn and F. Strassmann in January 1939 that Ba, Sr, La, and Y had been firmly identified, by chemical means, as products arising from the neutron irradiation of uranium led to a year of feverish activity. In this presentation, the questions that arose in 1939 will be addressed. These include: What is happening in the nucleus; are there neutrons emitted in the process; if so, how many neutrons are emitted; why is there a difference between neutron reactions with Th versus the result for U; could a chain-reaction weapon be devised; what about elements heavier than uranium for which E. Fermi had been awarded a Nobel Prize.

NUCL 32

Energy dependence of fission product yields for ^{235}U, ^{238}U, and ^{239}Pu with monoenergetic neutrons between thermal and 14.8 MeV

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Under a joint collaboration between TUNL-LANL-LLNL, a set of absolute fission product yield measurements has been performed. The energy dependence of a number of cumulative fission product yields (FPY) have been measured using quasi-monoenergetic neutron beams for three actinide targets, ^{235}U, ^{238}U and ^{239}Pu, between 0.5 and 14.8 MeV. This work has been done with the Triangle Universities Nuclear Laboratory (TUNL) 10 MV Tandem Van De Graaf accelerator on the campus of Duke University. In a quest to provide the most complete set of fission product yield data, we have measured the cumulative fission product yields for approximately 15 peak yield fission products as a function of incident neutron energy. Using a newly built rapid-transfer system, we are extending our previous measurements to consider the independent/cumulative yields of another dozen or more short-lived fission products with half-lives on the order of seconds-to-minutes. These new data, combined with our previously measured fission yields, will provide significant data and constraints to fission theory. To this point, theoretical modeling of fission has data sets of fission yields limited to thermal, fission and 14 MeV neutron energies, our new data will now provide theory an evolution of the fission yields over a wide energy range.

NUCL 33

Iridium: Important neutron flux monitor

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Iridium has been used for decades at Los Alamos as a fluence monitor in underground nuclear testing. Iridium can be used to monitor three neutron spectral groups at once, thermal/epithermal, 14 MeV, and fission spectrum (>2 MeV). The nuclear reaction Ir-193(n,n')Ir-193m has not had a model independent cross section, until recently. The first measurement of the cross section was made last fall at the Berkeley HFNG.

NUCL 34

Nuclear reaction studies with GODDESS

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One hundred years after Rutherford's first measurement, nuclear reactions continue to be a critical probe of the properties of atomic nuclei and informing the synthesis of elements in the cosmos. The frontiers involve reactions with unstable nuclei and pushing towards the limits of nuclear stability. To realize these studies requires the development of accelerated radioactive ion beams (RIBs) with sufficient intensity for measurements and high-efficiency, large solid angle arrays of detectors of nuclear radiations. Of particular interest is the measurement of neutron-transfer reactions often now with a RIB interacting with a CD_2 target to realize (d,pγ) studies. The Oak Ridge Rutgers University Barrel Array (ORRUBA), an almost a 4-π array of position-sensitive silicon strip detectors, has become a key instrument for these studies. It can now be coupled to large arrays of gamma-ray detectors, such as Gammasphere or GRETINA or in the future GRETA, to realize GODDESS: Gamma-array ORRUBA: Dual Detectors for Experimental Structure Studies. The GODDESS commissioning experiment identified new states in ^{135}Xe with configurations above the N=82 shell closure. The winter 2019 campaign studied the (d,pγ) reaction with beams of ^{30}P and ^{134}Te. The ^{30}P measurement populates ^{31}P states that are mirrors to states populated in the ^{30}P(p,γ)^{31}S reaction that is a potential bottleneck in nucleosynthesis in novae. The ^{134}Te(d,pγ) study could be interpreted as a surrogate for neutron capture on this fission fragment near the r-process path of nucleosynthesis. The present talk will provide an overview of the GODDESS instrumentation and capabilities. Preliminary results from the first measurements would be reported.

NUCL 35

Validation of an indirect method for constraining neutron-capture cross sections

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One of the prevalent questions in nuclear science is the origin of the elements. There are two stellar nucleosynthesis processes considered to be responsible for the production of the majority of the abundances of elements heavier than iron; the slow neutron capture process (s-process) and the rapid neutron capture process (r-process). Both of these processes are characterized by the successive capture of neutrons on

nuclei, with the major differences being the timescale over which they occur and the host environment. The s-process proceeds slowly along the valley of stability and the neutron captures involved are amenable to direct measurements. The r-process takes place in explosive events with high neutron densities which drive material far from stability. The recent observation of a neutron star merger event by LIGO and Virgo and the subsequent electromagnetic followup have demonstrated that the r-process can occur in these rare events, but it has not ruled out other potential astrophysical sites. In order to better understand and model the r-process, many nuclear properties are needed for a large number of nuclei, including neutron-capture cross sections. R-process nuclei are not viable for direct neutron-capture cross section measurements due to short half-lives, so the neutron-capture cross sections are theoretically predicted. Several indirect measurement techniques have been developed to provide experimental constraints on neutron-capture cross sections. One such method is the β-Oslo method, which uses β-decay to populate highly excited states of a nucleus. The resulting de-excitation via the emission of γ-rays is used to extract statistical nuclear properties of the daughter nucleus. These properties are then used as input in a reaction model to constrain the neutron-capture cross section. The β-Oslo method can provide a large number of constrained neutron-capture cross sections far from stability, but it is necessary to validate the method using a direct neutron capture measurement. This method will be validated in the A = 80 mass region with the ^{82}Se(n,γ)^{83}Se reaction. ^{83}Se can be accessed through the β-decay of ^{83}As, which has been studied at the NSCL with the total absorption spectrometer SuN. Using the β-Oslo method, the cross section of ^{82}Se(n,γ)^{83}Se was constrained. The comparison of this constrained neutron-capture cross section to a direct measurement of the neutron capture on ^{82}Se using DANCE at LANL will be presented.

NUCL 36

Constraining neutron-capture reactions through the surrogate reactions method

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While neutrons were not discovered until 1932 [1], already in 1920 Sir Ernest Rutherford had hypothesized the "possible existence of an atom of mass 1 which has zero nucleus charge" [2] to explain the constitution of elements heavier than hydrogen. Since then we have come to understand that nuclear reactions involving the capture of a neutron touch every area of modern life. We exist because many of the elements heavier than iron were created in stars in a process that involves the rapid capture of neutrons (the *r* process). Our understanding of neutron capture reactions plays an important role in safe nuclear power generation and in guaranteeing the reliability of our nuclear stockpile without a return to testing. However, it is not possible to constrain important neutron-capture cross sections on many of the isotopes of interest to these processes, due either to the unstable nature of the target or the neutron.

Because understanding the neutron-capture reaction is so important to our society, there has been an increased effort in recent years to develop indirect methods to constrain the cross section for this reaction on unstable nuclei. The surrogate reactions method, in which a reaction is chosen which will form the "same" compound nucleus as the desired (in this case neutron-capture) reaction, is one such technique. The decay of the compound nucleus is measured, and the resulting data are used to constrain the calculation of the neutron-capture cross section. This method has recently been benchmarked using a measurement of the ^{95}Mo(d,p) reaction against the available ^{95}Mo(n,γ) cross section. There is excellent agreement between the experimentally-constrained and known cross sections. A century after Sir Ernest's first reaction, this study opens the door to exciting new measurements in the vibrant field he was instrumental in creating.

NUCL 37

Shapes and transition rates in nuclear structure, the case of ^{78}Ge

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The discovery of nuclear reactions 100 years ago was understood to arise from the collision of two "undifferentiated objects undergoing an interaction leading to two new nuclei, but without distinction about the nature of the process. As the neutron had not yet been identified, or even postulated, shape and structure were not a part of the discussion. Research continued to reveal that nuclei appeared to be spherical, with neutrons and protons arranged in quantum-mechanically determined shells. Then, along came data showing not only spherical shapes, but also both football-shaped (prolate) and doorknob (oblate) shapes. In each case, transition-rate calculations were associated with collect motions of the neutrons and protons. In this presentation, the structure and transitions rates for ^{78}Ge will be discussed, which in the descriptions noted above, seems to be Tom Brady's football with too much air removed to resume a rigid prolate shape.

NUCL 38

Advances in nuclear astrophysics measurements in the FRIB era

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Since the discovery of the atomic nucleus, our appreciation of the role of nuclear physics in the universe has expanded dramatically. An understanding of the chemical evolution of the universe, and the energy generation and production rates of individual radionuclides, requires a detailed understanding of reaction rates involving very low

cross sections, or reactions involving unstable nuclei. Many of these unstable nuclei will be available with unprecedented intensities at the Facility for Rare Isotope Beams (FRIB), currently under construction, which will enable many of these reactions to be well-constrained for the first time. In addition to direct measurements at astrophysical energies, transfer reactions, such as (d,p) (d,n) and (3He,d) reactions, can provide constraints on the single-particle properties of bound and resonant states, and can be used are used for surrogate measurements of neutron capture. Advances in instrumentation, techniques and targetry to fully exploit the advances in radioactive beam production. To this end, new instrumentation such as GODDESS (a coupling of the Oak Ridge Rutgers University Barrel Array to GRETINA/GRETA gamma-ray tracking array), the Jet Experiments in Nuclear Structure and Astrophysics (JENSA) gas jet target, and advances neutron detection techniques have been developed. An overview of these devices and their physics in the FRIB era will be presented.

NUCL 39

^{4}He + ^{14}N --> ^{18}F*: What comes next?

***Paul J. Karol**, pk03@andrew.cmu.edu. Chemistry, Carnegie Mellon University, Palo Alto, California, United States*

Arguably more influential than his investigations into “disintegration of the elements and the chemistry of radioactive substances” that were recognized with the 1908 Nobel Prize in Chemistry is the work spawned by Rutherford’s exploration of alpha ray interactions with light elements, hydrogen, oxygen and nitrogen. In 1919, the latter result surprised the world by revealing the proton, by establishing artificial transmutation, and by revealing nuclear fusion reactions to the scientific world. Rutherford’s discovery essentially catalyzed an explosion of developments, many controversial, in nuclear science, a two decade old field which at the time was still very puzzling. Rutherford’s powerful insight foreshadowed the hypothesis of the neutron in 1920 as a neutral proton/electron doublet and the extension of nuclear reaction studies to neutron capture and copious energy release. An early advocate of accelerators, Rutherford by 1927 was urging his students to develop means of producing higher energy bombarding particles. Tracing the many developments germinated by Rutherford’s 1919 discovery, we will conclude with the apt fusion of californium and the three-alpha cluster, carbon-12, to produce the eponymous rutherfordium, element 104, a half century later.

NUCL 40

Measurement of neutron-capture cross sections of copper isotopes with DANCE for constraining s-process nucleosynthesis

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Understanding the origin of the elements comprising our universe as well as the environments in which they are synthesized is of paramount importance to the nuclear physics community. Most of the isotopes of elements heavier than iron are created via the slow (s-process) and rapid (r-process) neutron-capture processes, and thus accurate determination of the relevant neutron-capture cross sections is important. Two such isotopes, important for s-process nucleosynthesis, are ^{63,65}Cu where, until recently, large discrepancies between measured cross sections have introduced substantial uncertainties in s-process nucleosynthesis yields. In this talk a recent measurement of ^{65}Cu(n,g) using the Detector for Advanced Neutron Capture Experiments (DANCE) will be discussed. The impact of this work, coupled with two additional results from other recent DANCE measurements of ^{63}Ni and ^{63}Cu, was studied using s-process nucleosynthesis models. The results of that investigation will also be presented.

NUCL 41

Production of heavy actinides for support of superheavy element discovery

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The Radiochemical Engineering Development Center (REDC) in conjunction with the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) has supplied valuable and unique actinide materials to the scientific community for many years. Bombardment of actinide targets produced at ORNL with neutron-rich nuclear beams at Dubna, GSI, RIKEN, and other facilities results in the production of Superheavy Elements (SHEs) and has contributed to the discovery of elements 115 and 117. Experiments using ^{50}Ti, ^{51}V, and ^{54}Cr beams on ^{254}Es ($T_{1/2}$ 275.7 d) and ^{249}Bk ($T_{1/2}$ 329.9 d) targets may lead to the discovery of new elements Z=119, 120, and 121. Heavy actinides ^{249}Bk and ^{254}Es are currently produced as by-products during the biennial production of ^{252}Cf ($T_{1/2}$ = 2.7 y) from mixed curium targets. However, the quantities produced through this process are insufficient for expected future demand. In recent years the capabilities for isotope optimization have been improved and demonstrated through both modeling and simulation and small-scale experimental irradiations. These tools have been applied to the production of ^{249}Bk and have shown the potential for a threefold increase in the typically expected yield per unit of ^{248}Cm in the target through application of a 2 mm thick natural gadolinium filter. A target has been designed for experimental validation of this methodology, and irradiation is planned for later in 2019. Further research is under way to apply these techniques to the production of ^{254}Es.

NUCL 42

Laser-induced breakdown spectroscopy for nuclear forensics: Current trends, advancements, and challenges

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Laser-Induced Breakdown Spectroscopy (LIBS) and the related technique of Laser-Ablation Molecular Isotopic Spectroscopy (LAMIS) have seen significant progress in technological maturity and applicability to forensics. These techniques offer advantages including the potential for rapid chemical analysis with minimal or no sample preparation, the ability to identify several elements with a single measurement, and recently isotopic determination has become more reliable. Yet, critiques of the technique remain and must be addressed before widespread use is adopted. Recent progress in the development of LIBS and LAMIS for nuclear forensics applications and remaining challenges will be discussed.

NUCL 43

Handheld LIBS analysis of post-detonation synthetic nuclear melt glass

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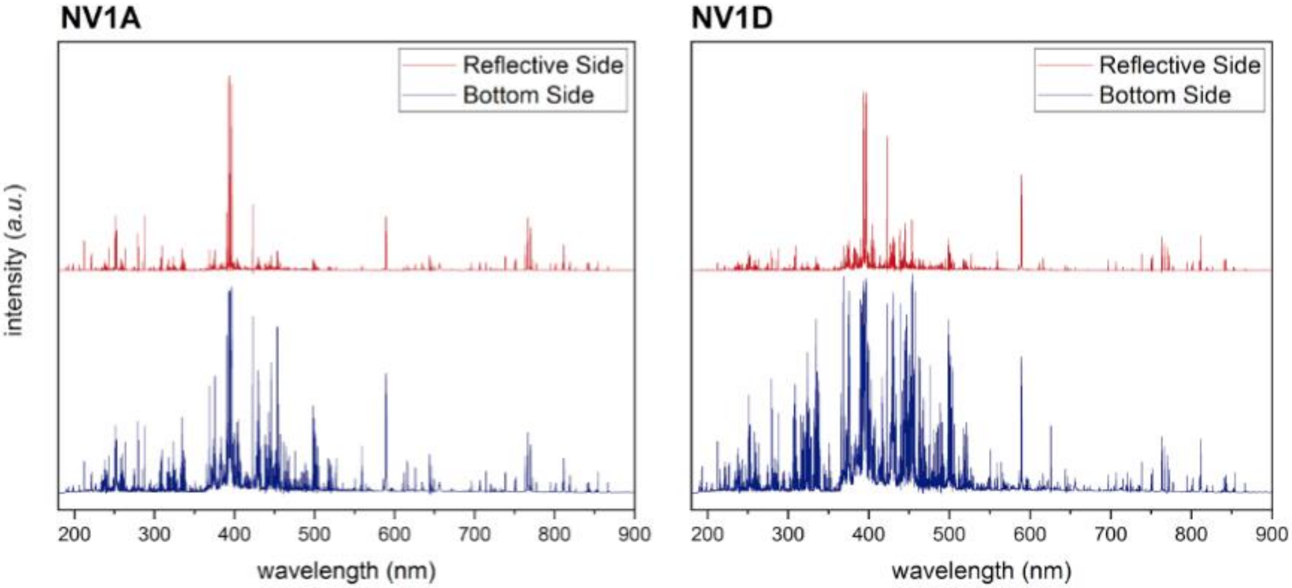
Nuclear debris, resultant in the event of a nuclear detonation, undergoes a complex formation process resulting in a glassy mixture of radioactive and non-radioactive components. The task once this process finalizes is to accurately identify from those glasses what type of device was used and where did the material originate from, which considers all avenues of procurement including material diverted from nuclear energy facilities. The determining factor of these two questions arise from an exact understanding of the glass composition, including types of elements and their abundance. In this study, the SciAps Z300 LIBS was utilized to measure a variety of post-detonation synthetic material. The LIBS contains a 3B laser with a wavelength of 1064 nm and an average power of 3.8E-01 W, capable of operating with no sample preparation, no calibration, and at ambient condition. The samples measured include underground test surrogates from an undisclosed location (LANL 1), as well as three underground Nevada Test Site surrogates (NV1X). Each of these samples were measured on the reflective top side and on the matte finished bottom side, and the data was processed instantaneously. The results of NV1A and NV1D are shown below with agreeable spectra. These LIBS software provides the relative abundance of elements which require a fair amount of sophisticated data processing in order to quantify. The methodology for accomplishing this is discussed in the following presentation.



NUCL 44

Production and characterization of uranium-containing particles for nuclear safeguard applications

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The International Atomic Energy Agency routinely performs the collection and analysis of environmental samples from declared nuclear facilities as part their international nuclear safeguards mission. The samples typically contain actinide-bearing particulates which are generated from facility activities. Secondary ion mass spectrometry (SIMS) is the primary analytical method used for the trace particulate characterization for these environmental samples. Although reference uranium oxide powders are available to support SIMS QA/QC, from both US and European government sponsored suppliers, they lack the desired monodisperse micron-sized characteristics and have limited isotopic compositions. Particulate materials with well characterized size, chemical/structural composition, and tailored isotopic content are needed for international proficiency testing and microanalytical method development activities. SRNL has engineered a production tool capable of synthesizing the required uranium particles called the monodisperse particle production and collection system (MPPaCS).

The system can produce highly monodisperse uranium-bearing particulates with tailored diameters between 0.5-5 microns and was engineered with in situ particle characterization capabilities, via an aerodynamic particle sizer. Generated particles are collected either by electrostatic precipitation with an SRNL-built collector or by impaction via commercial tools. To date, uranium particulates have been produced as UO_3 hydrate or uranyl oxalate dependent on MPPaCS operational parameters and feedstock chemical composition. Post production, the characterization of test particulates has been done with Raman spectroscopy, SEM/EDS, and SIMS. Related calculation methods have been developed to solve the optimization problem of feedstock generation via mixed ratio of certified reference materials. Future efforts will be discussed and include the development of plutonium and mixed actinide particle production methods.

NUCL 45

Optimizing ligand design for selective binding to lanthanides and actinides

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Selective separations of rare earth elements and actinides is needed for electronics, various energy needs, medical, military and nuclear applications. Computational methods have proven to be essential in optimization of selective binding and characterization of highly radioactive systems, and well as for those with short half-lives for which traditional experimentation is limited. Complexation of lanthanides and actinides in gas and liquid phases will be presented, with emphasis on electronic structure methods including single- and multi-reference descriptions including Density Functional Theory (DFT), coupled-cluster with single, doubles, and perturbative triples [CCSD(T)], second-order Møller-Plesset perturbation (MP2), Complete Active Space Second-Order Perturbation Theory (CASPT2), and Dirac-Hartree-Fock.

NUCL 46

Dynamic separation of Eu^{3+} and Nd^{3+} using bis-(2-ethylhexyl) phosphoric acid functionalized ordered mesoporous carbon nanoparticles

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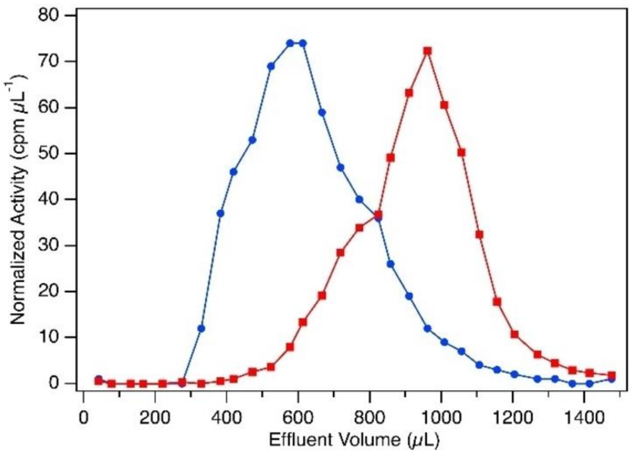
In a post-detonation event, attribution of the nuclear material must be done quickly. The presence of lanthanides contained within nuclear debris can serve as a characteristic “fingerprint” for the source material which, in turn, can provide valuable information regarding the nuclear material along with the device design. The rapid separation of lanthanides from post-detonation debris could be made possible through the use of small, unpressurized columns. The lanthanides, having a predominantly trivalent oxidation state, are notoriously difficult to separate. As such, small differences of their ionic radii and subsequent binding strengths are relied upon for separation. Bis-(2-ethylhexyl) phosphoric acid (HDEHP) demonstrates a difference of five orders of magnitude in selectivity between La^{3+} and Lu^{3+}. Here, ordered mesoporous carbon (OMC) nanoparticles were chosen as a chromatographic support for HDEHP due to their small particle sizes, large pore volumes, high surface areas, and inherent stability in acidic environments. The HDEHP-OMC materials were investigated for Eu^{3+} uptake and maximum adsorption capacities under static and dynamic conditions and compared to the current state-of-the-art lanthanide chromatographic resin, LN Resin. The dynamic separation of Eu^{3+} and Nd^{3+} suggests that HDEHP-OMC materials could be used in small, unpressurized column systems with an improved separation efficiency over the current state-of-the-art material.



Volume normalized chromatogram of a $^{147}Nd^{3+}$ (blue circles) and $^{154}Eu^{3+}$ (red squares) separation using HDEHP-OMC.

NUCL 47

Functionalized polymer thin films for plutonium capture and isotopic screening from aqueous sources

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The detection and screening of plutonium in environmental samples is critical for nuclear forensics and nonproliferation efforts. Direct measurement of waterborne plutonium is challenging due to its low solubility. Techniques for isolating and concentrating plutonium for isotopic screening are time-consuming and often have to be performed offsite. The ability to perform rapid, onsite analysis of plutonium in aqueous sources would be a powerful nuclear forensics tool, but currently no such technology exists.

In this study, we investigated the use of functionalized polymer thin films for the extraction and isotopic screening of waterborne plutonium via alpha spectroscopy. Polymer-ligand films were prepared by casting polystyrene and Pu-binding ligands onto 30 mm diameter silicon wafers through spin coating. This method of film casting provided a high-degree of control over the thickness and surface uniformity. Three polymer-ligand combinations were compared for their ability to capture plutonium from water at low and circumneutral pH, and the plutonium recovery and isotope peak resolution were determined for films with thicknesses from 25 to 250 nm.

Plutonium uptake studies were performed by exposing the polymer-ligand samples for 3 h to 0.5 mL of a ^{242}Pu solution, followed by a wash step to remove unbound plutonium from the surface. Isotope peak resolutions given as full width at half maximum (FWHM) for the samples containing di(2-ethylhexyl) phosphate, thenoyltrifluoroactetone, and dibenzoylmethane were measured to be 30-60 keV. At pH 2, only the films loaded with di(2-ethylhexyl) phosphate showed significant plutonium uptake ranging from 22 to 35%. Unexpectedly, FWHM and plutonium recoveries did not correlate with film thickness. Additional results will be presented from subsequent measurements designed to test the hypothesis that plutonium is isolated primarily at the polymer film-solution interface due either to slow diffusion through the film or accumulation of the ligands at the interface. These include results from tests performed at longer exposure times and circumneutral pH, along with spectroscopic measurements to quantify interfacial ligand concentrations.

NUCL 48

Potential strategies for uranium chronometry using nuclear counting techniques

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Over the last several years there have been successful efforts to develop new radiochronometry methods for uranium based on parent/progeny pairs of U-234/Ra-226, U-235/Ac-227, and U-235/Pa-231 beyond the more traditional U-234/Th-230. All of these newer methods have benefited from the significantly improved sensitivity of mass spectrometry instrumentation. However, they have also confined themselves to measuring radioactive decay progeny with longer half-lives: Ra-226 (1600 years), Ac-227 (21 years), Th-230 (75,380 years), and Pa-231
(32,670 years). This presentation will examine potential strategies for uranium radiochronometry determinations based on nuclear counting techniques.

NUCL 49

Characterization of chemical signatures from ADU and AUC materials

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There is a need to properly identify and characterize nuclear materials in order to understand how chemical signatures may be indicative of material origin. We have chosen to study two uranium materials common to the nuclear fuel process: ammonium diuranate (ADU) and ammonium uranium carbonate (AUC), which are precipitates formed during the production of UO_2. We prepared a series of ADU and AUC compounds using variations in temperature, pH, reaction stirring rate, rate of addition of reagents, and concentration of uranium starting materials. Each compound was characterized with powder X-ray diffraction (pXRD), scanning electron microscope (SEM) imaging, thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and SEM image analysis with Morphological Analysis for Material Attribution (MAMA) software. These characterization methods were used to identify differences in chemical composition and morphology, which may be correlated to the synthetic method. These differences and their potential correlations will be discussed.

NUCL 50

Selective separation of americium from europium using 2,9-diamide-1,10-phenanthroline in ionic liquids

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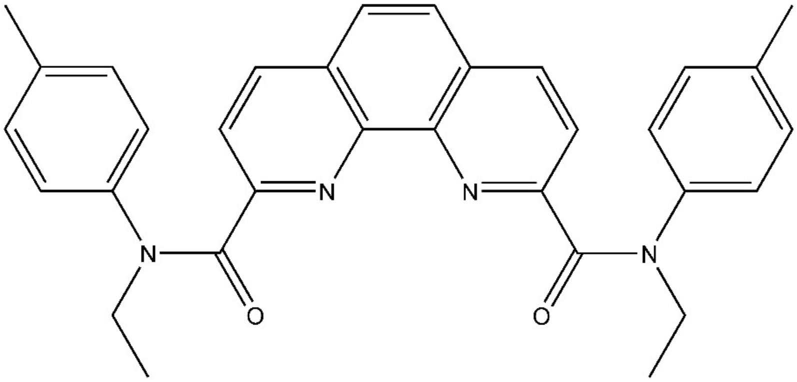
The extraction behaviour of Am^{3+} and Eu^{3+} by a novel phenanthroline based tetradentate ligand combining hard O-donor and soft N-donors in the same molecule,

N,N'-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen), from nitric acid medium (0.001 M to 2 M) was studied in ion liquids (ILs) to evaluate the feasibility of the Ln^{3+}/An^{3+} separation from nuclear wastes. The effects of contact time, temperature, extractant concentration, acidity, NO_3^- and NTf_2^- on the extraction were investigated. Significant enhancement in the extraction ability of Et-Tol-DAPhen dissolved in ion liquids was observed as compared to that in molecular diluents with a D_{Am} in excess of 200 at low extractant concentrations. The chemical stoichiometry of Am^{3+} and Eu^{3+} complexes with Et-Tol-DAPhen is determined to be 1:1 by the slope analysis of the extraction data. By comparing such results with the extraction in molecular diluents, the extraction mechanism of Am^{3+} and Eu^{3+} in ion liquids was determined. The present study suggests that Et-Tol-DAPhen/ILs system is promising to be used in the Ln^{3+}/An^{3+} separation and provides basis data required for developing chemical processes for separation.



The structure of Et-Tol-DAPhen

NUCL 51

Structural and thermodynamic factors underlying the Ln(III)/An(III) selectivity by Di-2,4,4-trimethylpentyl dithiophosphinic acid

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Complexation of trivalent lanthanides (Ln(III)) and actinides (An(III)) with a sulfur-bearing ligand, bis(2,4,4-trimethylpentyl) dithiophosphinate (C301), was studied by optical spectroscopy, microcalorimetry, luminescence lifetime measurement, and Extended X-ray Absorption Fine Structure (EXAFS). An(III) such as Cm(III) forms much stronger complexes with C301 than that of representative Ln(III) such as Nd(III). Moreover, in contrast to the general findings that heavier lanthanides form stronger complexes due to lanthanide contraction effect, the complexation strength between Ln(III) and C301 first increases from La(III) to Nd(III) and then decreases gradually toward heavier Ln(III) across the lanthanide series. The above trends agrees well with the results of solvent extraction using C301 as an extractant. The structural and thermodynamic factors underlying the Ln(III)/An(III) selectivity by C301 were further analyzed. A correlation between the thermodynamic trends and the coordination modes has been well established.

NUCL 52

Separation of transplutonium elements as part of the ORNL californium campaigns

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New neutral ligands are being investigated to separate trivalent actinides and lanthanides from other fission product and trivalent actinides from lanthanides but also to separate americium from curium. Production of californium-252 has been an ongoing process at the Radiochemical Engineering Development Center at Oak Ridge National Laboratory since the mid 1960s. The chemistry of the mandatory steps to go from the dissolution liquor of the irradiated curium targets to the purified californium product was established several decades ago, and only minor changes have been made along the way. New ligands are now available, and a new look is being taken to improve separations processes by eliminating the need for use of chloride and tantalum equipment, reducing the operation time in the hot cells, and making the waste stream less challenging to handle. Our goal is to take the acidic dissolver solution and use it immediately with minor feed adjustment. The ligand tetraoctyldiglycolamide (TODGA) is particularly attractive as its extractive properties match our requirements. Results obtained on a small scale with actual feed solution from two recent californium production campaigns showed promising progress and will be presented. Tests were also carried out with similar solutions containing only americium and curium using a ligand similar to TODGA but where the glycolic oxygen has been replaced by an amino group. These molecules have been shown to provide some separation of americium from curium at low levels and were tested with actual hot-cell solutions.

NUCL 53

Density functional theory analysis of the adsorption and surface chemistry of inorganic iodine species on graphite

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Releasing radionuclides of iodine (*e.g.*, ^{131}I) into the atmosphere presents a major concern during a nuclear emergency such as the Fukushima incident in 2011. Iodine's affinity for the thyroid gland makes radioiodine a significant, health concerning, biological hazard and necessitates important efforts to minimize its discharge into the atmosphere. Activated carbon, impregnated with KCl or DABCO (1,4-diazabicyclo[2.2.2]octane), routinely provides the means to hold up iodine-containing molecules and mitigate their release. The interactions between activated carbon and inorganic forms of iodine remain poorly understood. Using graphite or graphene as a surrogate for activated carbon, previous studies have analyzed the adsorption behavior of methyl iodide. However, these studies ignore the adsorption of acidic iodine species (*e.g.*, HI, HOI, HIO_2, and HIO_3) on activated carbon. We present a density functional theory analysis of the adsorption of these molecules on the basal (0001) plane of graphite. Characterizing the preferred adsorption sites, geometries, and binding mechanisms for these molecules on pristine graphite further clarifies the species that are most easily captured. We compare the binding energies between other common species to assess how reactive the surface is for the iodine-containing molecules. Additionally, we analyze the co-adsorption and select surface reactions between the most likely surface species. These effects help us predict the speciation of iodine on the surface and its influence on the molecules likely to be released from the activated carbon bed. Our computational analysis provides insights that will aid in the future design of capture materials based on activated carbon beds for the purpose of mitigating release of radioiodine into the atmosphere during a nuclear disaster.

NUCL 54

Radiation-resistant, ultra-microporous materials for efficient removal of krypton from nuclear reprocessing facilities

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Reprocessing of used nuclear fuel (UNF) is a prerequisite for any future expansion of civilian nuclear power. Major challenges during the reprocessing of nucler fuel is the release of volatile radio nuclides that must be captured and subsequently stored for an extended period of time before being released into atmosphere. While methods such as cryogenic distillation and fluorocarbon based absorption have been proposed and tested, solid state adsorbents in particular permanently porous Metal-Organic Frameworks (MOFs) are considered better alternatives in terms of cost and engineering control to capture these volatile radionuclide including ^{85}Kr (t1/2 = 10.8 years). However, because of presence of more polarizable Xe during the reprocessing, adsorbent materials including MOFs are found to be more Xe- philic than Kr. To address this challenge, a two-bed breakthrough method is being developed herein which leads to enhanced Kr adsorption and separation of ^{85}Kr during nuclear reprocessing. The extent of enhancement of Kr adsorption depends on the nature of adsorbing materials. Here, we evaluate the Kr adsorption capability of a series of hybrid ultra-microporous materials, namely SIFSIX-3-M (M= Zn, Cu, Ni, Co or Fe) for Kr adsorption and separation performance. The Fe-analogue in particular shows excellent Kr adsorption than the current benchmark materials: CC3, Ag-mordenite, NiMOF-74 and SBMOF-1, under simulated nuclear reprocessing off-gas conditions. The higher Kr adsorption and separation efficacy was attributed to the precise pore diameter of the Fe-analogue for such separation. All materials were systematically studied for gamma irradiation stability, which reveals that the metal center in these isostructural materials plays a crucial role in their irradiation stability. Zn and Ni analogues show phase change at 1KGy, while SIFSIX-3-Fe shows phase change at 3KGy. SIFSIX-3-Co structure was stable up to 10KGy before it undergoes phase change while SIFSIX-3-Cu was the most stable analogue. The phase change of all materials were interpreted using PXRD. These results attest the potential of these materials for Kr removal under the nuclear reprocessing conditions.

NUCL 55

New strategies in nuclear human decorporation using macromolecular systems

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The use of uranium and plutonium as a fuel for nuclear energy production or as components in military applications is under increasing public pressure worldwide. Associated nuclear risks include chronic or acute contamination in the nuclear industry, exposure in case of major accident or military attack, chronic low (to very low) dose effects from naturally (uranium, thorium) or artificially contaminated backgrounds due to mining activities. In case of human exposition, chemical toxicity as well as radiological toxicity (depending on isotopy) may contribute to deleterious health effects. However, the counter measurescurrently available are either not totally efficient or not very selective. Today, the only decorporation drug used in case of emergency is DTPA (diethylenetriaminepentaacetic acid, calcium form) injected intravenously.But it is only valid for removing actinide contamination from blood (mainly Pu), few minutes after contamination. In order to overcome these difficulties, news strategies must be elaborated. Macromolecular systems like biocompatible polymers or functionalized nanoparticles could represent an alternative strategy because of their tropism for specific target organs (bone, lungs, liver, kidneys...). For the skeleton for instance, we have recently explored the complexation properties of methylcarboxylated and methylphosphonatedpolyethyleneimine with uranium, thorium and plutonium. For the

pulmonary alveolar system in case of plutonium exposure, we have designed biocompatible chitosan nanoparticles that are able to release the decorporation agent directly into the macrophages.For all those macromolecular systems, the cation coordination site has been characterized with a combination of analytical and spectroscopic techniques, among which X-ray Absorption Spectroscopy plays a central role. Molecular dynamics and quantum chemical simulations have also been performed as a complement to better understand the atomic arrangement around the actinide cation. The physical chemical approach described here represents a necessary basic chemistry stage before envisioning further biological evaluations.

NUCL 56

Differential ability of leachate produced from leaf litter of different plant species to solubilize U from stable mineral forms

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Dissolved organic matter (DOM) has been shown to profoundly affect radionuclide mobility. Complexation of radionuclides by DOM in solution can increase the total amount of U available for transport. Organic compounds released during leaf litter drives major flows of DOM in soil systems. Based on the molecular composition of the leachable compounds that are present in the leaf litters at the time of senescence plants will exhibit contrasting ability to mobilize radionuclides.
This work, through a series of leaf litter decomposition, batch sorption and dissolution experiments, investigated the differential ability of leachate produced from leaf litter of different plant species to solubilize U form uranyl-phosphate mineral, Chernikovite. The DOC content in litter leachate was higher during the initial stages of decomposition, which decreased during the later stages. The amount of DOC, DON, water-soluble phenolic and tannins varied widely between species and decomposition stage. In most species, a higher amount of DOC (20-50%) and tannin (20-40%) leached from the litter in the first 48 hours of the experiment. Initially the amount of leachable phenolics were relatively low, but increases after 4 weeks. Dissolution of U was enhanced (30-60%) in the presence of all individual litter leachate from different species and the extent of dissolution varied based on the species and decomposition stage. The amount of dissolved U was significantly higher in the presence of leachate collected after 48 hours of incubation comparison to the leachate collected at later harvesting points. Comparable experiments examining the influence of tannins, purified from different species, on dissolution of U indicate the potential of tannin in mobilizing U irrespective of species of origin. Ongoing molecular characterization of litter leachate would generate predictive understanding on specific reactive moieties within litter leachates that enhance radionuclide mobilization from stable mineral forms. These comprehensive approaches provide valuable insight into the chemistry and molecular dynamics of mineral-organic matter interactions, fate, and transport of radionuclides in terrestrial and subsurface ecosystems.

NUCL 57

Leveraging radioanalytical and mass-spectrometry based technologies to investigate iron assimilation and allocation in rhizobacteria-associated maize

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Persistent high-density cultivation farming has led to depletion of essential microelements in soil which can result in decreased crop nutrition. Low nutrient crops contribute to severe, often fatal, micronutrient deficiencies in global populations. This work involves radioanalytical laboratory studies on maize inoculated with *Azospirillum brasilense*, a prolific grass root colonizing bacteria, to investigate bacterial influence on maize iron assimilation and allocation. Dynamic and quantitative maize ^{59}Fe ($t_{1/2}$ = 44.5 d) acquisition and root-to-shoot allocation studies with gamma detection reveal bacteria significantly promote whole-plant iron uptake and root-to-shoot allocation relative to non-inoculated controls. Studies with ICP-MS analysis of digested total plant tissues revealed bacteria inoculated plants had 3.8x more ^{56}Fe than non-inoculated controls, while spatial analysis using LA-ICP-MS of root and leaf sections revealed bacteria associated maize had 5.8x more iron in leaf tissue and significantly more iron in the root endodermis compared to control maize. Radio-HPLC and gamma detection were used in combination with radioactive ^{11}C ($t_{1/2}$ = 20.4 m) to investigate possible mechanisms underlying promotion of iron allocation in maize. $^{11}CO_2$ was administered to maize leaves and changes in partitioning of 'new' carbon into mobile substrate pools were quantified. Metabolism of key iron transport molecules like histidine, citric acid, and nicotianamine were significantly elevated in the presence of the bacteria. Nicotianamine is a precursor to root-excreted iron-chelating phytosiderophores. An increase in phytosiderophore production due to available nicotianamine would account for elevated maize iron uptake.

NUCL 58

Analysis of actinides other than uranium and plutonium by thermal ionization mass spectrometry

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Savannah River National Laboratory has been researching methods for determining the isotopic composition of actinide elements other than uranium and plutonium by thermal ionization mass spectrometry (TIMS). These actinide elements (e.g. americium and neptunium) have similar characteristics to plutonium but can have some analytical challenges. Some of these challenges include isobaric interferences, lack of reference materials for use in characterization or for use as a spike (to measure concentration/yield), and in TIMS it is more difficult to find a proxy element for use than in other forms of mass spectrometry. SRNL used available materials to characterize the ability of TIMS to measure some of the non-traditional actinide elements.

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Single-pass flow-through studies of simulated Hanford low-activity waste glass in varying pH, temperature, and presence of cement-contacted groundwater

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Long-term performance assessment (PA) models are used to assess contaminant and radionuclide transport from the integrated disposal facility (IDF), ensuring the safe disposal of immobilized low-activity waste (ILAW) glass wasteforms at the Hanford Site. Laboratory data is collected for various ILAW glass compositions to determine parameters to populate a rate model of glass dissolution that is used in the PA modelling efforts. To validate the laboratory inputs to the long-term dissolution models, a field demonstration is being performed at the Hanford field lysimeter test facility (FLTF) using glass and cementitious wasteforms.

Borosilicate glass dissolution reportedly occurs through pH-dependent mechanisms. Primarily, glass dissolution occurs through the hydrolysis of the Si-O bonds within the glass network (or other network formers). In the PA rate model, the dissolution rate is controlled by the [Si] in the near-field solution. The soon-to-be initialized lysimeter experiment at the FLTF will replicate the disposal scenario where the contact solution will be equilibrated with the surrounding backfill soil. One candidate configuration for an individual FLTF test cell (not yet planned for actual disposal in the IDF) stores cementitious-based material above glass waste material, and investigates how cementitious material affects the near-field solution and glass dissolution. Our objective is to quantify the effects of cement-contacted groundwater on glass dissolution in laboratory experiments to help design this potential cementitious/glass lysimeter configuration predict long-term glass dissolution in environments containing cementitious-based materials.

Single-pass flow-through (SPFT) experiments were carried out to determine the dissolution behavior of ILAW glass ORLEC28 in a wide range of pH (8-12) and temperature (25°C, 40°C, 70°C) to establish baseline dissolution behavior. The SPFT

method keeps the glass in dilute conditions, allowing determination of the dissolution behavior without precipitation or solution effects. The contact solution composition was then varied to mimic the equilibrated groundwater and presence of cementitious material.

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Dynamics of organic molecule-ion and water-ion complexes in concentrated aqueous salt solutions: 2D IR chemical exchange spectroscopy

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Aqueous salt solutions occur widely in systems ranging from industrial processes to biological materials. Prominent examples include batteries and the salt balance in living organisms. The properties of aqueous electrolyte solutions involve the dynamics of water and the dynamics of ions. In concentrated salt solutions, ions will associate with water as well as with polar organic molecule solutes. The dynamics of the formation and dissociation of complexes of Li^+ and water with methylthiocyanate (MeSCN) are explicated using two dimensional infrared (2D IR) chemical exchange spectroscopy. The CN stretch is used as the vibrational probe. Water forms a hydrogen bond (H-bond) with and Li^+ associates with the nitrogen lone pair of the CN moiety of MeSCN. These two complexes display distinct CN peaks in the FT-IR spectrum. In the 2D IR spectrum, at short time there are two peaks on the diagonal, corresponding to the two peaks in the FT-IR spectrum. At longer times, off-diagonal peaks grow in, which arise from the MeSCN-H_2O going to MeSCN-Li^+ and MeSCN-Li^+ go to MeSCN-H_2O. The growth of the off-diagonal peaks yields the rate constants for association and dissociation of the complexes. The concentration dependence of the exchange was studied and used to extrapolate to infinite dilution. Chemical exchange spectroscopy was also used to study the time for water to go from forming an H-bond bond to the anion, BF_4^-, to forming an H-bond with another water molecule. The OD stretch of HOD is used as the vibrational probe. Water-water and water-BF_4^- have distinct peaks in the spectra, and again the growth of off-diagonal peaks gives the chemical exchange time.

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Oxyanion aqueous solvation structure and alkali ion pair interactions in concentrated electrolytes

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An atomic-level description of ion pairing phenomena in solvated oxyanions salts (i.e sodium aluminate, calcium carbonate, potassium nitrate) remains a subject of intense

exploration due to cross-cutting importance across industrial processing conditions. Important questions surround the water solvation structure and dynamics under different electrolyte concentration regimes, the extent and energetics of ion-pair formation (i.e contact vs solvent separated ionic pairs) and reactivity. The aluminate anion is of particular interest for the nuclear industry due to its high concentration in Hanford nuclear waste tanks and its paramount influence in precipitation/dissolution processes that occur there and in aluminum processing conditions. In this work, we explore oxyanions' water solvation environment and ionic interactions with alkali metals through the lens of ab initio molecular dynamics. We primarily focus upon Na^+-aluminate interactions at the dilute limit and with the inclusion of OH^- species to simulate solvent basicity. Preliminary results show the different nature of aluminate ion-specific interactions (i.e Li^+, Na^+ and K^+) and the extent of disruption of the water solvation environment in each of these systems

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Towards a realistic modeling of ion hydration, one molecule at a time

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I will describe recent developments of our many-body molecular dynamics (MB-MD) methodology that enables computer simulations of ion hydration from the gas to the condensed phase, with chemical and spectroscopic accuracy. MB-MD is a unified molecular dynamics framework that combines many-body representations for potential energy, dipole moment, and polarizability surfaces that are derived entirely from correlated electronic structure data-driven approaches, with quantum dynamics methods that explicitly account for nuclear quantum effects. In particular, I will discuss the accuracy and predictive ability of the MB-MD methodology in the context of molecular modeling of aqueous ionic systems, from gas-phase clusters to bulk solutions and interfaces, with a particular focus on the relationships between structural and dynamical properties and vibrational spectra.

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Nonlinear optical studies of cooperative adsorption to lipid films: Role of buffers

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Surface-specific vibrational spectroscopy along with surface tension anddifferential scanning calorimetry measurements were employed to examine cooperative adsorption of glucuronic acid (GU) to lipid monolayers deposited on the aqueous/vapor interface. Experiments were performed using GU solutions prepared in Millipore water and in carbonate/bicarbonate solutions buffered to a pH of 9.0. The effects of GU on DPPC monolayer structure and organization were carried out with tightly packed monolayers (40 Å^2/DPPC) and monolayers in their liquid condensed phase (55 Å^2/molecule). Surface tension data show that GU concentrations of 50 mM lead to expanded DPPC monolayers with diminished surface tensions (or higher surface pressures) at a given DPPC coverage relative to monolayers on pure water. With unbuffered solutions, GU induces significant ordering within liquid condensed monolayers although the effects of GU on tightly packed DPPC monolayers are less pronounced. GU also induces a second, higher melting temperature in DPPC vesicles implying that GU (at sufficiently high concentrations) strengthens lipid-lipid cohesion, possibly by displacing water solvating the DPPC headgroups. Together, these observations all support a cooperative adsorption mechanism. In buffer solutions, the effects of dissolved GU on DPPC structure and organization are muted. Only at sufficiently high GU concentrations (when the solution's buffering capacity has been exceeded) do the data again show evidence of cooperative adsorption. These findings place limits on cooperative adsorption's ability to enrich interfacial organic content in high salinity environmental systems.

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X-ray emission spectroscopy at X-ray free electron lasers: Limits to observation of unperturbed electronic structures

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Modern free electron lasers provide intense X-ray pulses with ~10^{12} photons within ~10-100 femtoseconds. Such pulses enable new experimental techniques and provide unique opportunities for investigation of electronic and nuclear dynamics on their intrinsic time-scales. Interaction of ultra-bright, ultra-short X-ray pulses with matter can induce a multitude of nonlinear excitation processes which must be carefully considered when planning spectroscopic measurements and interpreting data recorded at XFELs. In most cases correct interpretation of the spectroscopic response and analysis of the electronic structure hinges on the assumption of single photon excitations. Here we attempted to answer the fundamental question on the limits to probing the ground (or native) electronic structure of a 3d transition metal ion at XEFL sources. Ions of the 3d transition metal (Mn^{2+}) in a lighter element (O, C, H) environment were used as a model system. X-ray emission spectroscopy recorded from Mn^{2+} at different pulse conditions demonstrate spectral changes as a function of increased pulse intensity and pulse duration. To explain these changes, we develop a rate equation based on sequential ionization and relaxation events forming multiply ionized states during a single pulse which agree with observed spectroscopic trends. The percentage of Mn Kβ emission recorded after the 1st, 2nd and 3rd 1s ionization events is calculated from the developed rate equation model and validated by experimental measurements. A method for estimating shifts in atomic X-ray emission lines from sequential ionization during a single XFEL pulse is given. From our data we infer that, in addition to multiple

ionization, the impact of electron cascades is more significant for longer pulses. We note that while use of shorter X-ray pulses will help to counteract additional effects of electron cascades it will not help to overcome the spectral shifts due to sequential ionization. Presented data and associated analysis will help with experimental designs at current and upcoming XFELs where even higher intensities and shorter pulses are expected. 3d elements have a variety of important applications such as in bio-inorganic catalysis, chemical catalysis and energy storage / conversion making robust protocols for their XFEL analysis of general importance

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Coarse-grained modeling of ion transport in complex fluids

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The dynamics of ions and mesoscale structure in complex organic fluids is a fascinating fundamental science problem with deep implications for many important energy, chemical, and biological systems. Many recent studies have indicated that ion dynamics and transport can be strongly influenced by the hierarchical mesoscale ordering and internal interfaces that often occur in these systems. In particular, it has been proposed that heterogeneous structure may produce heterogeneous dynamics, as well as strong solute size and charge dependence. Although the equilibrium structure and phase behavior of complex fluids has been the subject of much study, there is a need to characterize the dynamics to understand and control ion transport, complexation, and aggregation processes. We will present results from our recent work on the use of machine learned coarse grained models to describe water. We will also discuss our recent coarse-grained simulations performed over several microseconds timescales to elucidate the dynamics of the complexation and aggregation in reverse micelles as a function of surfactant, organic and water concentrations. The results of the simulations are validated using x-ray photon correlation spectroscopy (XPCS) to unravel the microsecond time scale dynamics inherent to nanostructured liquids.

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Investigations of the role of water for promoting hydride transfer during catalytic hydrogenation of CO_2

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This talk will describe recent efforts from our group to understand the role of water in the hydrogenation of CO_2 to formate using molecular catalysts. Hydride transfer is a critical step in hydrogenation of CO_2, and recent efforts from our group and others have demonstrated that water plays a key role in promoting hydride transfer from the catalyst

to CO_2. As one example, we recently reported that a cobalt phosphine catalyst is able to access a new catalytic pathway in water that is not available in organic solvent. Due to the change in mechanism in water, catalysis can proceed using bicarbonate as a base instead of a strong organic base, however, this benefit is partially offset by a decrease in the catalytic activity. Ongoing studies are focused on further improving catalysis by using binary mixtures of water and organic solvents.

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Salt solubilities in aqueous solutions of $NaNO_3$, $NaNO_2$, NaCl, and NaOH: Hofmeister-like series for understanding alkaline nuclear waste

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Non-electrolyte solubility in electrolyte solutions follow the Hofmeister Series, but the applicability of the Series to salt solubility has been less appreciated. This study, using solubility data for thirteen sodium-bearing salts, shows that salts are consistently salted-out by electrolytes important to alkaline nuclear waste in the order $NaOH>NaCl>NaNO_2>NaNO_3$ at 298.15 K, which is the same order as the Hofmeister Series. Graphical presentation allowed for easy separation of the common ion effect (caused by the addition of Na^+) from the salting-out effect (caused by the presence of anions) because there is a large difference between the solubility of a given salt in different background electrolytes at a common Na^+ molality. The trend persists even in very high electrolyte concentrations where essentially all of the water molecules must be in the coordination sphere of an ion, which means that the effect of electrolytes on “bulk water” is not the cause of the trend. These specific interactions more likely result from the sharing of water molecules between ions, augmented by differences in ion-pairing of the electrolytes. The Hofmeister Series has practical application to the management of alkaline high-level radioactive waste created at nuclear fuel reprocessing facilities, where a predictive understanding of salt solubility is essential for blending wastes of disparate compositions prior to treatment.

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Sorption behavior of Nd^{3+}, Th^{4+}, and UO_2^{2+} to dolomite in high ionic strength systems and the effect of EDTA

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The Waste Isolation Pilot Plant (WIPP) is a deep geologic repository that is currently accepting transuranic radioactive (TRU) waste from historic weapons production for long-term disposal. Development of an accurate risk assessment model is necessary for future performance assessments (PA) of the WIPP. To develop an accurate model, a better understanding of the fate of actinides and lanthanides in the WIPP environment is necessary.

The WIPP is characterized by high ionic strength solutions (up to 7.4 M) due to the high concentration of salt within the bedded salt formation. There is a need to investigate the complex WIPP environment including interactions in the presence of high ionic strength, carbonate, and potential ligands identified in waste disposed of at the WIPP (e.g. EDTA). Therefore, the focus of this work is to understand the interactions of stable oxidation state analogs for the actinides with carbonate and EDTA.

Batch experiments have been carried out to determine the behavior of Nd^{3+}, Th^{4+}, and UO_2^{2+} reacted with dolomite in the presence and absence of EDTA. The ionic strength of the system was varied (0.1 to 5.0 M NaCl). Additionally, two WIPP-relevant synthetic brines were studied, including the U.S. Energy Research and Development Administration Well 6 (ERDA-6, 95%) and generic weep brine (GWB, 95%). Dolomite from the Culebra formation above the WIPP was used as this is the most transmissive layer above the WIPP. Contaminant concentrations were varied from 10 µg/L to 1000 µg/L with Nd, Th, and U in the aqueous phase measured by ICP-MS.

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Exploring the role of electrolyte concentration in aluminate dimerization

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Essential to industrial processing of concentrated electrolytes that exist as nuclear waste (Hanford site, WA) or Bayer liquers alumina (Bayer process) is understanding the chemical transformations of Al(III). Herein, $Al(OH)_4^-$ is the predominant aqueous aluminum species under basic conditions, with Raman spectroscopy also supporting the presence of the dimeric aluminate species $Al_2O(OH)_6^{2-}$. No indisputable evidence exists for other dimeric or higher-order oligomeric species in these conditions, which hinders the understanding of the early stages of nucleation and crystallization of aluminum hydroxides and oxyhydroxides (e.g., gibbsite, boehmite). In this work, we explored the free energy profile of the dimerization by means of umbrella sampling density functional tight-binding using the monomer-monomer distance as a biasing collective variable. At infinite dilution, $Al_2(OH)_8^{2-}$ is formed and aluminate-sodium contact ion pairing interactions have no effect on the energetics of the dimerization itself. However, even at

moderate NaOH concentrations the $Al_2O(OH)_6^{2-}$dimer is systematically formed rather than $Al_2(OH)_8^{2-}$, consistently with the decreasing water activity. For a given reaction pathway, the NaOH concentration influences the reaction and activation energies, due to the varying charge transfer and polarization contributions.