American Chemical Society

Division of Nuclear Chemistry and Technology
248th ACS National Meeting, San Francisco, CA, August 10-14, 2014

J. Braley, Program Chair; P. Mantica, Program Chair

SUNDAY MORNING

Nuclear Fusion: From NIF To the Stars

M. Stoyer, Organizer; L. Bernstein, Organizer; L. Bernstein, Presiding; M. Stoyer, Presiding Papers 1-6

High-Level Waste Storage

N. Wall, Organizer; M. Boggs, Organizer; M. Boggs, Presiding; N. Wall, Presiding Papers 7-14

SUNDAY AFTERNOON

Comprehensive Test Ban Treaty Verification

H. Hall, Organizer; S. Liddick, Organizer; S. Biegalski, Organizer; H. Hall, Presiding; S. Liddick, Presiding; S. Biegalski, Presiding Papers 22-29

Nuclear Fusion: From NIF To the Stars

M. Stoyer, Organizer; L. Bernstein, Organizer; L. Bernstein, Presiding; M. Stoyer, Presiding Papers 15-21

MONDAY MORNING

A Lifetime of Contributions To Science, Summer Schools and Our NUCL Division Family: Symposium in Honor of Frank Kinard

P. Mantica, Organizer; P. Mantica, Presiding Papers 36-46

Nuclear Fusion: From NIF To the Stars

M. Stoyer, Organizer; L. Bernstein, Organizer; L. Bernstein, Presiding; M. Stoyer, Presiding Papers 30-35

MONDAY AFTERNOON

Nuclear Fusion: From NIF To the Stars

M. Stoyer, Organizer; L. Bernstein, Organizer; L. Bernstein, Presiding; M. Stoyer, Presiding Papers 47-53

A Lifetime of Contributions To Science, Summer Schools and Our NUCL Division Family: Symposium in Honor of Frank Kinard

P. Mantica, Organizer; H. Silber, Presiding Papers 54-63

TUESDAY MORNING

Environmental Radiochemistry

B. Powell, Organizer; D. Reed, Organizer; M. Zavarin, Organizer; R. Sudowe, Organizer; A. E. Hixon, Presiding; B. Powell, Presiding Papers 64-69

Young Investigators in Nuclear and Radiochemistry

C. Folden, Organizer; J. Terry, Organizer; A. Paulenova, Organizer; C. Folden, Presiding; W. Loveland, Presiding Papers 70-77

TUESDAY AFTERNOON

Environmental Radiochemistry

D. Reed, Organizer; R. Sudowe, Organizer; B. Powell, Organizer; M. Zavarin, Organizer; F. Bok, Presiding; M. Zavarin, Presiding Papers 78-84

Young Investigators in Nuclear and Radiochemistry

C. Folden, Organizer; A. Paulenova, Organizer; J. Terry, Organizer; K. Nash, Presiding; A. Paulenova, Presiding Papers 85-94

WEDNESDAY MORNING

Young Investigators in Nuclear and Radiochemistry

C. Folden, Organizer; A. Paulenova, Organizer; J. Terry, Organizer; H. Nitsche, Presiding; J. Braley, Presiding Papers 101-111

Environmental Radiochemistry

D. Reed, Organizer; M. Zavarin, Organizer; R. Sudowe, Organizer; B. Powell, Organizer; D. Reed, Presiding; X. Gaona, Presiding Papers 95-100

WEDNESDAY AFTERNOON

Environmental Radiochemistry

D. Reed, Organizer; R. Sudowe, Organizer; B. Powell, Organizer; M. Zavarin, Organizer; R. Sudowe, Presiding; S. Faye, Presiding Papers 112-117

Young Investigators in Nuclear and Radiochemistry

C. Folden, Organizer; A. Paulenova, Organizer; J. Terry, Organizer; J. Robertson, Presiding Papers 118-124

THURSDAY MORNING

Young Investigators in Nuclear and Radiochemistry

C. Folden, Organizer; J. Terry, Organizer; A. Paulenova, Organizer; J. Terry, Presiding Papers 125-130

NUCL 1

Present developments of the LMJ neutron diagnostics

Jean Luc G Bourgade[1], *gade@lle.rochester.edu, Tony Caillaud*[1]*, Bertrand Rossé*[1]*, Michelle Briat*[1]*, Isabelle Thfoin*[1]*, Vladimir Glebov*[2]*, Craig Sangster*[2]*, Greg Pien*[2]*, Philippe Legou*[3]*, Eric Delagnes*[3]*, Johann Frenje*[4]*, Maria Gatu-Johnson*[4]*, Dennis McNabb*[5]*. (1) CEA/DAM/DIF, ARPAJON, France (2) Laboratory for Laser Energetics, New York, United States (3) DSM/IRFU, CEA Saclay, Gif sur Yvette, France (4) MIT, Cambridge, Massachusetts 02139-4307, United States (5) Lawrence Livermore National Laboratory, Livermore, California 94450, United States*

The new Laser Mégajoule (LMJ) facility at CEA/CESTA center near Bordeaux in France will illuminate its first target at the end of 2014. As the present NIF facility at Livermore (CA), the LMJ will be partly devoted to studying Inertial Confinement Fusion (ICF) of DT mixtures by laser implosion. Diagnostics that record escaping fusion neutrons are of primary importance in understanding the internal conditions of thermonuclear plasma such as density, core temperature, imploding velocities, target shape and dimensions during the implosion.

For many years many experiments have been conducted on the OMEGA laser facility because of its ability to produce large bursts of thermonuclear DT, DD, TT, and D^{3}He neutrons which provided a unique capability to test our neutron diagnostics measurements principles on this reduced but sufficient scale in neutron yield.

A range of diagnostics have been developed including neutron time of flight (nToF) spectrometer (DEMIN), neutron imaging (NIS), and Doppler broadening measurements by fast photoconductors (SNANED).

The main characteristics of the LMJ facility will be presented with a summary of the present and future LMJ neutron diagnostics suite designed for measuring the escaping neutrons flux. DEMIN spectrometer, neutron core imaging, Yield, and ion temperature diagnostics developments will be discussed in detail.

NUCL 2

High intensity g-ray and neutron generation by ultra intense laser

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In nuclear synthesis experiments, particularly for the study of astrophysical nuclear synthesis such as neutron capture reaction under the high flux environmentof the γ-ray or neutron, an ultra-high intense neutron source is indispensable. The generation of high peak intensity neutron up to 10^9 neutron/shot within a 1.2-ps pulse duration from a 1-mm-sized gold target via photonuclear reaction was demonstrated by using LFEX laser. The hot electrons generated by LFEX laser irradiation creates γ-rays via Bremsstrahlung in the high Z material targets, and the γ-rays creates neutron via photo nuclear reaction from the material. The broad neutron spectrum from keV to MeV, which is preferable for the application of nuclear synthesis experiments was predicted by Monte Carlo simulation. The very stable neutron spectrum independent from the γ-ray spectrum was shown. The neutron flux at the target surface was 10^9/cm^2/ps, therefore 10^{21} neutrons /cm^2/s was estimated. The figure 1 shows the neutron spectrum generated from gold target via photo nuclear reaction, where black line and red line shows neutron generated by a γ-ray with the spectrum of 10-MeV-slope and 5-MeV-slope, respectively. The figure 2 shows the neutron yield obtained in the experiment by using 1-mm-thick 2-mm-diameter gold target and up to 1.6 kJ LFEX laser with the pulse width of 1.5 ps.

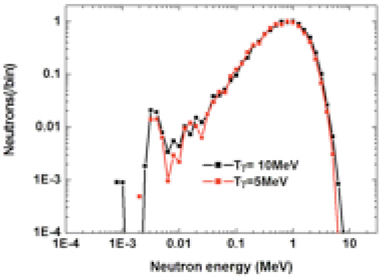

Figure 1. The photonuclear neutron spectrum from gold target. Every data plot indicates data bin. Black line shows neutron spectrum from 10-MeV-slope γ-rays and red line shows 5-MeV-slope γ-rays.

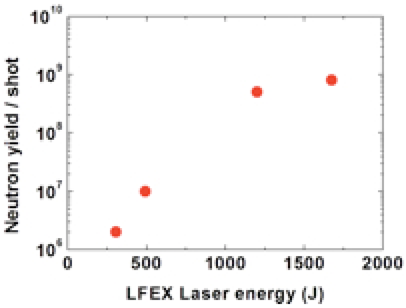

Figure 2. The neutron yield observed from the 1-mm thick gold disc target irradiated with LFEX laser.

NUCL 3

High energy density nuclear physics at UC Berkeley, LLNL, and LBNL

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Nuclear physics and diagnostics are playing an increasingly important role at the National Ignition Facility (NIF) in navigating the complex path towards ignition. They also offer an unprecedented opportunity to understand the role of high energy density plasmas in nuclear processes as they exist in astrophysical environments. Given the extraordinarily brief time scales, high neutron and gamma fluxes, and dynamic nature associated with inertial fusion events, extracting science from NIF requires significant advances both in nuclear instrumentation (neutron detection, radiochemical techniques, etc.) as well as greatly improved nuclear cross sections and other nuclear properties which underpin the analysis of NIF shots. A collaboration involving UC Berkeley, LLNL and LBNL has undertaken to exploit this unique HED environment for nuclear physics. As part of this program, we are designing and testing new detectors, and developing new platforms such as the High Flux Neutron Generator (HFNG) at UC Berkeley and a high intensity neutron beamline at the 88” cyclotron at LBNL to support the NIF nuclear physics program. This talk will particularly focus on the two new neutron sources which together provide a powerful new capability for studying neutron reactions from thermal energies to 50 MeV.

This work supported by a grant from the UC Office of the President, and the Laboratory Directed Research and Development program at LLNL.

NUCL 4

Laser nuclear experiments and facilities in Europe

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Short pulse lasers have become more and more involved in nuclear experiments. We report on the use of short pulse lasers as a powerful source of secondary radiation

(gamma, ions electrons neutrons) for nuclear experiments. We will present latest experiments with focus on neutrons and intense ion beams using relativistic transparency on high energy short pulse lasers.

Furthermore new facilities are currently been developed and are under construction in Europe, which offer unique capabilities for nuclear science in a hot and dense plasma. This would allow to explore nuclear reactions in highly ionized atomic states, at the presence of large magnetic fields and in an intense x-ray flux environment.

The international FAIR facility (Facility for Antiproton and Ion Research) in Germany and the ELI-NP (Extreme Light Infrastructure - Nuclear Pillar) in Romania will become operational in the next few years. While ELI is addressing intense laser beams (2 x 10 PW and an electron accelerator) for nuclear physics the FAIR facility offers the most intense ion beam, from Hydrogen to Uranium, and two kJ laser beams with either long pulses of multi PW capability at a 10 minute repetition rate.

We report on the status of the facilities and first experiments planned in the context of nuclear physics.

NUCL 5

Enhanced ion heating in short-pulse laser-driven buried-layers for NEET/NEEC

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The generation of keV temperture, solid-density plasma, transiently in the interaction of ultra-intense lasers with heterogenous targets is proposed as a means to study NEET/NEEC in buried layers, using high repetition-rate (1-10 Hz) 100 TW to PW class laser systems. By using layers of significantly different electron density, heating from the bulk return currents can produce extreme pressure gradients, with corresponding expansion/compression inside the solid target. Rapid collisional coupling efficiently heats the ions in the compressed regions, leading to extreme temperatures at about solid density. Particle-in-Cell simulations will be presented which address all aspects of the precise ion heating dynamics [1]. The prospect of directly probing the buried layer dynamics with coherent diffraction techniques at hard x-ray FELs will be discussed. And the feasibility of an experiment designed to realize NEET/NEEC at the HZDR DRACO laser system will be presented.

[1] L. Huang et al, Phys Plasmas **20** , 093109 (2013).

NUCL 6

Diagnostics on the National Ignition Facility have built the user community

***Joe Kilkenny**, kilkenny1@llnl.gov. General Atomics, United States*

The National Ignition Facility at Lawrence Livermore National Laboratory is a 1.8 MJ, 192 beam laser that has been in use since 2009. A comprehensive set of about sixty diagnostics has been installed with major contributions from the users outside of LLNL.

New diagnostics have been developed and tested on smaller facilities at Universities, Companies and then integrated into the NIF facility. The scientists who have created the science and technology of the new diagnostics have become integral to the science programs on NIF. Some examples are:

-Time gated x-ray imaging has been extended from 100 psec to 10 psec by scientists at General Atomics and Kentech Instruments Ltd in the UK, using drift tube time dilation. Working with LLNL scientists this technology is used in the DIXI diagnostic which is now operational on NIF taking time gated imaging as short as 10 psec, a requirement now the neutron yield approaches 10^{16}. A related instrument will be operational in a DIM, TIM or a SID allowing a Single Line of Sight framing camera or a DIXI close to target chamber center.

-Neutron spectroscopy has been developed by scientists at MIT and the University of Rochester. A magnetic recoil spectrometer (MRS) was first tested on OMEGA. Another MRS was designed and built by MIT and U of R staff and working with LLNL scientist installed on the NIF. Time integrated neutron spectra are now recorded from below 6 MeV to well above 14 MeV.

-Gamma spectroscopy has been developed by scientists at LANL, LLNL and GA. A prototype Gamma Reaction History (GRH) diagnostic was tested at OMEGA. A GRH was then installed on NIF. GRH now measures 17 MeV burn gammas but also 4.4 MeV neutron induced carbon gammas. The yields are increasing and GRH higher resolution gamma spectroscopy developed by LANL and GA will measure neutron induced gamma spectroscopy allowing time resolved mix measurements.

A new set of diagnostics will need to be installed on the NIF over the next decade. A community program is developing the new instruments which will extend the science program on the NIF.

NUCL 7

Geochemical aspects of nuclear waste disposal

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This presentation will provide an overview of the geochemical aspects of disposal of nuclear waste. The broad categories of waste, their quantities, and their origins will be reviewed, followed by the desired attributes of a geologic repository. With emphasis on matching the waste form to the geochemical environment, various geochemical and materials processes that may occur in the near-field and far-field will be examined, as well as factors that determine the relative importance of these processes in determining repository performance.

NUCL 8

Retardation and release study of uranium(VI) on phlogopite at the presence of HA: Batch and TRLFS study

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Batch sorption experiments and time-resolved laser-induced fluorescence spectroscopy (TRLFS) technique were applied to investigate uranium(VI) sorption and desorption on phlogopite in the presence of humic acid (HA). The results showed that HA inhibited U(VI) sorption on phlogopite above pH 4 and such effect became much more pronounced by increasing HA concentration from 20 mg/L to 50 mg/L. Below pH 4, the presence of HA made little difference on U(VI) sorption. Thus the cause of the inhibition effect was likely due to the formation of soluble U(VI)-HA binary complexes. Time-resolved U(VI) fluorescence spectra clearly indicated formation of multiple U(VI) surface complexes, including ternary U(VI)-HA-phlogopite species. Results of U(VI) desorption experiments showed that U(VI) sorption in the presence of HA was reversible while introduction of HA after U(VI) sorption completion did not cause U(VI) desorption from phlogopite within 48 hr, providing further evidence that U(VI) sorption involved U(VI)-HA-phlogopite ternary complex (SO-OOC-HA-U(VI)).

NUCL 9

Long-term diffusion of U(VI) through bentonite: Effect of density

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Bentonite shall be used as backfill material in repositories considered for the storage of high-level nuclear waste (HLW) in deep geological formations. It presents a part of the barrier system needed to guarantee the safe isolation of the waste for the next million

years. Within a repository, bentonite can acquire different densities depending on compaction level. This could influence the diffusion properties of contaminants.

One of the main constituents of HLW is UO_2. After interaction with water this could oxidize to U(VI) which forms mainly mobile species under environmentally relevant conditions.

For safety assessment it is essential to know if waste-released U(VI) can be transported into the geo- and biosphere surrounding the repository. In this study, long-term diffusion experiments with U(VI) through bentonite with densities of 1.3, 1.6, and 1.9 g/cm^3 were performed for about 6 years under bentonite pore water conditions (pH 8, $I \sim 0.3$ M). Using the profiles of the diffused U(VI), values for the diffusion parameters (effective diffusion coefficient, D_e; distribution coefficient, K_d) were determined.

The sorption of U(VI) onto bentonite is observed to be very weak (low K_d values) and decreases with increasing density. This can be explained by the present speciation. At 1.3 g/cm^3, $Ca_2UO_2(CO_3)_3$(aq) (84%) and $UO_2(CO_3)_3^{4-}$ (13%) are the dominant species. At 1.9 g/cm^3, their fractions shift to $Ca_2UO_2(CO_3)_3$(aq) (71%) and $UO_2(CO_3)_3^{4-}$ (26%). The neutral U(VI) species is known to sorb only weakly to clay. The negatively charged U(VI) species seems to be completely repulsed by the negative clay surface.

The obtained D_e values decrease with increasing density. They are very low compared to literature values for experiments performed on a shorter time scale. This can be interpreted by blocked diffusion paths which hinder the further migration of U(VI) through bentonite. This result can only be observed from performance of long-term experiments.

Prepared by LLNL under Contract DE-AC52-07NA27344. This work was supported by the Used Fuel Disposition Campaign of the Department of Energy's Nuclear Energy Program and the U. S. DOE Office of Biological & Environmental Sciences, Subsurface Biogeochemistry Research Program. Funding by the European Commission (Project NF-PRO under contract C2-ST-C-01) is gratefully acknowledged by HZDR.

NUCL 10

Tin(II)apatite mediated reduction and sequestering of pertechnetate

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Sn(II)apatite reduces pertechnetate from the mobile +7 state to the non-mobile +4 state, as evidenced by a black precipitant. As would be expected, the apatite has much lower distribution coefficients at the pH extremes. However, at pH > 1.3 and pH < 11.4, distribution coefficients were measured at 170,900. When subjected to a nitric acid wash, less than one weight percent of technetium was released from the apatite. The technetium-apatite complex was also subject to air sparging in a water column with 8.5 mg/L dissolved oxygen concentration. Subsequent measurements for technetium were below the detection limit of 0.01 mg/L. The mechanism by which technetium is sequestered and protected from re-oxidation appears to be a mole for mole exchange with phosphate in the apatite lattice. The Sn(II)apatite would be efficacious in the following scenarios: water elution from pertechnetate resins such as SuperLig© 639, treatment of pertechnetate containing waste streams from the Effluent Treatment facility, treatment of the secondary waste stream from the Waste Treatment Plant, and as a permeable reactive barrier to prevent pertechnetate mobility in the environment.

NUCL 11

Flammable gas hazard in Hanford waste tanks

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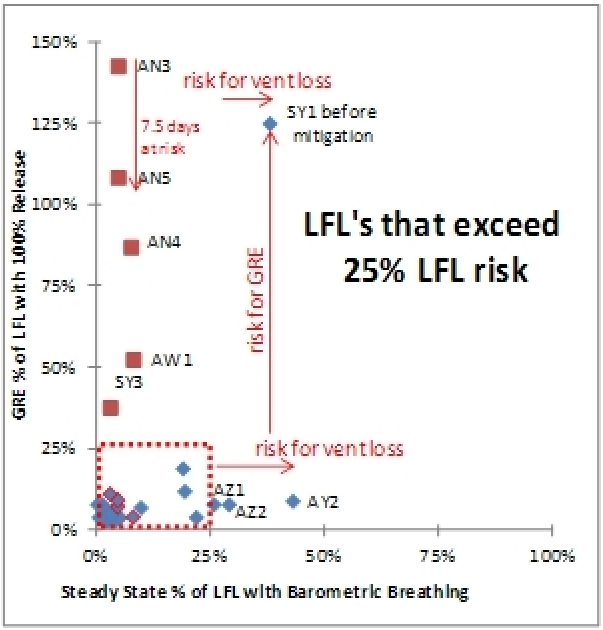
All aqueous radioactive solutions generate radiolytic hydrogen and Hanford underground waste tanks have a long history of dealing with this hazard. Currently there are a set of very conservative operational controls that have successfully maintained all tank headspaces at or below 25% of the lower flammability limit for hydrogen, or below 10,000 ppmv hydrogen. In the coming years, these waste liquids and solids will be retrieved and processed into stable waste forms and it is very likely that improved hazards analyses will increase operational flexibility with waste retrieval and treatment without jeopardizing safety.

This paper will discuss three areas where more realistic hazard analyses will increase operational flexibility without compromising safe operations. For example, the passive ventilation rate measured in tank headspaces have half lives of 10-20 days or less. Yet the time-at-risk for off normal events uses the much more conservative barometric ventilation limit of about 130 days, one order of magnitude greater time at risk. More realistic passive ventilation rates will lower these time-at-risk scenarios for off normal events.

Finally, retention of flammable gases in sediments and the subsequent sudden release into tank headspaces has limited tank operations significantly for certain high solids tanks. However, only precipitated solids with sodium nitrate and nitrite coupled with significant gas generation rates show sudden flammable gas releases.



In particular, simple oxide sludges do not show spontaneous gas release events even for tanks with quite large gas generation rates. Better defining the actual hazards of flammable gas generation will make it possible to increase operational flexibility without compromising safe operations in processing tank wastes.

NUCL 12

Incorporation of iodine in phosphate-based glasses

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Nuclear industry uses glass matrices for long-lived nuclear wastes immobilization; in particular borosilicate composition is the glass reference for such wastes. However, immobilization of I-129 in borosilicate glasses can be difficult, due to high glass processing temperature. This work aims at understanding phosphate glasses for ^{129}I wastes. Phosphate glass can be prepared at lower temperature (under 700˚C) allowing for minimization of iodine volatilization and incorporation of high iodine contents. In the present study, the structure and thermal properties of $AgI\text{-}Ag_2O\text{-}P_2O_5\text{-}Al_2O_3$ glass system have been studied and chemical durability (i.e., aqueous resistance) determined. The effects of the incorporation of Al_2O_3 (up to 5 mol%) and silver iodide (up to 30 mol%) on micro and local structures were measured. An absence of AgI clusters within the glass was clearly demonstrated and a shortening of phosphate chains upon AgI incorporation was also proven. However, the formation of aluminophosphate-based crystallizations was observed for an Ag_2O/P_2O_5 ratio of 1, explained by a competition process between Al_2O_3 and AgI in the glassy network. DSC analyses further revealed the correlation between glass structure modifications and thermal properties. Results show that T_g decreases upon AgI incorporation but increases with Al_2O_3 content. Static eaching tests in pure water (MCC1-like test) conducted at 50˚C showed the formation of a thin layer containing γ-Agi and the initial rate was estimated to be 6 $g.m^{-2}.d^{-1}$.

NUCL 13

Examination and reactivity studies of the metallic residues of a high burn-up BWR fuel

***Bruce K. McNamara**, bruce.mcnamara@pnnl.gov, Edgar C Buck, Chuck Z Soderquist, Frances N Smith, Edward J Mausolf. Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Wa 99352, United States*

We discuss the microscopic examination and the unusual reactivity of the metallic alloy residues from the dissolution of a high burnup, boiling water reactor fuel (~70 MWd/kgU). Exposure of the metallic phase for instance to a weak fluorinating reagent, 10% NF_3 in argon, removed molybdenum and technetium near 400°C as their volatile fluorides, and ruthenium near 500°C as its volatile fluoride. Depletion of the volatile fluorides resulted in substantial exothermicity. The conditions specified for the fluorination reaction are a recipe to separate these metals from each other and from the nonvolatile residue. Post-fluorination, only two products were present in the residual nonvolatile fraction. These were identified as a nano-crystalline, metallic palladium cubic phase and a hexagonal rhodium trifluoride (RhF_3) phase. Physical characterization of the metallic phase and its thermal behavior are consistent with high kinetic velocity reactions encouraged by the nanoparticulate phase or perhaps catalytic influences of the mixed platinum metals with nearly pure phase structure.

NUCL 14

New ligand designs for recovery of precious metals from spent nuclear fuel

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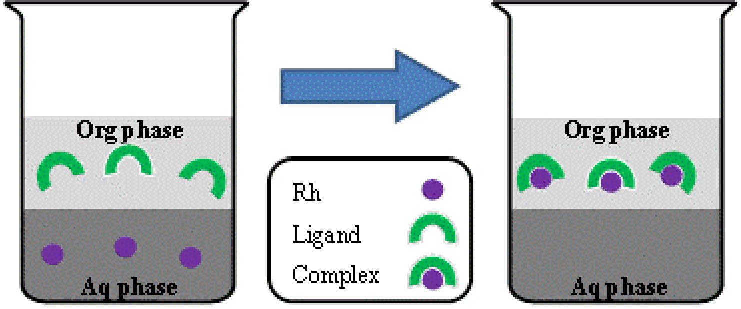
Precious metals (Rh, Ru, Pd, Ag, Pt) represent critical components in the construction of new energy materials (e.g., catalysts, batteries, electronics, solar cells) that will remain essential as energy needs continue to increase. While conventional mining remains the current source, an untapped resource for these elements can be found in the fission products of spent ^{235}U fuel rods used in power reactors. Formed in high percentages in the light fission fragment (~100 MW), precious metals are found in greater concentrations in spent nuclear fuel than terrestrial sources. Used in conjunction with recovery of fissile material in reprocessing, selective recovery of precious metal

offers a unique venue to harvest these high value materials from the waste stream while reducing the overall long term waste storage. Utilizing the affinity of precious metals for soft donors, novel ligands containing nitrogen and sulfur donors were designed and synthesized. The initial complexation studies were conducted with the 1st generation ligands and rhodium (III). Macroscopic prepared Rh complexes were characterized by standard spectroscopic techniques (NMR, IR, UV-Vis, X-ray) and compared to solution speciation. Complexation reaction formation rates were also determined under pseudo-first kinetics. Preliminary extraction studies were also carried to examine the feasibility of these ligands to transfer rhodium from aqueous phase to the organic phase.



NUCL 15

Measuring bulk fuel velocity at the National Ignition Facility with neutron activation

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Neutron yields and fuel areal densities are measured at the National Ignition Facility by an extensive suite of neutron activation diagnostics. Neutrons interact with materials whose reaction cross sections threshold just below the fusion neutron production energy, providing an accurate measure of primary unscattered neutrons without contribution from lower-energy scattered neutrons. An array of up to seventeen zirconium samples are located on ports around the chamber to measure activation via ^{90}Zr(n,2n) reactions and provide a global map of neutron yield and relative anisotropies. A dipole perturbation in zirconium activation around the target chamber on DT glass-capsule exploding pusher implosions is indicative of bulk core velocity. The relatively low areal density (10-50 mg/cm^2) allows measurement of the Doppler energy shift of the primary fusion spectrum, contributing systematic low-mode variation to the activation anisotropy. Quantification of this few-percent perturbation is a challenge as measurements are made on the calibration shots themselves. A calibration technique using a global fit to all exploding pusher shots and vector summing to zero net velocity allows measurement of core velocity as low as tens of kilometers per second. Velocities higher than 200 km/s have been observed on shots with known drive asymmetries due to dropped laser bundles or misaligned capsules.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratories under contract DE-AC52-07NA27344.

NUCL 16

Thulium activation by reaction-in-flight neutrons

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In highly compressed NIF capsules deuterons and tritons can be imparted high kinetic energy by elastic scattering with 14 MeV neutrons. The energetic ions can then interact with stationary fuel resulting in fusion while emitting a neutron from a moving reference frame. This results in neutrons with a kinetic energy in excess of 14.1 MeV and up to 22 MeV. Thulium is mono-isotopic and has two threshold reactions that can be used for neutron spectral measurement. The (n,2n) reaction has a threshold of 8 MeV and produces Tm-168 that decays with a 93.1 day half-life. This reaction is used to measure the 14.1 MeV neutron fluence. The (n,3n) reaction has a threshold of 15 MeV and produces Tm-167 that decays with a 9.24 day half-life. This reaction is used to measure Reaction-in-Flight, RIF, neutrons. The difficulty in making this measurement is observing Tm-167 in the presence of 5 orders of magnitude more Tm-168 atoms. The Los Alamos 4-Pi clover gamma ray spectrometer is uniquely able to discriminate gamma ray on the basis of decay scheme and energy. The measurements, the method and the results of RIF neutron production as a function of different laser pulse structures will be described.

NUCL 17

Prompt gamma-ray measurements in inertial confinement fusion experiments

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The primary objective of the NIF Gamma Reaction History (GRH) diagnostic is to provide bang time and burn width information in order to constrain implosion simulation parameters such as shell velocity and confinement time. This is accomplished by

measuring deuterium-tritium (DT) fusion gamma-rays with energy-thresholded Gas Cherenkov detectors that convert MeV gamma-rays into UV/visible photons for high-bandwidth optical detection. Burn-weighted CH ablator areal density is also inferred based on measurement of the $^{12}C(n,n')$ gammas emitted at 4.44 MeV from DT fusion neutrons inelastically scattering off carbon nuclei as they pass through the plastic ablator. This requires that the four independent GRH gas cells be set to differing Cherenkov thresholds (e.g., 2.9, 4.5, 8 & 10 MeV) in order to be able to unfold the primary spectral components predicted to be in the gamma ray energy spectrum (i.e., DTγ; ^{27}Al & ^{28}Si (n,n')γ from the hohlraum thermo-mechanical package (TMP); and $^{12}C(n,n')\gamma$ from the ablator). The GRH response to $^{12}C(n,n')\gamma$ is calibrated in-situ by placing a known areal density of carbon in the form of a puck placed ~6 cm from a DT exploding pusher implosion. Additional puck materials are used to make nuclear cross section measurements for 14.1 MeV DT fusion neutrons. Comparisons between inferred gamma fluences and simulations based on the nuclear cross sections database will be presented.

NUCL 18

Characterization of a stilbene-doped bibenzyl single-crystal organic scintillator for fast neutron spectrometry

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The neutron time-of-flight (nTOF) diagnostics used to characterize implosions at the National Ignition Facility (NIF) has necessitated the development of novel scintillators that exhibit a rapid temporal response and high light yield. One such material, a bibenzyl-stilbene mixed single-crystal organic scintillator grown in a 99.5:0.5 ratio in solution, has become the standard scintillator used in the nTOF diagnostic at NIF. The prompt fluorescence lifetime and relative light yield as a function of proton energy were determined to calibrate this material as a neutron detector. The temporal evolution of the intensity of the prompt fluorescent response was modeled using first-order reaction kinetics and the prompt fluorescence decay constant was determined to be 2.46 ± 0.01 (fit) ± 0.13 (systematic) ns. The relative response of the bibenzyl-stilbene mixed crystal generated by recoiling protons was measured, and results were analyzed using Birks relation to quantify the non-radiative quenching of excitation energy in the scintillator. The relative response data, while similar to previously reported values for a xylene-based liquid scintillator, differ in their overall energy dependence. The implications of this difference will be discussed, and plans for future highly-segmented nTOF systems will be presented.

NUCL 19

Neutron spectrometry using neutron time-of-flight detectors at the National Ignition Facility

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The neutron time-of-flight (NTOF) detectors at the National Ignition Facility (NIF) make the highest resolution measurement of the neutron energy spectrum from NIF implosions. This spectral information provides insight into the fuel assembly at bang time of the implosion. The workhorse detectors are a suite of three detectors that are fielded at ~20m from the target. These detectors have been used since late 2012 to measure traditional fusion variables such as neutron yield, ion temperature and fuel areal density. The high quality, high signal-to-background data of the newly-implemented detectors have enabled measurement of portions of the neutron spectrum that were previously challenging or impossible; remaining ablator areal density, D(n,n) and T(n,n) backscatter edges, hot spot velocity, and high-energy reaction-in-flight neutrons are measured routinely. Thermal components of the spectrum (≤100keV) have yet to be measured due to the lack of sensitivity of the detectors to those neutrons, but we plan to field a low energy neutron spectrometer to facilitate these measurements. The low energy portion of the neutron spectrum will be critical in understanding cross section measurements in a NIF target capsule.

NUCL 20

Radiochemical measurements of neutron reaction products at the National Ignition Facility

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The National Ignition Facility (NIF) is currently the world's most powerful laser, capable of producing very large quantities of neutrons via the fusion of deuterium and tritium fuel. The neutron luminosity of a NIF ignition can produce observable concentrations of activation products from nanogram quantities of radiochemical detector isotopes loaded in the innermost layer of the capsule ablator (closest to the DT fuel) or on the outside of the hohlraum. The production of 14 MeV neutrons in a single pulse creates an opportunity to measure neutron activation and neutron capture reaction rates in an environment where the contribution from lower-energy, scattered neutrons is insignificant. Using the Solid Radiochemistry (SRC) and Radiochemical Analysis of Gaseous Species (RAGS) diagnostics at NIF, initial results obtained during high neutron

yield shots have shown collection of activated hohlraum material, as well as neutron capture products both in the hohlraum and in the collector material itself. As neutron yields continue to increase, there is also the possibility of measuring cross sections from excited nuclear states. These results motivate using NIF as a source for the measurement of nuclear data that is not obtainable at traditional reactor or accelerator facilities. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NUCL 21

Demonstrating capability for radiochemical analysis of gaseous samples at NIF

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The Radiochemical Analysis of Gaseous Samples (RAGS) system provides the capability to measure time-resolved and integral quantities of gaseous nuclear reaction products generated in NIF experiments (e.g., xenon and krypton products from n,2n reactions or 14 MeV fissions). RAGS collects gas from the target chamber after a shot and separates a noble gas fraction for in-situ counting and off-line counting and noble gas mass spectrometry. We characterize the system performance under different operating conditions and optimize parameters to maximize sample collection. Faux shots, control tests without laser operation, inject known amounts of stable and radioactive xenon isotope tracers into the target chamber and provide maximum sample recovery. During a 15 minute gas collection, greater than 90% of the radioactive tracer is collected on cold copper foam located beneath the in-situ germanium counter, and more than 50% of the radioactive and stable tracers are subsequently collected in the off-line sample. On recent NIF shots with laser operation and RAGS participation, sample recovery is lower and varies from shot to shot compared to the faux results. Data analysis of these shots is underway to identify the factors affecting sample recovery. These shots also collected data to optimize the in-situ detector performance for measurement of n,2n reaction cross sections and 14 MeV fission yields, as well as shot-background products ^{18}F, ^{23}Ne, and ^{19}O. In addition to identifying short-lived fission products, such as 8.6-second ^{91}Kr, we are working toward quantifying them on upcoming depleted-uranium hohlraum shots. Another shot will examine target mix by neutron activation of two xenon isotopes implanted at different distances from the inner surface of a symcap target; ^{124}Xe at 45 microns and ^{136}Xe at 70 microns.

NUCL 22

Radionuclide detection and measurement techniques for use in Comprehensive Test Ban Treaty on site inspection

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Conduct of an On Site Inspection (OSI) under the Comprehensive Test Ban Treaty (CTBT) is expected to employ an inspection team (IT) and a system of techniques designed to localize regions in an inspection area (IA) and detect/assess whether signatures present are consistent with a nuclear explosion. A number of radionuclide (RN) detection and characterization techniques are planned to be part of the overall OSI system. The RN techniques under consideration include aerial and ground-based gamma survey, in situ gamma spectroscopy for field characterization, and even collection of physical samples (surface and subsurface, including noble gases) and capability to analyze all of the previous at a base of operations laboratory. Many of these techniques are slated for testing and demonstration during an upcoming Integrated Field Exercise planned for later this year. As introduction to the session, this presentation will describe a number of the planned RN techniques, their intended application within OSI and draw analogies to the U.S. response to Fukushima which similarly employed many of the same techniques and processes. LLNL-ABS-652150. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC.

NUCL 23

Subsurface gas-phase transport and detection of noble gas signals from underground nuclear explosions

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The Non-Proliferation Experiment (NPE) involved detonating 1 kiloton of chemical explosive in a subsurface cavity that also contained bottles of tracer gases. That experiment provided an improved understanding of transport processes relevant to the detection of noble gas signals at the surface that might emanate from a clandestine underground nuclear explosion (UNE). As an alternative to performing large chemical detonations to simulate gas transport from UNEs, we have developed a test bed for gas transport, release and detection studies using a former UNE cavity. The test bed site allows for the opportunity to evaluate pathways to the surface created by the UNE as well as possible gas transport mechanisms including barometric pumping and cavity pressurization. With the test bed we have monitored long-term chemical tracers as well as newly injected tracers. In order to perform high temporal resolution tracer gas monitoring at the test bed site, we have also developed a Subsurface Gas Smart Sampler (SGSS), which has potential application during an actual On Site Inspection (OSI) and will be deployed in OSI field exercises planned for 2014. With gas transport

characteristics inferred from these experiments we have also performed a variety of computer simulations that provide an improved understanding of how Xenon isotopic ratios, potentially relevant to determining the source of a radioxenon signal detected at the site of an OSI, may be affected by transport in the subsurface.

NUCL 24

Nevada National Security Site and Comprehensive Nuclear Test Ban Treaty Organization (CTBTO) support capabilities

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Introduction

The Nevada National Security Site (NNSS), formerly known as the Nevada Test Site (NTS) is now much more than a nuclear testing site. It is where the Department of Energy, Department of Defense, Department of Homeland Security, and other government agencies experiment, train, and demonstrate vital global security capabilities. The Site is Big: 1,360 square miles of federally owned land, Remote: with the nearest McDonald's restaurant 40 miles away from the work areas (as the crow flies), Safe: has an outstanding safety record, Secure: is surrounded by Nellis Test and Training Range, and Versatile: contains a variety of geologies, topographies, environments, personnel, and facilities. The NNSS brings unique capabilities to the table that exist nowhere else in the United States. Its personnel consist of a wide variety of scientists, engineers, technicians, and infrastructure support craft workers. The Site's core competencies include world-class instrumentation development, fielding, data acquisition, and data reduction in support of nonproliferation treaties with regard to modeling and verification under a CTBT regime.

Description of CTBTO needs that NNSS can fulfill

The CTBTO International Monitoring System can locate a potential underground nuclear explosion within an ellipse comprising no more than 1,000 square kilometers. Should a suspected nuclear explosion be detected, the CTBTO may choose to deploy equipment and an inspection team to collect evidence leading to a fact-based determination of whether a violation of the Treaty has occurred. The first task of the inspection team is to narrow the search area quickly and efficiently. An overflight is permitted with equipment specified in the On-Site Inspection Protocol to the Treaty for the purpose of orienting the team and locating the artifacts and indications of a nuclear explosion. Once the inspection area has been reduced to a size practical for ground based detection equipment to be deployed, other activities such as passive seismic, radiation monitoring, and environmental sampling may be deployed to further narrow the inspection area. If credible evidence of a nuclear explosion is found, the inspection team may deploy active seismic, magnetic and gravitational field mapping, ground penetrating radar, and electrical conductivity measurements at the surface and from the air, as appropriate, to detect anomalies or artifacts. Finally, the team can perform drilling to obtain a core sample from the suspected nuclear explosion for radiochemical analysis.

Conclusions

The NNSS, as the former United States nuclear testing site, has the requisite land area, flight expertise, and skill sets to exercise every aspect of an on-site inspection under the CTBT from warehouse deployment to the inspected state, initial briefing and equipment inventory, base camp setup, and working in a remote inspection area. In addition, the NNSS has real artifacts of nuclear testing useful for determining if inspection personnel, equipment, and procedures work well in the field.

Keywords: NNSS, NTS, CTOS, RSL, STL, LO, LAO, RSLA, CTBT, CTBTO, Verification, Treaty, RNCTEC, CTOS, NCNS, NPTEC

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NUCL 25

Development of novel radioxenon detectors for nuclear explosion monitoring

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The Comprehensive Nuclear-Test-Ban Treaty Organization deploys a variety of radioxenon detection systems as part of its International Monitoring System to detect nuclear explosions. To achieve the high sensitivity required, the systems extract xenon from several cubic meters of air and look for characteristic radioactive emissions from 4 Xe isotopes of interest. Existing systems use either high resolution high purity germanium gamma detectors or multiple scintillators for high efficiency beta/gamma coincidence detection.

Several new radioxenon detectors are currently being developed at XIA with the multiple goals of improving discrimination between the Xe isotopes, simplifying detector designs and/or adapting them for portable applications. First, a silicon detector with PIN diodes for X-ray/beta/conversion electron coincidences has been designed, assembled, and tested; providing unprecedented resolution for conversion electron lines. The probability for detecting higher energy gamma rays is low, but backgrounds are practically zero so that overall the minimum detectable concentration is estimated to be well below 1 mBq/m^3. Second, an earlier phoswich detector design has been modified for field measurements to reduce size, weight, cost, complexity, and memory effect with only a minor impact on the sensitivity. The detector and its lead shielding are packaged in a carrying case with total weight of 32 kg. Third, geometric partitioning is being explored in a detector design that uses 12 independent scintillators to reduce backgrounds, distinguish triple coincidences (from Xe beta emitters) from double coincidences (from Xe metastables), and make use of additional decay paths not distinguished in existing detectors. We will present design considerations based on Monte Carlo simulations, results from Xe measurements with these detectors, and estimates of efficiencies and minimum detectable concentrations.

NUCL 26

Absolute efficiency calibration of gas beta-gamma detectors using nuclear reactor irradiated radioxenon sources

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Abstract : The automated radioxenon collection and quantification systems (SAUNA[1] and ARIX[2]) are part of the International Monitoring System of the Comprehensive Nuclear-Test-Ban Treaty Organization used to detect underground nuclear explosions. The systems use beta-gamma coincidence detectors and calibration of these detectors is performed as part of the initial system field setup and then annually thereafter. The detectors are typically calibrated with xenon isotope standards: Xe-135, Xe-133, and Xe-131m to accurately determine the detection efficiency and the energy range. However, maintaining the gas standard's high accuracy in the field is difficult. To overcome this obstacle methods have been developed that do not require detailed knowledge of the amount of the radioactive gas that has been injected into the beta detection cells The simplest of the methods relies on the geometry of the two detectors, the beta-gamma coincidence decay signature of radioxenon isotopes, and the production of isotopically pure Xe-133, Xe-135, and Xe-131m via neutron activation from stable xenon isotopes.[3] To test and verify the calibration method, a beta-gamma simulation code was developed that produces two-dimensional beta-gamma histograms with known activities for each isotope. The code is also used to verify various interference terms that arise from multiple isotopes in the counting cell during routine sample analysis. In this talk we will discuss past calibration methods using NIST traceable standards, the absolute calibration methods developed, and the simulations code used to test and verify the new methods.

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NUCL 27

Uniform deposition of trace and ultratrace levels of uranium hexafluorides

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Detection of uranyl fluorides species in support of nuclear safeguards efforts at uranium enrichment facilities is an international analytical challenge. Quantitative generation of uranyl fluoride samples for methods calibration, standardization and fundamental studies is challenging due to the chemical reactivity of uranyl fluoride species and the radioactivity of the isotopic mixtures We report a convenient method for the generation of fluorinated uranium species and their subsequent uniform deposition at ultratrace levels on surfaces. Conditions for uniform, low level depositions are demonstrated for uranium materials all of which can be made volatile by fluorination. Reproducible depositions with mass between 1.4e-3 ng*cm^{-2} and 14.1 ng*cm^{-2} were obtained and the deposition mass quantified by radiometric detection as aided by use of high specific activity isotopes. The data suggests that the method can be used to achieve uniform depositions at the low femtogram and attogram levels on varied surfaces. The method reported has application to analytical chemistry, nuclear forensics, corrosion science, and other fundamental disciplines.

NUCL 28

Measurement of U and Pu isotope ratios in hair and nail samples of occupationally exposed workers and controls

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A non-invasive bioassay capable of monitoring occupational or environmental exposure to special nuclear materials would be a useful tool for nuclear nonproliferation programs. Hair and nail are potential, non-invasive biomonitors of exposure to U and

Pu. A method was created to measure isotope ratios of ultra-trace concentrations of U and Pu in hair and nail samples. The method uses multiple extraction chromatography resins to separate and recover U and Pu fractions from the sample matrix. The U recovery was quantitative while the Pu recovery ranged from 81-109%, with a U decontamination factor of 5 x 10^4. Following the separation $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{240}Pu/^{239}Pu$ were measured in human hair and nail samples using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). Volunteers were recruited from the national laboratories and the Columbia, Missouri area under an IRB approved protocol. We present the U and Pu isotope ratios in human hair and nail in a control group and an occupationally exposed group.

NUCL 29

Attribution of Iridium-192 sources via QD-ICP-MS

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Iridium-192 sources are some of the most commonly used radioactive sources in the private sector. Because of the potential for these sources to be used in a radiological dispersal device, we are investigating the use of trace and isotopic analysis of spent Ir-192 sources as a way to provide information about the source of the radioactive material. An electrochemical dissolution procedure has been developed that can be employed in a remote handling (hot-cell) environment. This procedure has been used in conjunction with quadrupole inductively-coupled plasma mass spectrometry (QD-ICP-MS) to determine the trace-element and isotopic composition of decayed industrial Ir-192 sources. Significant differences are observed in the isotopic signatures of both iridium and trace platinum group elements between natural and irradiated iridium.

NUCL 30

NEET in plasma: The case of ^{84}Rb

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The development of high-intensity lasers is opening up new opportunities for nuclear-physics studies. Lasers are promising tools to study nuclear properties in extreme plasma conditions, which cannot be reached with conventional particle accelerators. In a plasma, the interaction between a nucleus and its electronic cloud can be influenced by its environment and unusual excitation processes such as nuclear excitation by electronic capture (NEEC) and nuclear excitation by electronic transition (NEET) should be observed. Indeed, NEEC (unobserved) and NEET (observed in ^{197}Au [1], ^{189}Os [2,3]

and ^{193}Ir [4] in accelerator based experiments) are exotic processes relevant to astrophysics, which can be dominant in particular plasma conditions of temperature and density [5], and therefore it is highly desirable to study them. These two processes involve a coupling between the nucleus and the electronic cloud. In the case of the NEET, a bound-bound atomic transition leads to a nuclear excitation if the two transitions are resonant and have the same multipolarity. The NEEC process is equivalent to the NEET process with the difference that the atomic transition is bound-free. We have undertaken a joint experimental and theoretical program to investigate the ^{84m}Rb excitation rate in laser produced plasma.

The long-lived isomeric state of the ^{84}Rb (energy of 463.6 keV, $T_{1/2}$=20.26min) can be excited towards a higher lying short-lived state. According to the literature, the nuclear transition energy involved in this excitation is 3.05 (20) keV. It is possible to find atomic transitions, which match this nuclear transition for charge states between 27^+ and 32^+ allowing the NEET process to take place [6].Searching for the NEET process in plasma requires an accelerator to produce the ^{84}Rb isomeric state and a high-energy- high-intensity laser to create the plasma with the required charge states. This kind of facility exists at GSI (Darmstadt, Germany) where the PHELIX high-energy laser is combined with the UNILAC ion accelerator.

To prepare the NEET experiment, nuclear and atomic physics experiments were conducted. We have made experiments at ELSA (CEA/DAM, Bruyères-le-Châtel) and at TANDEM/ALTO (Orsay) accelerators to measure the nuclear transition energy with high accuracy. Indeed, the accuracy of this transition energy in the tables was insufficient (200 eV) in comparison with the accuracy of the atomic data (few eV) [7]. We have also measured the X-ray spectra emitted by a Rb plasma at PHELIX. These spectra will be compared with theoretical ones to determine plasma conditions (charge states, temperature…) reached during the experiment. The results of these experiments will be presented.

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NUCL 31

P {margin-bottom: 0.21cm; direction: ltr; widows: 2; orphans: 2;} indirect deexcitation of ^{84}Rb in a plasma created at PHELIX (GSI)

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Rubidium 84 is one of a few nuclei exhibiting both an isomeric state with a 20 minute half-life and an upper level lying very close above it at 3.05 keV. This isomeric state can be produced at GSI with the LINAC accelerator and then be irradiated by the PHELIX laser to excite the upper level which decays down to the ground state through two gammas with energies above 200 keV.

Nuclear excitation in plasmas [1] code ISOMEX predicts a NEET (Nuclear Excitation by Electron Transition) rate around 10^{-4} s^{-1}. It is corroborated by MCDF (Multi-Configuration Dirac Fock) calculations [2] and should occur for rubidium charge states between 27^{+} and 30^{+}. A preliminary experiment was performed at GSI in September 2013 and May 2013 in which radiative spectra of rubidium around 3 keV have been measured. During this workshop, I will discuss the theoretical approach which has been used to predict the transition rates and put the emphasis on the DLA (Detailed Level Accounting) technique used to interpret the results.

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NUCL 32

P {margin-bottom: 0.21cm; direction: ltr; widows: 2; orphans: 2;} nuclear excitation of ^{169}Tm in hot dense plasma

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The high power laser facilities LMJ and NIF offer the opportunity to study atom-nucleus coupling effects in hot dense plasma. The ^{169}Tm nucleus has a low-lying isomer located at 8.41 keV above the ground state, with a 4.09 ns lifetime. This isomer decays down to the ground state level via a M1+E2 multipolarity transition.

Some calculations with the system code ISOMEX have been performed to estimate the pertinent thermodynamics parameters (density, electronic temperature and correlated charge state) areas to determine the most appropriated atomic transitions able to excite efficiently the ^{169}Tm. In addition, MCDF (Multi-Configuration Dirac Fock) calculations indicate a 53$^+$ - 59$^+$ charge state range to reach.

Hydrodynamics calculations indicate that LMJ/NIF shots in a capsule containing ^{169}Tm seem to be a good way to excite significantly the isomer via electronic processes such as NEEC or NEET. Theoretical aspects will be discussed to determine excitation and de-excitation rates in plasma.

NUCL 33

Search for nuclear excitation by electronic transition (NEET) in 201Hg

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The development of high intensity lasers has permitted the study of matter in extreme conditions of density and temperature. These conditions can allow nuclear excitation of isomeric states in plasma.
201Hg is a good candidate for this study. The first excited state of 201Hg is an isomeric state of 1.565 keV excitation energy with a lifetime of 81 ns [1]. In a neutral atom, the deexcitation of this state occurs mostly by internal conversion. In specific plasma conditions of temperature and density, this nuclear state can be populated preferentially by the NEET effect (Nuclear Excitation by Electronic Transition) [2]. This is a resonant process where an atomic deexcitation may cause a nuclear excitation provided that energy and angular momentum conditions are fulfilled. In the case of 201mHg, for a charge state of 42+, the 6s1/2 to 4s1/2 atomic transition is resonant with the nuclear one [1].
To highlight the production of 201mHg in a plasma, the detection of the internal conversion electron produced during this nuclear state deexcitation is necessary. The lifetime of 81 ns is not long enough to avoid the electron background due to the plasma radiation produced during the laser interaction. However, it has been shown that for charge states higher than 30+, the deexcitation by internal conversion of 201mHg is blocked and the isomeric state lifetime increases to a few milliseconds [3]. In this condition, the ions of interest can be transported far away from the laser interaction site with an electrostatic analyzer [4].
So far, we have built an analyzer and characterized it with plasma ions produced with a Nd-Yag laser. In a first study with have considered a laser intensity of 1013 W/cm^2 and different targets (13Al, 29Cu, 48Cd, 73Ta). In few weeks, the spectrometer will be used on a 1014 W/cm^2 intensity laser to make sure that high charge states of 201Hg are produced (>30+). An X-ray spectrometer will be used to measure the charge states reached inside the plasma. The results of all these experiments will be presented.
In previous study [5], the NEET rate was calculated using the average atom model. To determine if the average atom model is relevant for NEET rate calculations, we have

developed a new code based on DCA calculations around the average atom model to calculate the NEET rate. A comparison between the two models will be made. Then we will present an estimation of the number of excited nuclei during a laser pulse by coupling the calculations with a hydrodynamic code.

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NUCL 34

Nuclear excitation with zeptosecond multi-MeV laser pulses

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The ongoing construction of the Nuclear Physics Pillar of the Extreme Light Infrastructure (ELI) offers unprecedented possibilities for nuclear physics experiments. The facility holds promise to deliver in the not-too-distant future coherent gamma ray pulses with energies of several MeV per photon. Coherence strongly amplifies nuclear absorption and if the latter occurs comparably fast to nuclear equilibration, it leads to the formation of a compound nucleus with excitation energy several hundreds MeV above yrast in a so far totally unexplored regime.

We investigate theoretically the outcome of nuclear reactions induced by the strong zeptosecond laser pulse in the quasiadiabatic regime where the photon absorption rate is comparable to the nuclear equilibration rate. A quantitative description of the absorption and equilibration processes requires knowledge of the density of states, so far unavailable for this parameter regime. Our new approach yields approximate analytical expressions for the total and partial level densities [1,2] and allows the semiquantitative study of the competition between photon absorption, photon-induced nucleon emission, and neutron evaporation. With neutron evaporation overtaking photon absorption at energies below the saturation of the latter for medium-weight and heavy nuclei, we find that neutron-poor nuclei far from the valley of stability may be produced [3]. Experiments planned at ELI thus promise to shed light on the structure of such nuclei and on the time scales involved.

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NUCL 35

Searching for nuclear-plasma interactions on highly excited states with radiochemistry

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Current solid debris collected from the gold holhraum at the National Ignition Facility suggest that highly excited ^{196}Au nuclei populated via the ^{197}Au(n,2n) reaction may be interacting with the high energy density plasma, leading to a modification of the population of the $J^{\pi}=12^{-}$ isomer relative to the $J^{\pi}=2^{-}$ ground state. Due to large statistical and systematic uncertainties, these results remain inconclusive. In order to independently verify these results, we have performed a series of experiments designed to measure nuclear plasma interactions on highly excited states in ^{196}Au and the related nucleus ^{198}Au with a well controlled, beam-foil configuration. A quasi-plasma environment is generated by directing a beam of highly excited ^{196}Au and ^{198}Au onto a thick, metal backing, where nuclear excitation by electron transition or capture can occur between electrons in the backing and vacancies in the gold atom. The effects of these interactions can be seen by comparing the isomer to ground state ratio with and without interactions with the quasi-plasma. We will report on the results from several experiments, including optimizing the ^{196}Au and ^{198}Au beam through neutron transfer between ^{197}Au and ^{13}C, and the outlook of investigating nuclear-plasma interactions with radiochemical methods.

NUCL 36

Frank Kinard and The San Jose State University Nuclear Summer School

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The SJSU Nuclear Summer School has existed to help meet a National Need to train undergraduates for a career in nuclear sciences and radiochemistry. Because SJSU lost its faculty in nuclear sciences, I stepped in to save the Nuclear Summer School with Dr. Robert Silva as the primary instructor. When it was becoming too much for Dr. Silva, I asked Professor Frank Kinard to help for two weeks. The following summer, Dr. Silva turned the entire teaching program over to Dr. Kinard and a true cooperative venture was born. I will describe the evoilving interactions between us that was a true

collaboration, remembering that Frank was the heart and soul of the program. His ability to interact and nuture the outstanding Summer School Students is greatly missed. This Summer School has been supported by the American Chemical Society through grants from the Department of Energy.

NUCL 37

Remembering Frank: Thirty years of the Summer Schools, NUCL service, and friendship

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I met Frank Kinard at the first Summer School in Nuclear Chemistry at San Jose State University, where I was invited to make a presentation on the process of applying to graduate schools, a fundamental goal of the Summer School. Since that time, I have made many visits (twenty, according to my count) to the Summer School at SJSU, and Frank was my host on most of these occasions. His contributions to the early Summer Schools were many and included helping with the labs and providing transportation for students to/from the airport or for weekend excursions. Frank later became the primary instructor at SJSU and the face of our field to Summer School students. He also served as the Secretary of the Division of Nuclear Chemistry and Technology (NUCL) from 1996 to 2013. His longevity in both positions and his many contributions led NUCL to establish the W. Frank Kinard Service Award in his honor. Recollections and reminiscences of these and other activities will be presented.

NUCL 38

From the ACS Nuclear Chemistry Summer School to actinide chemistry at UC Berkeley

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The ACS Nuclear Chemistry Summer Schools provide an excellent pipeline for undergraduate chemistry majors to graduate programs in nuclear and radiochemistry around the country. I attended the summer school in San Jose in 2010, when Frank Kinard taught the entire curriculum. Frank's love of teaching radiochemistry and his unfailing belief in the ability of his students greatly contributed to my decision to pursue a doctoral degree in radiochemistry. The summer school introduced me to many aspects of the field and gave me the skills required for my present research, which is focused on the chemistry of the actinides in nuclear reprocessing. The summer school also helped me to foster a special interest in nuclear security and energy policy.

In my research, I am developing functionalized mesoporous silica materials for the selective extraction of actinides and lanthanides from acidic media. Functionalized mesoporous silica has many advantages as a solid extractant. Compared to solvent extraction systems, these solid-phase extractants have the potential to maintain the selectivity of the functional moieties while eliminating third-phase formation, to significantly reduce the amount of mixed hazardous waste produced, and to increase the efficiency of extraction due to their very high surface areas (>800 m^2/g). Compared to coated extraction chromatography beads, they are potentially more stable over repeated use. Preliminary work has focused on functionalizing the silica with a phosphonate ligand, characterizing the material using solid-state MAS NMR and IR, and conducting batch contact experiments with uranium and europium.

NUCL 39

Bridging the gap in nuclear chemistry and radiochemistry education

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Since the 1940s our nation recognized the strategic need for research and training in nuclear science, nuclear chemistry and radiochemistry for our national security, energy independence, and modern health care. Over time, however, funding to universities and National Laboratories declined in these areas and a manpower shortage resulted. For three decades, the American Chemical Society Summer Schools in Nuclear and Radiochemistry has helped bridge the gap by exposing outstanding undergraduate science and engineering majors to this critical area. As the primary instructor for one of the two summer school sites for many years, Dr. Kinard had a significant impact on the nation's current nuclear workforce. This talk will highlight some of Frank's innovations in the classroom and instructional laboratory and how those innovations are being employed in the radiochemistry courses at the University of Missouri.

NUCL 40

Frank Kinard: His influence on a generation of nuclear chemists through the ACS Nuclear Summer School

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We will remember Frank as a great educator, humanist, and friend. His decade-long devotion to the ACS/San Jose State (SJS) Nuclear Summer School has influenced many young students to join the field of nuclear and radiochemistry for graduate studies. His efforts helped to provide the pipeline for young faculty and staff at universities and national nuclear laboratories. This talk will give an outline of Frank's

achievements, and provide an analysis of the students' careers related to nuclear science.

NUCL 41

Importance of service and education to Frank Kinard

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Many nuclear chemistry students were encouraged by Frank Kinard to pursue the scientific careers of their dreams. While I never had the pleasure of taking a course taught by Frank, I nonetheless felt such support in my nuclear chemistry career through significant professional interactions with him. These included: 1) discussing my LLNL applied nuclear chemistry work or the latest super heavy element (SHE) developments as a guest lecturer during various SJSU Nuclear Chemistry Summer Schools (NCSS); 2) helping host and arrange tours of LLNL and the National Ignition Facility (NIF) for NCSS students; and 3) serving on the executive board of the ACS NUCL division together. I will discuss these long-standing interactions during this talk. As an example of the latest science topic used to engage students, I will present a summary of SHE research over the last 10-15 years on the synthesis of elements 113 – 118, including the recent IUPAC acceptance of element names for 114 (flerovium) and 116 (livermorium). Elements 113-118 have been synthesized and characterized using fusion-evaporation nuclear reactions of ^{48}Ca beams on actinide targets (^{237}Np, ^{242,244}Pu, ^{243}Am, ^{245,248}Cm, ^{249}Bk, and ^{249}Cf, respectively) at the U400 cyclotron located at the Flerov Laboratory of Nuclear Reactions in Dubna, Russia [1].

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NUCL 42

Nuclear science education through lanthanide research with undergraduate students

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Georgia Regents University has unique facilities and programs supporting nuclear science education for undergraduates. GRU itself is the result of a consolidation between the institutions formerly known as Augusta State University and the Medical College of Georgia. The Savannah River Site Community Reuse Organization is

funding a nuclear science education program at GRU with grants from the Department of Energy. Students majoring in chemistry or physics can choose to pursue a nuclear science track within the respective degrees. Despite this unique focus on nuclear science, many of the students at GRU had only thought of nuclear science research from a physics or from a medical perspective. Interest in radiochemistry and topics associated with radiochemistry has been increased in the student body by involving undergraduates in spectroscopy and electrochemical research on lanthanide coordination. Guest lectures on the nuclear fuel cycle and on the discovery of the lanthanides have been given in a Applications of Nuclear Science class and a Historically Significant Experiments in Science class, respectively, and have also been successful at increasing student interest in f-element chemistry and radiochemistry.

NUCL 43

Educating the next generations of nuclear scientists

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Frank Kinard contributed to nuclear chemistry in so many ways, not the least of which was his involvement in the ACS-DNCT Summer School in Nuclear Chemistry. Summer programs such as this are invaluable in helping to attract young individuals to nuclear science. The Texas A&M Cyclotron Institute has run a complementary program in the form of an NSF Research Experiences for Undergraduates program in nuclear science for the past 13 years. This talk will demonstrate how these programs excite the next generation of chemists and physicists about nuclear science.

NUCL 44

Training the next generation of radiochemists: Education efforts at Lawrence Livermore National Laboratory

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Currently, the National Laboratories lose nuclear scientists significantly faster than they can recruit top replacements. The number of university nuclear chemistry programs has decreased significantly over the past decade and as a result fewer PhDs are being awarded in nuclear chemistry and radiochemistry. Frank Kinard worked tirelessly to reverse this trend and we owe him a great debt. An enthusiastic educator who enjoyed teaching students at the College of Charleston SC, Dr. Kinard also successfully directed the ACS Nuclear and Radiochemistry Undergraduate Summer School held during the summer at San Jose State University for over 15 years.

Additional efforts to help increase the number of young scientists introduced to the field of radiochemistry and nuclear forensics are underway at the Seaborg Institute at LLNL. Several programs are designed to give graduate students an opportunity to come to LLNL either in the summer or for the full year for a hands-on research experience. Students conduct research with a staff scientist, attend weekly lectures, interact with other students, and present their work as a poster at the end of the program. Our graduate fellowship program is designed to provide an opportunity for students to carry out more in-depth research in nuclear chemistry, while getting their PhD. Each year the Frank Kinard and the undergraduate students from San Jose State's radiochemistry summer program came to LLNL to meet the current graduate and postdoctoral students and learn about the research our students were doing and deciding if that is something they wanted to do next.

As Dr. Kinard knew, the challenge of attracting the next generation of top students into nuclear science and reversing the declining trend in PhD's awarded is to develop and sustain successful undergraduate programs such as the one Dr. Kinard directed at San Jose State University.

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NUCL 45

Thermodynamic features of lanthanide and actinide aqueous complexes: A tribute to Frank Kinard

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Our friend and colleague, Prof. Frank Kinard, was well known for his decades-long contributions to the ACS/DOE Nuclear and Radiochemistry Summer School and to the ACS Division of Nuclear Chemistry and Technology (NUCL, aka DNCT). In the first role he was an important first contact and mentor for many nuclear chemistry novices who later became familiar faces at our meetings, coworkers, and colleagues. In the second role, Frank at some point became the face of NUCL, providing a lasting presence as Secretary for more than sixteen years. His upbeat spirit and friendly manner were for some of his colleagues reason enough to plan to attend ACS National meetings. His untimely passing caught us by surprise and left a gap that will not be easily filled. Frank Kinard was also a very competent and careful scientist, having spent numerous summers working with colleagues at the DOE national labs working on diverse projects in actinide research. He began his actinide/solution chemistry career in the laboratory of Professor Greg Choppin atFloridaStateUniversity, investigating the thermodynamics of f-element complexation and leading the Choppin-group “touch” football team to frequent victory over other departments in Saturday morning games. In this presentation, the focus will be on the thermodynamics of lanthanide complexation reactions, including some of Professor Kinard's contributions.

NUCL 46

Thermodynamics of actinide interactions with soft donors: Observations of our friend, Frank Kinard, and future directions

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While Frank would eventually contribute significantly to our Division of Nuclear Science & Technology (NUCL), both as long time NUCL Secretary and educator at the San Jose Nuclear Chemistry Summer School, his early technical contributions were in the lab of Gregg Choppin examining the solution thermodyanamics of f-element complexation. This presentation will examine his contributions in the broader scope of using thermodyanamics to understand actinide covalency – particularly in the vein of (poly)aminopolycarboxylate (APC) ligands. Courtesy application of APC ligands in over fifty years of actinide separation science, the best defined interactions of actinides with soft donors in aqueous solutions involve APC ligands. These interactions are usually defined in terms of stability constants, especially for the trans-americium actinides, with minimal dialogue regarding enthalpic and entropic contributions to the binding. To better understand the role of covalency in the binding of actinides heavier than Cm, radiotracer techniques, such as those used by Frank, will be necessary due to limited material availability and radiological hazards. An argument is presented that expansion of APC thermodynamic data with heavier actinides could be instructive regarding fundamental f-element science. The benefit of producing lanthanide-normalized linear free energy diagrams to describe actinide covalency is also highlighted

NUCL 47

How ICF targets implode to the conditions exceeding those of the center of sun, in order to achieve fusion ignition: A mini tutorial

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In this overview / tutorial we present the basics of the Inertial Confinement Fusion (ICF). We motivate, via simple models, how an ICF target can produce more energy than the laser energy that drives it, and in so doing release an unprecedented fluence / flux of neutrons of probable use in Nuclear Chemistry research. We concentrate on “Indirect Drive” in which a sphere that contains the DT fuel sits in the center of a small gold can. The laser heats the gold creating a 300 million degree “ x-ray oven”, and those x-rays drive the sphere. The “exhaust gas” from the heated surface of the sphere drives the rest of the sphere inward in a rocket-like reaction. Upon implosion, we consider the ultra high energy density state of the DT fuel, assembled into a configuration consisting of a central igniting hot spot surrounded by a shell of ultra-dense cold fuel. This ignited assembly can undergo further fusion via a thermonuclear burn wave propagating outward from the central hot spot and into the main dense fuel. We quantify the yield

from such a process. We present experimental results summarizing our progress towards that goal at the National Ignition Facility.

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Nuclear physics at the National Ignition Facility

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Although the primary use of nuclear physics-based techniques at the National Ignition Facility (NIF) has focused on their use as ignition implosion diagnostics, the recent development of robust, higher yield platforms provides a possible avenue to investigate more fundamental issues. The availability of a high neutron flux in a plasma environment is an attractive alternative to accelerator-based studies if it can be practically accessed. An overview of currently achievable implosion conditions will be presented with an emphasis on those capabilities of most interest to nuclear physics experiments such as the available neutron energy spectra and burning plasma conditions. Additionally, ongoing experimental results from neutron-activated capsule dopants will be reviewed to demonstrate the feasibility of applying specific radiochemical techniques to NIF experiments.

NUCL 49

Measurement of the T+T neutron spectrum using the National Ignition Facility

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Neutron time-of-flight spectra from inertial confinement fusion experiments with tritium-filled targets have been measured at the National Ignition Facility. These spectra represent a significant improvement in energy resolution and statistics over previous measurements, and afford the first definitive observation of a peak resulting from sequential decay through the ground state of ^{5}He at low reaction energies $E_{c.m.} < 100$ keV. To describe the spectrum, we have developed an R-matrix model that accounts for interferences from fermion symmetry and decays channels, and show these effects to be non-negligible. We also find the spectrum can be described by sequential decay through l=1 states in ^{5}He, which differs from previous interpretations.

NUCL 50

Nuclear astrophysics studies with charged particles in hot plasma environments

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With the advent of the next generation of Inertial Confinement Fusion facilities such as the National Ignition Facility, studies of nuclear reactions of astrophysical interest could, for the first time, be performed in the same temperature conditions as the stellar cores in their quiescent burning phase. Those studies range from charged particle reactions in the hydrogen and helium burning phase of the stellar evolution to neutron captures reactions on the path of the s-process.

Beside the possibility to study charged particle reaction rates at stellar temperatures, the effect of the free electron cloud on reactions can be evaluated. Currently, most of the stellar hydrodynamic calculations are performed assuming the Debye-Hückel phenomenological expression for the electron screening. In order to experimentally evaluate the electron screening in plasmas, a comparison between experiments at accelerator facilities and at facilities such as the National Ignition Facility (NIF) is needed.

This talk will address steps towards an experimental nuclear astrophysics program to study low energy charged particle reactions at Inertial Confinement Fusion facilities.

NUCL 51

Charged-particles diagnostics for NIF capsules

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Reaction-in-Flight Neutrons and knock-on charged particle reactions probe the stopping power in ICF capsules. The stopping can be altered by hydrodynamical mixing and simultaneous measurements of these two diagnostics provide unique information on the state of the plasma formed. In this talk I present the formalism relating stopping power and charged-particle diagnostics and discuss possible stopping power experiments at NIF.

NUCL 52

Nuclear fission inside astrophysical plasmas

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Is nuclear fission a fundamentally different process when it takes place inside a high-density plasma? Fission plays a critical role in

the formation of heavy elements in the universe by 1) placing a limit on the heaviest elements that can be produced, and 2) re-seeding the astrophysical r-process, which is responsible for the formation of about half the neutron-rich nuclei heavier than iron. However, most fission calculations to date do not fully account for the fact that this process takes place in very high-density plasma environments (e.g., in core-collapse supernovae and inside the crusts of neutron stars). Inside these plasmas, the fission process can be modified by electron screening effects and by multiple collisions with neutrons, photons, and electrons that can excite the fissioning nucleus into an initial state not normally encountered in terrestrial laboratories.
At LLNL we are extending a fully quantum-mechanical and dynamic theory of fission, that we have implemented for normal (non-plasma) conditions, to the regime of extreme astrophysical plasmas. We will present first results from calculations using this approach, as a function of the plasma conditions.

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NUCL 53

Neutron-induced nucleus fission in stellar processes

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Taking into account the existence of a correlation between the abundance of the elements in the Universe and the mass distribution of the products obtained with neutron-induced nuclear fission of heavy nuclei, and also taking into consideration the ongoing search for the mechanisms of heavy elements formation in the Universe, we can develop a hypothesis that:

- formation of chemical elements nucleus that are heavier than ferrum, especially nucleus with masses in intervals 80 <M <105 and 125 <M <160, occurs not only in the ***s*** -, ***r*** - and ***p*** -type processes, but also in the process of neutron-induced nuclear fission with masses M ≥ 228. Strong argument for formation of elements that are heavier than ferrum in the neutron-induced fission reactions of actinides is proved by the existence of a correlation between the abundance of chemical elements in the Universe and the mass distribution of the products obtained with neutron-induced nuclear fission of heavy nuclei. The feasibility of a stellar nuclear fission chain process requires additional research;

- in the process of stellar evolution the conditions are realized not only for the occurrence of ***s*** -, ***r*** - и ***p*** -processes, but also for the synthesis of elements nuclei heavier than silicon, including actinides with nuclear masses M ≥ 228, in reactions involving three or more nuclei occurring in ultrastrong (>10^{13} Gs) magnetic fields.

NUCL 54

Nuclear Security Science & Society: The Nuclear Policy Working Group

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The Nuclear Policy Working Group (NPWG) is an extracurricular educational programming effort sponsored by the Nuclear Science and Security Consortium (NSSC) with the aim of equipping students with the tools needed to engage in the ongoing debate on nuclear security policy. Through lectures from academics and practitioners, as well as from the students themselves, the NPWG provides members with a background in U.S. nuclear policy, the international nonproliferation regime, and technical and policy issues related to the U.S. nuclear stockpile. As a complement to the classroom-based instruction, students from both the technical and social sciences collaboratively engage in interdisciplinary nuclear security policy research projects in the technical areas of nuclear physics, nuclear engineering, nuclear chemistry and radiation detection and instrumentation. This talk will feature an overview of the NPWG's mission, educational programming and research projects in nuclear security policy. Ongoing expansion efforts of the NPWG to implement the working group model at the six partner academic institutions in the NSSC will be outlined. The NPWG complement the technical training afforded by the NSSC with education in nuclear security policy to address the need for knowledgeable practitioners in the nonproliferation field. This work continues the tradition of Dr. Kinard to provide quality education and hands-on training for students in the nuclear sciences, and to train the next generation of nuclear security experts.

NUCL 55

Use of inductively coupled plasma mass spectrometry for the pretreatment of high-level wastes at the Savannah River Site

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Residues from processing irradiated nuclear materials at the Savannah River Site (SRS) contain a majority of the elements found in the periodic table. These residues are stored in underground carbon steel tanks as precipitated metal hydroxides and hydrous oxides, concentrated supernatant liquids and saltcake. The disposition strategy for these chemical residues concentrates the radioactive elements into a small volume for

incorporation into a highly durable borosilicate-glass wasteform. The decontaminated residues or low-activity wastes are disposed of as a cementitious wasteform in a near-surface engineered vault. Successful radiochemical separations require accurate and precise measurements of a large number of elements and radioisotopes that are present in the high-level waste (HLW) supernatants. Inductively coupled plasma mass spectrometry (ICP-MS) is an attractive analytical technique because of the relatively simple sample preparation, speed, and simultaneous acquisition of a large fraction of elements found in HLW solutions. This paper will present examples where the use of ICP-MS analyses proved invaluable in developing pretreatment processes at the SRS.

NUCL 56

Method improvements on inductively coupled plasma-mass spectrometry for analysis of actinides at the Savannah River National Laboratory

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Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is used at the Savannah River National Laboratory (SRNL) to support numerous programs for the Savannah River Site (SRS). The ICP-MS instrumentation at SRNL has been upgraded to address the needs for increased sensitivity and capability to meet SRS demands for elemental characterization. An important ICP-MS application at SRNL is to analyze actinides for high-level nuclear waste characterization required by the Defense Waste Processing Facility and for H-Canyon dissolution processes. ICP-MS determinations of actinides complement those from other techniques at SRNL such as separation chemistry and nuclear counting methods. The discussion details recent developments and improvements of ICP-MS techniques for analyzing actinides.

NUCL 57

Digestion and analysis of high temperature gas reactor nuclear fuels

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The Savannah River National Laboratory (SRNL) and Forschungszentrum Jülich GmbH (Jülich) are partnering in the development of a digestion technology for the processing of graphite-based high temperature gas reactor (HTGR) nuclear fuels. SRNL has proposed a chemical oxidation process for digesting the graphite and SiC, and for placing the nuclear fuel into a chemical state compatible with existing Savannah River Site (SRS) H-Canyon process equipment. The HTGR fuel consists of small kernels of uranium/thorium encased (U/Th) in a large-volume sphere of dense graphite (referred to as “pebbles”). SRNL has successfully demonstrated the oxidation of the graphite in HTGR fuel with a mixture of molten salts. Tests were performed in the SRNL shielded

cell facilities to evaluate the behavior of irradiated fuel and its fission products during molten salt digestion. The experimental design and methods used to measure the radionuclides will be discussed.

NUCL 58

Studies of the corrosion and long term behavior of glasses and glass ceramics for immobilization of defense nuclear high level waste and used fuel reprocessing waste

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Scientists at the Savannah River National Laboratory (SRNL) in Aiken, South Carolina have studied the corrosion of simulated wasteforms (glass, glass-ceramics) using various short and long term techniques involving static and flow conditions. This program is sponsored by both the Nuclear Energy and the Environmental Management of the Department of Energy (DOE-NE & EM). Glasses studied include the French SON-68 and an Advanced Fuel Cycle Initiative (AFCI) glass for incorporation of fission fragments, lanthanides and transition metals. A six-component simplified 'International Standard Glass' (ISG) has also been fabricated and distributed to both U.S. and international labs for comparative testing. Comparative long term accelerated corrosion tests performed at high surface area to volume ratio at 200°C for over 2 years show that the AFCI glass undergoes complete reaction within 90 days while the SON-68 glass does not appear to reach complete dissolution. Leachate analyses and leached glass characterization via X-ray diffraction (XRD) and microscopy will be presented. A forward rate for the AFCI glass via Single Pass Flow Through (SPFT) methodology has been estimated based on analyzed leachate Si concentrations using glass particles at 90°C and buffered leachant at pH 10.3. Glass-ceramics are being corrosion tested from 7 days to over 1 year using standard Product Consistency Test (PCT) static powder methods with the inclusion of a small monolithic coupon in the leachate of each vessel. Short and long term corrosion are investigated using leachate composition analyses and leached coupon and powder surface analyses. Leachate analyses are facilitated with ICP-AES and ICP-MS.

NUCL 59

Enabling personalized medicine: Simultaneous imaging and treatment with tin-117m based radiopharmaceuticals

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The high-LET conversion electron (C.E.) emitter Sn-117m (t½ 14d, γ 159keV, 86%), in addition to being a good therapeutic agent for cancer, also shows considerable promise for the noninvasive molecular imaging and treatment of active atheromatous disease [vulnerable plaque (VP), also known as thin-cap fibroatheroma (TCFA)], in the coronary and carotid arteries. The VP's form below the lumen in coronary artery walls, and inflammation is the main driver. Unfortunately, a majority of all significant cardiac events (~70%) leading to MI, including sudden death, are caused by the rupture of these thin-cap fibroatheroma lesions, not lumen atherosclerosis. The C.E. from Sn-117m are ideal for treating VP's, as their discrete range in tissue (~300 μm) is approximately the same as the VP thickness in human carotid and coronary arteries. We have developed and used (i) Sn-117m electroplated coronary stents (Sn-117m stents), and (ii) Sn-117m-DOTA –Annexin [TA] for evaluating the possibility of simultaneous imaging and therapy of VP with this dual-purpose (theragnostic) radionuclide.

The TA was synthesized by attaching Sn-117m to a bifunctional chelating agent (aminobenzyl-DOTA) using a microwave reactor at elevated temperatures and then purified using HPLC. Conjugation of this chelate to the biological molecule (annexin V-128) was accomplished by preparing the isothiocyanate version of the chelate and then reacting it with lysine residues on the annexin for 90 min at 37°C. Several analytical methods (cell binding, electrophoresis, gel permeation chromatography) were used to evaluate the cGMP TA that was produced.

Studies in a hyperlipidemic rabbit model, 3d after Sn-117m- stent implantation [4 doses: 0 (cold tin), 30, 60, and 150μCi Sn-117m per 15-mm stent], upon histochemical analysis of proliferating macrophages and smooth muscle cells, demonstrated that inflammatory cells in the Sn-117m-stented segments were dramatically reduced in a dose-dependent manner. In recent studies in an Apo-E mouse VP model, systemically administered TA has demonstrated a significant anti-inflammatory therapeutic effect. The plaque composition showed significantly less expression of macrophages in all treatment groups as compared to the control group. A phase I clinical trial with TA, in which human carotid endarterectomy patients were dosed and imaged for VP, with histology as the comparison, has demonstrated promising results.

NUCL 60

Transport of plutonium and neptunium of varying oxidation states in the vadose zone using field lysimeters

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Understanding subsurface migration of actinides is vital for the protection of human and environmental health during disposition of actinide bearing wastes. The sensitivity of actinide elements to redox reactions and the profoundly different geochemical behavior

of differing actinide oxidation states complicates our understanding of Pu transport. Thus, data collected under realistic field conditions is vital for model refinement. The transport of neptunium and plutonium has been monitored for over 2 years in a unique series of field lysimeter experiments at the Savannah River Site. The field lysimeters (60-cm x 10-cm PVC pipe) were packed with a sandy loam soil and a Np(IV), Np(V), Pu(V), Pu(IV), or PuO_2-nanocolloids, source was placed approximately 30 cm above the base. Then 25 cm of clean soil was packed above the source. The lysimeter design allows for the collection of effluent rainwater from the bottom of the pipe after it has percolated through the soil and source. Quarterly collections of effluent samples are analyzed for Np, Pu, selected major ions, as well as pH and dissolved oxygen measurements. As expected based on the low mobility and high solid phase affinity of tetravalent actinides, no measureable Np or Pu has been found in the effluent from lysimeters containing Np(IV), Pu(IV), or PuO_2-nanocolloids. However, breakthrough of Np(V) occurred after approximately one year in the field and the concentration of Np in the aqueous effluent has increased steadily for each sampling event thereafter. Unlike Np(V), Similar breakthrough of Pu(V) has not been observed. Thus, is appears that Pu(V) reduction to Pu(IV) is occurring within the lysimeters, consistent with previous observations with pure mineral phases and soils. The data are discussed in terms of conceptual model development and modeled using the 1D transport code HP1 (Hydrus-PHREEQ-1D). These radiological field lysimeter experiments will be continued for a total of 10 years and represent the first of their kind in >30 years.

NUCL 61

Trace metal concentrations in South Carolina streams: Statewide, ecoregion, and ecobasin relationships

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Terrestrial anthropogenic activities can have deleterious effects on aquatic habitats. The work presented represents data from the analysis of water samples from over 200 small streams in South Carolina. South Carolina is a diverse state with two distinct geographical and ecological areas, the upstate and the coastal plain, and it contains seven US EPA ecoregions and seven major river basins. The term ecobasin is used to identify the overlap of particular ecoregions and river basins. Samples were collected and analysis was performed using ICP-MS and ICP-AES. Analytes included more common ions such as calcium and magnesium as well as trace elements such as aluminum, cadmium, chromium, copper, iron, lead, manganese, nickel, silver, and zinc. The National Land Cover Data Set (NLCD) was used to determine major land uses for the watershed areas corresponding to each sample location. The closed data were transformed using statistical methods and linear correlations between stream water composition and land use activities in individual and combined watersheds were investigated. Results indicate that changes in land use can partially explain pollutant loads which sometimes impact the quality of the stream habitats. Cadmium, copper, lead, nickel, and zinc are positively correlated with urbanization and negatively correlated with forest land cover. Calcium and magnesium decreased with increasing urbanization in the upstate, however the opposite was observed in the coastal plain. The overall results are interpreted in terms of land use and hydrogeologic characteristics of the regions.

NUCL 62

Scientific signature of Frank Kinard on the San Jose State University summer school and the scientific community

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Frank Kinard was the central figure in the San Jose State University (SJSU) Summer School sponsored by the American Chemical Society. It was largely through Frank's foresight, dedication and effort that the impact of the west coast summer school rippled well beyond those actually involved in the summer school. It was clear that the installment of his fundamental passion for science with all things radioactive into the students, from solid chemical and physical standpoints, was his mission in the weeks he spent in San Jose each summer. One of the most telling signs was the loyalty of the guest instructors that appeared in San Jose each year and how important they believed the summer school was to the fields it served. This loyalty to and the overall quality of the summer school revolved around Frank along with those assisting him at the SJSU. The impact of the summer school has been clearly felt in the fields it served, with several students having gone on to leadership roles. It has been the overall larger and extended impact, not just limited to the summer school students but extending to the entire scientific community engaged in the summer school, fostered by Frank, that was so exceptional and carries his legacy forward. A simple and small example, the relationship established between SJSU staff, Lawrence Berkeley National Laboratory summer school guests, and U.C. Berkeley led to a scientific project that measured and discovered the first circularly polarized luminescence from curium [J. Amer. Chem. Soc. **134** , 15545 (2012)].

NUCL 63

Monitoring solar photodegradation of pharmaceuticals in environmental samples: Analytical and environmental chemistry research at the College of Charleston

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Dr. Kinard's legacy of environmental chemistry is alive and well at the College of Charleston. In this presentation, research conducted with C of C undergradaute researchers in the area of pharmaceutical analysis with environmental implications will be described.

The twentieth century saw a growth in the development, availability, and use of pharmaceuticals to treat and cure disease. Now the release of these pharmaceuticals into the aquatic environment is a twenty-first century problem of worldwide concern. Natural processes occurring in the environment, including solar photodegradation, can result in chemical transformation of the pharmaceutical into structurally similar compounds that are both more persistent and more toxic to the aquatic environment.

In this work, HPLC and LC-MS were used to identify and monitor the phototransformation products of several PhACs with a focus on those with chemical structures suggesting a potential for environmental persistence and/or ecotoxicity. Investigations to assess the environmental fate of these degradates, including the toxicity of some of these compounds to amphibians commonly found in the South Carolina Lowcountry, will be described.

NUCL 64

Radiation release at the nation's only operating deep geological repository: An independent monitoring perspective

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The Waste Isolation Pilot Plant, also known as WIPP, is a transuranic (TRU) waste repository operated by the U.S. Department of Energy (DOE). The repository is emplacing defense-related TRU wastes in the Salado Formation, a bedded salt formation approximately 655 m (2150 ft.) below the surface of the Earth. Located near Carlsbad, New Mexico, an area with less than 30,000 people, the WIPP facility is the world's first underground repository licensed to accept TRU waste. Many factors contribute to the success of this project; an important one being the local acceptance engendered by an independent environmental monitoring program in the vicinity of the WIPP.

For the first time in its almost fifteen years of operation, there was an airborne radiation release from the WIPP. An independent study released by CEMRC confirmed detection of trace amounts of ^{241}Am and $^{239+240}$Pu in the air samples collected about half a mile from the WIPP site. The likely causes of the accident is currently unknown, but it is believed that it may involve the collapse of a section of roof in the active waste emplacement area, damaging one or more drums containing a type of waste readily dispersed into the ventilation air.

This paper presents the data and makes an evaluation of the data in the wake of this incident. At this point in time the concentrations of radionuclides in air and other samples have been very small and well below any level of public-health or environmental concern. Results to this time have been both low and localized. CEMRC's independence and its extensive monitoring program and constant public engagement provide confidence to the local public. CEMRC's independent monitoring program is a potential model for nuclear facilities, and especially nuclear waste repositories, elsewhere in the world.

NUCL 65

Measurements of fission products from the Fukushima Daiichi reactor accident in the San Francisco Bay area

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A variety of environmental media and foodstuffs have been analyzed for radionuclides resulting from the Fukushima reactor accident. Low background gamma-ray measurements were performed at UC Berkeley and at the Low Background Facility at Lawrence Berkeley National Laboratory. Materials tested include environmental air filters, automobile filters, rainwater, soil and sediment, as well as a variety of fish, dairy products, and plant material. Using a chemical separation and low-level beta counting procedure, a search was also made for Sr-90 in local rainwater collected soon after the Fukushima accident. Results of these measurements will be presented and comparisons will be made to the levels of naturally occurring radioisotopes found in these materials and to contamination levels observed in the San Francisco Bay Area after the Chernobyl nuclear accident.

NUCL 66

EMSL Radiochemistry Annex: A new user-facility for the study of radiological samples

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The Radiochemistry Annex, a new state-of-the-art laboratory to facilitate application of advanced analytical methods to environmental samples containing radionuclides, has been established at EMSL, a U.S. Department of Energy Office of Biological and

Environmental Research user facility located at Pacific Northwest National Laboratory in Richland, Washington. It supports world-class research in the biological, chemical and environmental sciences through integration of computational and experimental capabilities, as well as collaborating among disciplines to yield a strong synergistic scientific environment.

Critical determinants of radionuclide mobility are oxidation state, chemical speciation, and formation of surface and aqueous complexes. Understanding how environmental conditions impact these determinants is key to predictive modelling of radionuclide fate and transport in environmental systems as well as stability of wasteforms. Unfortunately, the application of new advances in molecular characterization to radiochemistry, particularly in the area of evaluating the importance of interfacial processes, has lagged behind other areas of environmental science due the need for dedicated equipment and facilities for such studies, and the fundamental difficulties of observing molecular level processes for radionuclides that are often present in very minor amounts in the interfacial region of bulk wastes or geologic materials.

A major objective of EMSL's Radiochemistry Annex is to provide a specialized environment where scientists can apply advanced experimental resources for imaging and spectroscopy to studies of radionuclides in environmental samples and waste forms. The user facility consists of approximately 6000 sq ft of lab space for NMR, EPR, XPS spectroscopies and AFM, EMP, FIB/SEM, SEM, and TEM imaging. Together with NWChem, EMSL's premier computational modelling code, users are able to address radionuclide systems from both experimental and computational vantage points. An overview of research projects and science areas ideally suited to the capability will be provided as well as modes of user access.

NUCL 67

Selectivity studies of ion-exchange resins for uranium recovery from acid mine drainage effluents

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Acid mine drainage (AMD) is a pervasive issue for mining operations worldwide. Characterized by elevated concentrations of heavy metals dissolved in its acidic medium, AMD effluent poses a significant environmental threat. In this research, AMD leachate from uranium mines is specifically targeted for the metal's toxicity, as well as for the potential development of additional remediation techniques. The AMD effluent from a typical uranium mine was modeled in the laboratory by creating a pH 3.0 sulfuric acid solution containing uranyl and various metal ions. This solution was then contacted with a series of polymer-supported, aminophosphate complexants. Affinity and selectivity of these resins for uranyl was studied by contacting them with the AMD effluent model and individual metal ion solutions.

NUCL 68

Column-scale evaluation of in situ uranium immobilization in sediments amended with phosphate

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Phosphate amendments can be added to U(VI)-contaminated subsurface environments to promote *in situ* remediation. The transport of U(VI) in phosphate-treated systems can be controlled by non-equilibrium processes involving advective and diffusive transport and adsorption-precipitation or desorption-dissolution reactions. The primary objective of this study was to evaluate the impacts of phosphate addition on the transport of U(VI) in contaminated sediments. Sediments (< 2 mm size fraction) from sites in Rifle, Colorado and Hanford, Washington, were used in column experiments with flow rates that corresponded to a typical groundwater velocity of 1 m/day. First, columns were loaded with uranium-containing influent until uranium breakthrough occurred. Following this loading stage, uranium-free influents were introduced with and without phosphate. In the absence of phosphate, all of the U(VI) was desorbed from the sediments within two weeks. In contrast, a significant amount of the adsorbed uranium was retained in the sediments when phosphate was present in the uranium-free influent. In a separate set of experiments with an influent containing both uranium and phosphate, significant continued uptake of uranium was observed.

After different durations of uranium loading and phosphate treatment, sediments were retrieved at various depths within columns and characterized using laser induced fluorescence spectroscopy, X-ray absorption spectroscopy, electron and X-ray microprobe analysis, and sequential extractions. The results provided insights into uranium-phosphate reactions and the dominant mode of immobilization (i.e. adsorption/precipitation). The response of dissolved uranium concentrations to stopped-flow events indicated that intraparticle diffusion is a rate-limiting step for uranium adsorption-desorption and affected uranium transport in the sediments. Finally, a one dimensional reactive transport model was developed for interpreting the fate and transport of uranium under subsurface environments upon addition of phosphate amendments. The results obtained can be used to design effective remediation strategies for phosphate based *in situ* remediation.

NUCL 69

Extraction of uranium from low grade ores using naturally produced siderophores

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An increase of nuclear power has resulted in a large demand for high grade uranium ores. Generally, the uranium in these ores is extracted through a dynamic treatment where the rock is crushed and mechanically ground prior to extraction with organic solutions, ion exchange, or acid leaching. We are exploring a green alternative using biohydrometallurgy techniques to naturally extract uranium from low grades ores, specifically black shale. Black shale, also known as alum shale, is primarily composed of clay minerals such as smectite and illite. Initial studies have focused on characterizing the complexation of the fungal bacteria with lanthanides and uranium using potentiometric titrations, absorption spectroscopy and mass spectrometry. In addition, the concentration and chemical form of uranium in various black shale has been characterized with electron microscopy.

NUCL 70

Harvesting radioisotopes at the National Superconducting Cyclotron Laboratory

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A remotely-operated liquid water target system for harvesting radioisotopes at the National Superconducting Cyclotron Laboratory (NSCL) was designed and constructed as the initial step in proof-of-principle experiments to harvest useful radioisotopes from the Facility for Rare Isotope Beams (FRIB). FRIB will be a new national user facility for nuclear science to be completed in 2020 at which radioisotopes can be collected synergistically from the water in cooling-loops for the primary fragmentation target. To develop the radiochemical expertise required to harvest long-lived radioisotopes of interest in this environment, the water target system was constructed and has been successfully used to collect beams of ^{24}Na and ^{67}Cu ions produced at the NSCL. Initial experiments included collection of an analyzed ^{24}Na test beam and collection and extraction of analyzed ^{67}Cu, a radioisotope with medical applications. The collected radioisotopes were characterized using low-background gamma spectroscopy at both Hope College and Washington University. The analyzed ^{67}Cu, counted offline, indicated that over 80% of the beam produced at the focal plane was delivered into the water cell. Analysis of the extraction technique indicated over 95% of the delivered copper isotope was successfully removed from the water, and made available for antibody labeling. The final test run, where ^{67}Cu was delivered with a higher rate of unanalyzed beam, contained a cocktail of contaminant beam particles that had to be radiochemically separated from the isotope of interest. The unanalyzed ^{67}Cu collection, with a beam rate ~100 times more than the analyzed ^{67}Cu collection, required circulation of the water in

the target during beam collection to minimize localized heating. Preliminary results from each of these experiments will be presented.

NUCL 71

Light charged particle emission following fusion of ^{18}O ions with ^{12}C nuclei at energies near and below the Coulomb barrier

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Measuring the de-excitation of neutron-rich light nuclei at low excitation energies is important in nuclear science as it provides an important test of the statistical model in this domain. Competition between various decay channels for such excited nuclei can be determined by identifying the emitted light charged particles (LCPs). In order to measure the LCPs evaporated from ^{30}Si at low excitation produced in the fusion of ^{18}O ions with ^{12}C target nuclei an array of CsI(Tl) detectors with photodiode readout has been developed. Using pulse shape discrimination, evaporated protons and alpha particles are resolved. Emitted LCPs have been measured in coincidence with the resulting evaporation residues allowing one to distinguish between different decay paths. Comparisons with a statistical decay model will be presented.

NUCL 72

Coincident spectroscopy in neutron-deficient actinides: A new opportunity

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The study of many neutron deficient isotopes is limited by particle stability along the proton drip line, short half-lives or very small production cross sections. These limitations do not necessarily apply to the neutron deficient actinides. However, many of the neutron deficient actinides remain unstudied due to the fact that they often decay via electron capture. Because of high γ-ray background rates heavy element production facilities are usually not sensitive to this type of decay. We have developed new capabilities at the Berkeley Gas Filled Separator (BGS) that allow us to study these isotopes. High-intensity stable ion beams from the 88-Inch Cyclotron at the Lawrence Berkeley National Laboratory (LBNL), together with the highly selective and efficient separation of compound nucleus evaporation residue products using the BGS and the

rapid delivery to a low-background detector facility, opens up many new possibilities for nuclear decay and structure studies in the neutron deficient actinides. These actinides predominantly decay via electron capture which produces vacancies in the *K*-shell resulting in x-rays uniquely identifying the Z of the decay products. We present the first results of this new methodology in studying the decay of nobelium-254 that was produced in the reaction $Pb^{208}(Ca^{48},2n)No^{254}$. By observing the gamma rays in coincidence with fermium x-rays the background was reduced to near non-existent levels and the nuclear level structure of ^{254}Fm produced in the electron capture of ^{254}Md was measured. The decay spectra correctly reproduce all currently known transitions as well as a new level that was previously unknown. Coincident gamma-decay spectroscopy gives us a new tool to study the nuclear structure of previously inaccessible systems.

NUCL 73

Nuclear structure of $^{132,134}Xe$:Relevance to shape transitions and neutrinoless double-beta decay

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The stable isotopes of xenon span a region which exhibits an evolution of nuclear structure from spherical to gamma-soft behavior; thus these nuclei may provide insight into the nature of this transition. Highly enriched (>99.9%) ^{132}Xe and ^{134}Xe gases were converted to solid $^{132}XeF_2$ and $^{134}XeF_2$, and were used as scattering samples for inelastic neutron scattering measurements at the University of Kentucky Accelerator Laboratory. Lifetimes of levels up to 3.5 MeV in excitation energy in ^{132}Xe and ^{134}Xe were determined using the Doppler-shift attenuation method. Gamma rays corresponding to new transitions and levels have been observed and reduced transition probabilities have also been determined. This new information will be examined in an effort to elucidate the structure of these transitional nuclei.

The nuclear structure of ^{134}Xe is also of relevance for neutrinoless double-beta decay experiments, specifically those searching for the decay of ^{136}Xe to ^{136}Ba. For example, the detector constructed by the EXO collaboration utilizes liquid xenon as the source and detector and is enriched to 80% in ^{136}Xe, while the remaining 20% is ^{134}Xe. As neutrons may be produced by either incident muons or natural radionuclides present in the surroundings, excited states in either isotope may be populated by inelastic neutron scattering. Therefore, γ rays emitted upon de-excitation of ^{134}Xe which have energies near the neutrinoless double-beta decay end-point energy, 2458.7 keV, may obscure the observation of this rare decay. New γ rays corresponding to transitions in ^{134}Xe have been observed in this energy region, within the resolution of the EXO detector. Gamma-ray production cross sections have been measured and will be discussed.

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NUCL 74

Inelastic neutron scattering cross sections for ^{76}Ge relevant to neutrinoless double-β decay background

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The observation of neutrino oscillations has revealed that neutrino flavors mix and that neutrinos have mass; however, the absolute mass scale remains unknown. Double-β decay with the emission of two β^- particles particles and two electron antineutrinos is among the rarest forms of radioactive decay and has been observed for only a handful of nuclei. Neutrinoless double-β decay, 0νββ, a lepton-number-violating nuclear process, will occur only if the neutrinos have mass and are Majorana particles, i.e., they are their own antiparticles. The observation of 0νββ provides the best method for obtaining the mass of the neutrino, and it is the only practical way to establish if neutrinos are Majorana particles. For a variety of reasons, several 0νββ searches focus on the decay of ^{76}Ge. The “signal” in these searches is a single peak at $Q_{\beta\beta}$, 2039 keV, in the spectrum of the ^{76}Ge-enriched HPGe detectors. As even weak background γ rays occurring near $Q_{\beta\beta}$ can complicate the analysis of 0νββ experiments, it is important to assess, quantify, and eliminate these possible obstacles. Furthermore, recent work has indicated that inelastic neutron scattering may become a significant contributor to backgrounds in tonne-scale experiments such as MAJORANA and GERDA. We have searched for the production of interfering γ rays through the ^{76}Ge(n,n′γ) reaction with monoenergetic accelerator-produced neutrons. The identification of γ rays in the 2040-keV region suggests that assessing the background contributions in ^{76}Ge 0νββ-decay searches may be more challenging than previously anticipated.

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NUCL 75

Development of a chemical system for rutherfordium

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Studies of the chemical properties of the transactinide elements ($Z \geq 104$) have always been difficult due to the short half-lives of the nuclides and the low nuclear cross sections involved. To solve this problem, atom-at-a-time methods have been used to determine the properties of short-lived isotopes. Extremely fast kinetics for the chemical reactions studied (on the same order as the nuclide's half-life) are required and the chemical system should also have potential for automation. One particular separation technique, extraction chromatography, shows promise for the investigation of the chemical properties of element 104, rutherfordium, without the solvent waste generated in liquid-liquid extractions. A fast systematic study involving the use of a ligand with a high inner group selectivity is necessary to learn more about element 104. Utilizing the homologs of rutherfordium, zirconium and hafnium, studies can be performed using liquid-liquid extractions and extraction chromatography. From literature reviews, thiacrown ethers, tertiary amines, and calixarenes show promise in extracting group 4 elements. The development of an extraction system for rutherfordium based on these extractants can further elaborate on its properties.

The goal of this research is the evaluation of these ligands to establish their suitability for future studies with rutherfordium. The ligands are tested in batch experiment with ^{89}Zr and ^{175}Hf and various concentrations of mineral acids to elucidate trend in extraction behavior.

NUCL 76

Selenides of the superheavy elements copernicium and flerovium

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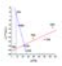
Recently, flerovium ($Z = 114$) and copernicium ($Z = 112$), which can be produced simultaneously in ^{48}Ca induced nuclear fusion reactions with ^{242}Pu and ^{244}Pu [1] were chemically identified for the first time [2-4]. Surprisingly, gas phase adsorption chromatography experiments revealed about equal interactions of Fl and Cn with gold surfaces. The aim of this work is to study furthermore the chemical behavior of Fl and Cn, in comparative gas chromatographic experiments. As stationary surface selenium was chosen. Extrapolative predictions, based on mutual correlations of thermodynamic state functions, showed that the formation of FlSe is expected to be highly favored, while the interaction between Cn and selenium is expected to be weak.



First results on the preparation of stable stationary Se surfaces and on the offline investigation of the interaction of elemental ^{197}Hg with red amorphous selenium will be presented. Further experiments will concern ^{185}Hg deposition in on-line experiments, as well as the coverage of silicon PIN diodes with thin layers of Se for on-line thermochromatographic studies with SHE.

NUCL 77

FIONA: A mass analyzer for superheavy elements

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Six new superheavy elements (Z = 112 - 118) and over fifty new transactinide isotopes ($Z \geq 104$) have been synthesized in compound nuclear fusion reactions using ^{48}Ca on actinide targets in the last decade. Because there are no direct mass determinations available, their *A* assignments are still unconfirmed. These SHE are short-lived, with their resulting decay chains ending in spontaneous fission before reaching a known mass region. Their production reactions have picobarn to femtobarn cross sections. To synthesize the SHEs at a rate of atoms per week, they require a dedicated accelerator able to produce high intensity beams (10^{13} particles per second). The resulting SHE must then be separated from the beam and unwanted transfer reaction products. At the Lawrence Berkeley National Laboratory (LBNL), we use the 88"-cyclotron to produce heavy ion beams and the Berkeley Gas-Filled Separator (BGS) when studying the transactinides. Unfortunately, the BGS's high beam suppression come at the cost of mass resolution. Ongoing upgrades to the BGS, including beam thermalization and fast ion transport, will allow us to couple a dedicated mass analyzer to the BGS. Known as FIONA (Facility for Identification Of Nuclide *A*), the analyzer is a novel mass separator based on an unbalanced Wien velocity filter. It has been designed for 100% transmission with an expected mass resolution of 2000 $A/\Delta A$. We present the current progress in commissioning the FIONA mass analyzer using a ^{nat}Xe ion source and the future directions of the project, including the first direct mass measurement of a superheavy element.

NUCL 78

Sorption data: Ways from a plain collection to recommended values

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For geochemical modeling of scenarios for the disposal of hazardous radioactive and (chemo)toxic waste, comprehensive and consistent thermodynamic data are required as well as sorption data for the surrounding host rocks. Whereas there are several projects running world-wide to arrive at the comprehensive and consistent thermodynamic data base for the aqueous phase and forming solids, the situation is much worse concerning the reactions on the mineral-water interface. For important processes such as sorption, ion exchange or surface precipitation incompleteness and inconsistencies, restricted ranges of variation (temperature, density, pressure, ionic strength) are abundant leading to hardly comparable results in geochemical modeling.

RES³T – the Rossendorf Expert System for Surface and Sorption Thermodynamics (http://www.hzdr.de/res3t) – is a free-for-use digitized thermodynamic sorption database utilizing surface complexation models (SCM). It is mineral-specific and can therefore also be used for complex real systems such as rocks or soils. Data records comprise of mineral properties, specific surface area values, characteristics of surface binding sites and their protolysis, sorption ligand information, and surface complexation reactions. An extensive bibliography is included, providing links not only to the above listed data items, but also to the primary reference. Currently efforts started to combine RES³T with the thermodynamic database THEREDA (http://www.thereda.de) to provide a comprehensive and consistent database for a holistic geochemical modeling.

Sorption speciation calculations of radionuclides on mineral surfaces will be presented, showing the actual consequences of inconsistent and scattered sorption data that can be found in literature, as well as the possibilities of the RES³T database for calculating radionuclide sorption onto complex geologic formations, *e.g.* the overburden of a nuclear waste disposal. Generally, RES³T proved to be a powerful tool for identifying data gaps for combinations of minerals and sorbing radionuclide essential for the risk assessment of waste disposals or in accident analysis.

NUCL 79

Ab initio calculations and experimental studies of uranyl sorption to graphene oxide

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Ab Initio calculations were performed to model the sorption of uranyl pentahydrate ($UO_2(H_2O)_5$) onto the carboxyl functional group of graphene oxide, and these calculations were compared with experimental batch sorption and FTIR spectra. The models were utilized to characterize the sorption reactions in terms of energetics, changes in molecular geometry, and vibrational peak shifts. The calculations performed used Gaussian09, the B3LYP functional, and 6-311++G(d,p) and LANL2DZ basis sets.

The modelling found sorption onto a carboxyl group oriented approximately parallel to the plane of the graphene sheet to be energetically favorable ($\Delta E_{sorption} = -113.4$ kJ/mol). The model for the parallel orientation showed that the uranyl asymmetric stretch vibrational peak shifted lower with sorption, from 1003 cm^{-1} to 934 cm^{-1}. Though the exact wavelengths do not match, this redshift is consistent with experimental results, where a shift in the uranyl asymmetric stretch from 937 cm^{-1} to 912 cm^{-1} was observed upon sorption.

NUCL 80

Sorption studies of actinides onto clay minerals under saline conditions

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Actinide retention at clay mineral surfaces is a well established process, which has been intensely investigated in the context of nuclear waste disposal. Up to now, however, no mechanistic sorption model exists describing reliably actinide retention under ionic strength conditions in groundwater up to ~ 5 mol/kg. Such conditions are to be expected e.g. in the vicinity of a repository in rock salt formations, in the Jurassic and lower Cretaceous clay rock layers in Northern Germany or in sedimentary rocks in Canada, all identified as potential host rocks for high level nuclear waste disposal.

Within the present study lanthanide/actinide ion (Eu(III), Cm(III)) interaction with montmorillonite and illite in aqueous solution ($I \leq 4.5$ mol/kg NaCl, $CaCl_2$ and $MgCl_2$) in absence of carbonate is investigated. Batch sorption and time-resolved laser fluorescence spectroscopy (TRLFS) experiments are carried out for a given ionic strength at fixed metal concentration and constant solid to liquid ratio for $3 < pH_m < 12$ (for $MgCl_2$ solutions up to pH=8). Highly saline conditions have a surprisingly small impact on K_d—values in the NaCl system. A significant decrease in sorption extent is observed in solutions with elevated Mg/$CaCl_2$ concentrations, notably for the trivalent cations. Nonetheless, K_d values remain high ($\log K_d \geq 4.5$) for all systems in the pH range 7-11. TRLFS studies using Cm(III) as a fluorescent probe point to the invariant metal ion first coordination sphere at given pH_m if ionic strength is increased. As a consequence, we assume no significant change in the speciation of surface sorbed Cm(III) at elevated ionic strength. Sorption data are described using the non-electrostatic 2SPNE/SC CE approach. The impact of elevated ionic strength on dissolved metal ion activity is taken into account by applying the specific ion interaction theory as well as the Pitzer approach.

NUCL 81

Study of the thermodynamics of Pu(IV)/Th(IV) sorption to goethite using variable temperature batch sorption and calorimetry experiments

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Due to the elevated temperature expected in nuclear waste repositories, there is need for a better understanding the behavior of radionuclides at elevated temperatures. In this work, sorption of Pu(IV) and Th(IV) to goethite was monitored at variable temperatures (15 °C to 65 °C) and across the pH range 1 to 6. Both Pu(IV) and Th(IV) showed an increase in sorption to goethite with increasing temperature. Van't Hoff plots were used to estimate the sorption enthalpies and entropies for both Pu-goethite and Th-goethite surface complexes. For the Pu-goethite complex, the average entropy and enthalpy values were 173.4 J/K/mol ± 28.4 and 27.9 ± 11.8 kJ/mol, respectively. The entropy and enthalpy for the Th-goethite complex increased with increasing pH value, and have average values of 249.6 ± 68.5 J/K/mol and 57.8 ± 18.4 kJ/mol, respectively. The changes in enthalpy and entropy values with increasing pH are hypothesized to be due to changes in thorium and plutonium aqueous and solid phase speciation. These data also indicate that Pu(IV) and Th(IV) sorption on goethite are both endothermic and the surface complexes are strongly driven by the positive sorption entropies. This reaction is hypothesized to be mechanistically driven by displacement of solvating water molecules from the actinides and mineral surface during sorption. The enthalpy values determined using the van't Hoff relationship are compared with those determined from isothermal titration calorimetry (ITC).

NUCL 82

Effect of natural organic matter on the sorption of plutonium to goethite

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The effect organic matter on plutonium sorption to the iron oxyhydroxide mineral goethite was studied at a bulk and molecular level. Batch sorption experiments quantified sorption of plutonium (10^{-11} M) to goethite ($0.1\ g \cdot L^{-1}$) in the presence of representative natural organic matter (NOM) with respect to NOM concentration, pH, and time. Leonardite humic acid, Suwannee River fulvic acid, citric acid, and deferoxamine-B (DFOB) were considered at concentrations of $5\ mg_C \cdot L^{-1}$ and $50\ mg_C \cdot L^{-1}$. Plutonium and NOM sorption was measured after 1, 7, 14, and 30 day sorption periods by measuring the loss of plutonium and NOM from the aqueous phase. Radiolabeled organic ligands provided a complimentary and simultaneous study of ligand sorption to goethite to inform possible ternary surface-ligand-plutonium complex formation. Generally, sorption of plutonium was decreased at circumneutral pH values relative to a ligand free system. The magnitude of the decrease in plutonium sorption followed the trend DFOB > fulvic acid > humic acid > citric acid. Thus the influence of NOM on plutonium sorption follows the strength of the aqueous Pu-NOM complexes. Modeling exercises considering plutonium speciation using FITEQL were performed using aqueous, including complexation with NOM, and surface complexation constants from

open literature. The model could not accurately predict the increased sorption of plutonium observed at low pH values where the ligands exhibit significant sorption. Thus, it appears ternary surface-ligand-Pu complexes may be responsible for increased sorption of plutonium at low pH values. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to probe the sorption mechanisms of organic matter to the goethite surface at the molecular level. Carboxylic acid and carboxylate ion stretches were found to be the molecular vibrations of greatest sorption significance. A change in the relationship between the asymmetric and symmetric carbonyl vibrations upon sorption to goethite of an NOM species was used to propose mondentate, bidentate-mononuclear, and bridging-bidentate surface complexes.

NUCL 83

Microbial sorption of plutonium and the role of extracellualr polymeric substances

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Decades of nuclear weapons testing and production have left a legacy of radionuclide contamination at many sites around the world. One of the most pressing concerns is the eventual fate of the radionuclides released into the environment. Plutonium (Pu) is of particular concern as over 2000 metric tons have been deposited in the subsurface worldwide. Its long half-life (^{239}Pu – 2.4 x10^4 yr) coupled with high toxicity makes it of particular concern for long-term risk assessments. Complications in predicting environmental behavior of Pu arise from its ability to exist in different oxidation states (III, IV, V, and VI) and the resulting differences in geochemical behavior. Additional complexities in Pu behavior occur in the presence of microbes and microbial exudates.

In this study, we examined the sorption of Pu (IV) and Pu(V) to an aerobic bacterium *Pseudomonous sp*, isolated from Pu-contaminated groundwater collected at the Nevada National Security Site (Nevada, USA). To quantify the contribution of extracellular polymeric substances (EPS) to Pu sorption, we compared Pu sorption using cells with and without bound-EPS. Our results showed that while bound-EPS contributes significantly to Pu(V) sorption across a wide concentration range, cells with and without EPS showed the same sorption capacity towards Pu(IV). Oxidation state analysis of Pu in the supernatant indicates near complete reduction of Pu(V) in the presence of cells containing bound-EPS, but not with EPS-free cells, suggesting that bound-EPS promotes Pu(V) reduction. Bound-EPS extracted from *Pseudomonous sp.* also promoted rapid reduction of Pu(V). With ^{13}C labeled glucose as the carbon source, we extracted ^{13}C enriched bound-EPS and examined its composition using Nuclear Magnetic Resonance spectroscopy (NMR). While the bound-EPS is primarily comprised of polysaccharides, a number of low molecular weight compounds, and aromatic functional groups, phosphorous functional groups were identified. The potential roles of these functional groups in Pu complexation and reduction will be discussed.

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NUCL 84

H_2O_2 catalyzed desorption of plutonium from mineral surfaces

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Understanding the stability of plutonium (Pu) adsorbed to mineral surfaces is key to understanding the environmental tranport of Pu. Previously, hydrogen peroxide (H_2O_2) has been shown to alter the redox state of arsenic adsorbed to mineral surfaces, thus affecting its sorption behavior. Here we demonstrate that environmental concentrations of H_2O_2 can affect the stability of Pu adsorbed to goethite, montmorillonite and quartz across a wide range of pH values. In batch experiments where Pu(IV) was adsorbed to goethite for 21 days at pH 4, 6, and 8, the addition of 5 – 500 µM H_2O_2 resulted in significant Pu desorption. At pH 6 and 8 this desorption was transient, with re-adsorption of the Pu to goethite within 30 days. At pH 4, no Pu re-adsorption was observed. Experiments with both quartz and montmorillonite at 5 µM H_2O_2 desorbed far less Pu than the goethite experiments, highlighting the contribution of Fe redox couples in controlling Pu desorption at low H_2O_2 concentrations. Plutonium(IV) adsorbed to quartz, and subsequently spiked with 500 µM H_2O_2 also resulted in significant desorption of Pu, demonstrating the complexity of the desorption process. Our results provide the first evidence of H_2O_2 catalyzed desorption of Pu(IV) from mineral surfaces. We suggest this reaction pathway coupled with environmental levels of hydrogen peroxide may contribute to Pu mobility in the environment.

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NUCL 85

Speciation of lanthanides in proposed ALSEP organic phases

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A new combined separation scheme called the Actinide Lanthanide SEParation (ALSEP) process has been developed to partition minor actinides and lanthanides. The neutral ligand in this process is proposed to be either tetraoctyldiglycolamide or tetra(2-ethylhexyl)diglycolamide, collectively referred to as DGAs, alongside the acidic extractant 2-ethylhexyl phosphonic acid mono(2-ethylhexyl)ester, or HEH[EHP], both of

which have been proven effective individually. When DGAs and either HDEHP or HEH[EHP] are combined in dodecane however, non-idealities exist in metal extractions (particularly with TODGA-HDEHP combinations), possibly indicating the presence of inter-molecular adducts. IR and UV-Vis spectroscopy were used to assess the coordination of neodymium in a post-extraction ALSEP organic phase to determine the contribution of individual extractants and adducts. This analysis is useful to determining the viability of certain extraction mixtures for the ALSEP process.

NUCL 86

Development of a malonate buffer system for use in advanced TALSPEAK separations

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Separation of the trivalent actinides and lanthanides remains a challenging task in the implementation of a fully closed nuclear fuel cycle. Recently, variations of the standard Trivalent Actinide-Lanthanide Separations by Phosphorous-reagent Extraction from Aqueous Komplexes (TALSPEAK) method have been proposed, substituting bis(2-ethylhexyl)phosphoric acid (HDEHP) with 2-ethylhexylphosphonic acid mono-2-ethylhexl ester (HEH[EHP]). Several advantages in what has been deemed as Advanced TALSPEAK can be noted by using HEH(EHP) rather than HDEHP, including a flatter pH profile, more predictable thermodynamic extraction behavior, and faster extraction kinetics relative to traditional TALSPEAK. The work presented here attempts to extend Advanced TALSPEAK from the traditional lactate media to a malonate buffer system, allowing separations using lower pH ranges than normally required with lactic acid. The partitioning and separation of the trivalent lanthanide elements and americium between an aqueous phase and n-dodecane diluent using a combination of HEHEHP, malonic acid, and N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) are reported. A thermodynamic model for the prediction of the extraction behavior at various conditions and the role of ternary complexes present in the aqueous phase are also discussed.

NUCL 87

Dipicolinate-based separation of trivalent actinides from lanthanides using mixed extractant solvent extraction

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Combined extractant systems have been shown to offer some advantage in lanthanide actinide separations in TALSPEAK-like systems. To provide additional options for conducting these separations, a series of novel aqueous holdback reagents have been synthesized using the dipicolinic acid (2,6-pyridinedicarboxylic acid) backbone. The functionalization of dipicolinic acid focused on minimizing changes in the coordination environment while adjusting the acidic media solubility of the holdback reagent. Functionalizing at the 4-position of the pyridine ring minimizes changes in the coordination environment. By varying the functional groups the acid solubility can be tuned. The ligands synthesized focus on the incorporation of oxygen and nitrogen bearing substituents. The functionalized dipicolinic acid derivatives simplify the complex chemistry of TALSPEAK-like systems by removing the need for buffering that is essential for the traditionally-used polyaminopolycarboxylate holdback reagents. The separation potential of these holdback reagents were characterized by application in conjunction with the promising HEH(EHP)/Cyanex-923 combined extractant system in a reverse-TALSPEAK stripping regime to separate the actinides from the co-extracted lanthanides.

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NUCL 88

Probing ligand exchange reactions of lanthanide-HEH[EHP] complexes in organic solvents using ^{31}P NMR spectroscopy

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Advanced TALSPEAK processes are currently being investigated as a method for separating trivalent lanthanides from trivalent actinides. These solvent extraction methods partition the lanthanides and actinides between an organic phase containing an organophosphorus extractant and an aqueous phase. In order to effectively design these processes it is important to have insight into the interactions between the metal ions, extractant molecules, solvent and any other solute molecules that could be present. Though NMR spectroscopy has been applied infrequently to characterize solvent extraction systems, such investigations could provide useful insights into ligand exchange reactions in the organic phase. In this study, ^{31}P NMR has been applied to probe the interactions between (2-ethylhexyl) phosphonic acid mono (2-ethylhexyl) ester (HEH[EHP]) and lanthanide(III) cations. Fresh insights into complex formation reactions in the apolar organic phase have been developed. Through investigations at variable temperatures, exchange rates and activation parameters can be calculated using the complete band shape analysis by the Rogers and Woodbrey general equations for an uncoupled two-site exchange. Results of investigations probing the effect of increasing the polarity of the organic phase on the ligand exchange reactions will also be reported.

Work performed at Washington State University with support from the US Department of Energy, Office of Nuclear Energy, Nuclear Energy University Program (NEUP) as an element of project number DE-AC07-015ID145517.

NUCL 89

Investigating the coordination of lanthanides in ionic liquids through spectroscopy and electrochemistry

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Georgia Regents University, the result of a consolidation between the institutions formerly known as Augusta State University and the Medical College of Georgia, is a primarily undergraduate institution with respect to chemistry degrees. Research on lanthanide coordination was started in the Fall of 2013 with one undergraduate participant, and was expanded to three undergraduate participants in Spring of 2014. To allow students to learn how to use the spectroscopy instrument, and how to perform data analysis, aminopolycarboxylic acids were used with lanthanides in aqueous systems through Spring 2014. In the Summer of 2014 lanthanides and lanthanide aminopolycarboxylic acid complexes were introduced to ionic liquids to study their spectroscopy and electrochemistry. Results from aqueous and ionic liquid systems will be discussed and related to prior literature. Future directions for this work, especially as it relates to solvent extractions, will also be discussed.

NUCL 90

Electrochemical studies of technetium-ruthenium and rhenium-ruthenium alloys in nitric acid: Implications for the long term behavior of metallic technetium waste forms

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In order to predict the durability of metallic technetium waste form, understanding of the corrosion properties of technetium metal is of importance. One parameter that needs to be considered in those predictions is the building of ruthenium that occurs from the decay of technetium. In this context, the corrosion behavior of technetium-ruthenium and rhenium-ruthenium alloys (rhenium was used as a technetium surrogate) alloys were studied in nitric acid. Technetium-ruthenium and rhenium-ruthenium alloys with various compositions were prepared and their corrosion behavior was studied by electrochemical methods in 1M HNO_3.

Dissolution potentials of the alloys were determined by linear voltammetry. Result shows that the dissolution potential of the alloys increase with the ruthenium content. In order to understand the dissolution mechanism, electrolysis experiments above the dissolution potential were performed; the corrosion products of the alloys were characterized on the surface of the electrodes by scanning electron microscopy and Energy dispersive X-ray spectroscopy and in solution by UV-visible spectroscopy and electrospray ionization mass spectrometry. The speciation of technetium, rhenium and ruthenium was studied after dissolution of the alloys at 1.2 V/ (Ag/AgCl). Results show the formation of permetalates for rhenium and technetium and RuO_4

NUCL 91

Speciation of low valent technetium-99 with tri-substituted and lacunary Wells-Dawson polyoxometalates

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Technetium-99 (^{99}Tc) is a long-lived ($t_{1/2}$ = 2.13 x 10^5 years) β-emitting (E_{max} = 294 keV) radionuclide formed during the fission of ^{235}U and fallout from nuclear weapons testing. Due to its long half-life and the high mobility of the pertechnetate (TcO_4^-) anion in the environment, ^{99}Tc management is an issue for immobilization and long-term storage. Metal oxides are found in the environment and are considered for ^{99}Tc waste forms. It is important to understand the speciation and mobility of ^{99}Tc in metal oxides. Specifically, we are interested in the speciation and reactivity of the technetium(I) tricarbonyl moiety with polyoxometalates (POMs). POMs are commonly used as model systems for metal oxide solid-state matrices. Here, we report on the investigation of technetium (I) and rhenium (I), tricarbonyl ($M(CO)_3^+$, M=Tc,Re) with the tri-substituted Wells Dawson ion, $[P_2W_{15}Nb_3O_{62}]^{9-}$, and the lacunary Wells-Dawson isomer, α_2-$[P_2W_{17}O_{61}]^{10-}$.

NUCL 92

Determination of radioisotopes in complex saline matrices using extraction chromatography and liquid scintillation counting

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Nuclear operations conducted over the past seventy years have resulted in the contamination of the environment with potentially hazardous radioactive species. Atmospheric testing of nuclear weapons along with accidents such as the ones that occurred in Chernobyl, Ukraine and Fukushima, Japan are some of the major sources of anthropogenic radionuclide contamination in the environment. Sea and ocean water cover more than two-thirds of the Earth's surface and are therefore the major recipients of radionuclide contamination in the environment through either atmospheric or aquatic pathways. Some of the radioactive species that are associated with these nuclear operations possess long half-lives as well as potentially high levels of mobility within the environment. Therefore, it is critical to conduct research into the separation and rapid determination of radioactive species from highly saline matrices.

A number of radioanalytical techniques are commonly used to determine radioisotopes within a variety of matrices. However, the elevated salinity of sea and ocean water imparts a complex matrix that could affect the isolation, characterization, and determination of the radioisotopes of interest. Modern radioanalytical separation techniques employ novel extraction chromatographic resins in order to separate radionuclides from sample matrices. Batch experiments were conducted in order to determine the retention capabilities of the extraction chromatographic resins for the radioisotopes of interest, particularly isotopes of plutonium and strontium. The selective extraction of the radioisotope was assayed by liquid scintillation counting (LSC) to determine the retention capability of the resin. The research investigated the effect that sodium, magnesium, and calcium constituents had on the retention capabilities of the resins. The retention capabilities of the resins were measured by determining the capacity factor, k', which is the free column volumes to peak maximum. The greater the value of the capacity factor, the more affinity the resin has for the radioisotope of interest.

NUCL 93

Desorption of radionuclides from minerals: The effect of mineral competition

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Understanding the adsorption and desorption processes is essential for predicting the mobility of radionuclides in the environment. Typically, adsorption/desorption reactions are studied in single mineral systems. Here we investigate desorption of plutonium in bi-mineral experiments in an attempt to move towards understanding radionuclide desorption in complex mineral environments. Pu(IV) was adsorbed to goethite, quartz or montmorillonite for a period of 21 days. After this adsorption period, an aliquot of the mineral suspension was placed inside 5 mL dialysis bags with a cut-off size of 3.5-5 kD. The dialysis bags were then placed inside cells containing a 175 mL plutonium-free mineral suspension of montmorillonite outside of the dialysis bag. The desorption of plutonium initially adsorbed to goethite, quartz, or montmorillonite placed inside the dialysis bag was monitored by measuring the bulk suspension of plutonium sorbed onto the montmorillonite suspension outside the dialysis bag. The plutonium sorbed onto the montmorillonite suspension outside the dialysis bag was less than expected. In addition, parallel experiments using radioactive cesium are underway to optimize the quantification of desorption rates based on this experimental framework. Cesium was chosen because of its expected simpler adsorption/desorption behavior. Ultimately we aim to use our data to improve adsorption/desorption parameters for environmental transport models and evaluate the impact of desorption rates on radionuclide transport.

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NUCL 94

Growth and characterization of palladium and silver coated silicon carbide thin films for nuclear fuels applications

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High temperature gas-cooled nuclear reactors (HGTRs) utilize tri-structural isotropic (TRISO) coated particle fuels. The SiC layer acts as the main barrier to the diffusion of fission products, provides mechanical support, and maintains structural rigidity of the TRISO fuel. Previous studies have demonstrated that chemical interactions of nuclear fission products with the SiC layer of TRISO fuel limit cell performance. In particular, palladium may corrode and fracture the SiC, while silver diffuses through the layer and may contaminate the reactor, posing a safety hazard for workers. An understanding of the reaction mechanisms and kinetics of these interactions under normal operation as well as accident conditions is critical for the development of advanced nuclear reactors, but currently is not well understood.

We have grown SiC thin films using pulsed laser deposition. By depositing 0.5 - 5ML of palladium or silver onto the thin films, we can characterize the chemical interactions between the metal fission products and the SiC layer using x-ray photoelectron spectroscopy (XPS) in order to determine how the structural integrity of TRISO fuels is reduced. Results will be compared to theoretical calculations conducted by the Stoller group at Oak Ridge National Laboratory.

NUCL 95

Colloid-facilitated Pu transport mechanisms at the Nevada National Security Site: Linking field evidence, laboratory desorption kinetics, and Pu desorption from glass alteration products

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At the Nevada National Security Site (formerly Nevada Test Site), colloid-facilitated Pu transport has been identified as the dominant mechanism leading to downgradient migration of Pu. In 1999, the transport of Pu from the Benham underground nuclear test to a well 1.3 km downgradient (ER-20-5) was detected. Since that time, several new wells have been drilled nearby. Groundwater from one of these wells, ER-20-7, located 300 meters downgradient from ER-20-5, was found to contain Pu. Isotopic ratio measurements have identified the source of Pu as the Benham test. These results, combined with tritium data, indicate that trace Pu is migrating at this location.

To elucidate the mechanisms controlling Pu transport at the NNSS (and other field sites), we have investigated the Pu desorption rates from montmorillonite colloids under controlled laboratory conditions. These data suggest that Pu desorption rates are slow enough that colloid-facilitated transport of adsorbed Pu is possible at the field scale (km distances and decade timescales). However, the transport distances are very sensitive to the desorption rates and flow velocities expected in the field.

An alternative scenario at the NNSS is Pu incorporation into secondary mineral colloids during nuclear melt glass alteration processes which can lead to irreversible association of Pu with colloids. This mechanism is being investigated through longterm hydrothermal alteration experiments and Pu desorption/extraction experiments. We will summarize the field and laboratory investigations of Pu colloid-facilitated transport and discuss the underlying mechanisms controlling Pu transport at the NNSS and other field sites.

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NUCL 96

Plutonium interactions with iron oxide nanoparticles: An investigation into reduction mechanisms

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Previous work has shown that mineral surfaces, including non-reducing mineral surfaces like hematite, can facilitate surface-mediated reduction of plutonium. Several theories have been proposed to describe the mechanisms of plutonium reduction,

including 1) Thermodynamic favorability of Pu(IV) hydroxide complexes, 2) Self-reduction via radiolysis byproducts, 3) Presence of trace reductants such as Mn(II) and Fe(II) on the surface, 4) Electron shuttling from semiconductor materials, and 5) Plutonium disproportionation. This work investigates reduction mechanisms via trace reductants and electron shuttling on α-Fe_2O_3 and demonstrates reduction of sorbed plutonium via spectroscopy measurements by Fourier transform infrared attenuated total reflectance infrared spectroscopy (FTIR-ATR). Though high concentrations of Pu are required for this measurement, FTIR-ATR provides a direct, laboratory-based, and rapid determination of Pu(V/VI) reduction via observation of the decrease in the asymmetric stretches of the axial oxygen bonds of sorbed Pu between 915 and 925 cm^{-1}.

In this work batch sorption experiments were conducted with hematite (8.5 mg/L α-Fe_2O_3) nanoparticles and plutonium (^{238}Pu(V) at $9.2x10^{-11}$ mol/L) at pH 3.5, 5.5 and 7.5 with variable trace Fe(II) content and light. The results of this work show that α-Fe_2O_3 nanoparticles are capable of shuttling electrons similarly to previous work on bulk α-Fe_2O_3 and that there can be variable trace Fe(II) content in synthesized α-Fe_2O_3. In addition Fe(II) is present in large enough quantities that small differences do not affect kinetics [a ratio of $7x10^{-5}$ to 1 for a mole to mole ratio of Pu:Fe(II)]. FTIR-ATR measurements were also taken over time for five subsamples pulled at sequential times over 20 days from one sample at pH 7.0 with $6.5x10^{-5}$ mol/L ^{242}Pu(VI) and 60 mg/L of α-Fe_2O_3 nanoparticles. The spectroscopy demonstrates for the first time that reduction of plutonium can be determined over time based on a decrease of the sorbed, antisymmetric PuO_2^{2+} peak measured between 915 and 925 cm^{-1}.

NUCL 97

Kinetics of plutonium(V) sorption and reduction on hematite as a function of total Pu concentration

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Surface-complexation models are generally informed through controlled batch-sorption studies, and more recently, spectroscopic methods that provide a molecular-level understanding of processes at the mineral-water interface. However, these spectroscopic methods have high detection limits and require plutonium concentrations that are six to fifteen orders of magnitude higher than observed plutonium concentrations in groundwater. Therefore, it is important to know if observations at high plutonium concentrations can be extrapolated to low plutonium concentrations.

The purpose of this work was to determine the reaction order with respect to plutonium for Pu(V) adsorption and reduction on hematite (α-Fe_2O_3). Changes in aqueous- and solid-phase plutonium oxidation state were monitored as a function of time and plutonium concentration in hematite suspensions containing initially Pu(V). Batch kinetic experiments were conducted at plutonium concentrations between 10^{-8} and 10^{-6} M at pH 5 and 0.3 g/L (9.3 m^2/L) hematite. Surface-mediated reduction of Pu(V) was observed under all conditions studied. However, differences in the reaction kinetics demonstrate that the mechanism of Pu(V) reduction changes as a function of plutonium concentration. Adsorption of Pu(V) was found to be the rate-limiting step at plutonium concentrations less than approximately 10^{-7} M Pu(V). Plutonium reduction in these systems was attributed to trace amounts of Fe(II) in the hematite structure. Reduction of Pu(V) was found to be the rate-limiting step at concentrations higher than approximately 10^{-6} M Pu(V) and is attributed to the formation of $PuO_{2+x}\bullet nH_2O$ nanoparticles and the Nernstian favorability of Pu(IV) surface complexes. The reaction order with respect to plutonium concentration was found to be -0.68 ± 0.09, indicating that there is a concentration dependence in these systems. This work strongly suggests that the kinetics of experiments carried out under high plutonium concentrations (i.e., > 10^{-7} M Pu) cannot be directly extrapolated to environmental concentration of plutonium.

NUCL 98

Recent advances in aqueous chemistry and thermodynamics of neptunium

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Actinide aqueous chemistry is a relevant, multifold and challenging research field of inorganic chemistry. In the context of nuclear waste disposal, actinides arise as potentially relevant dose contributors in the long term. Because of their specific electronic configuration, several oxidation states of actinides (+III to +VII) can exist in aqueous solution. This imposes a differential chemical behaviour as a function of the boundary redox conditions, which is of special concern for the safety case of repositories for nuclear waste disposal. In this framework, it is essential to continuously reduce experimental and systematic uncertainties, fill existing gaps in thermodynamic databases and improve knowledge and available data for more complex and relevant (geo)chemical systems.

This presentation focuses on aqueous neptunium chemistry as a relevant case of actinide science and good example of the experimental and conceptual approaches employed at KIT-INE for investigating actinide solubility and thermodynamics. Based upon experimental studies characterizing neptunium redox transformation processes, separate series of solubility experiments were performed involving Np(V), Np(VI) and Np(VII) in dilute to concentrated saline systems. Investigations with other actinides (U, Pu) are discussed in order to support the interpretation of the Np studies. Solubility experiments were complemented with advanced spectroscopic techniques to gain insight on the chemical models governing the investigated systems. Examples will highlight studies related to:

- Np(V) solubility in NaCl solutions: formation of ternary Na–Np(V)–OH solid phases

- Redox chemistry of Np(V/VI) under near-neutral to hyperalkaline pH conditions

- Np(VI) chemistry in alkaline NaCl media

- Formation of Np(VII) under hyperalkaline pH conditions

All studies included in this presentation aim at deriving comprehensive thermodynamic models of the investigated systems, which can be implemented in thermodynamic databases for geochemical model calculations.

NUCL 99

Biogeochemistry of neptunium in high ionic-strength brine systems

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The solubility, redox behavior and microbial interactions of neptunium (IV and V) in high ionic-strength brine systems are being investigated as an analog for plutonium (IV and V). The spectroscopy of Np(V) as a function of ionic strength and temperature has been quantitatively established and leads to small, but measurable, shifts in the absorption spectrum that need to be accounted for in complexation studies. The biosorption of Np(V) with halobacteria and archaea has also been established. Halobacteria show sorption trends that are comparable to past studies for soil bacteria whereas archaea show significantly different and much lower sorption. Solubility and complexation studies with Np (IV) are underway as an analog for Pu(IV) and progress in these experiments will be statused. These studies support the ongoing recertification efforts for the WIPP project and improve our overall understanding of actinide behavior in the unlikely event that brine saturation occurs.

NUCL 100

Interactions of Np(V) with hematite at elevated temperatures and ionic strengths

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The use of nuclear waste repositories requires good stewardship and waste management to minimize the effect on the environment. To accurately predict actinide affinity and mobility in nuclear waste repositories, it is important to understand actinide behavior with engineered barrier materials under repository conditions of high temperatures and high ionic strengths. While previous work has been performed on neptunium (Np) interactions to mineral surfaces, the majority of data has been collected at room temperature. In this study, the sorption behavior of Np(V) onto the surface of hematite ($Fe(III)_2O_3$) is being investigated as a function of temperature and ionic strength. The hematite mineral was chosen as a representative iron oxide byproduct from the corrosion of steel containment vessels. The synthesized mineral was characterized with respect to the powder X-ray diffraction (XRD) pattern, point of zero charge, surface area, and elemental content. Batch sorption studies of Np(V) are being performed from pH 4 to pH 10 at low and high ionic strengths and temperatures ranging from 15°C to 80°C. To complement the information garnered from the sorption studies, X-ray absorption spectroscopy (XAS) will be used to further characterize the sorption samples and gain a molecular-level understanding of actinide sorption. Extended X-ray absorption fine structure (EXAFS) will reveal the local coordination environment and determine whether the sorbed Np is bound to the mineral surface in an inner- or outer-sphere coordination. Results from the batch sorption studies and XAS experiments will be presented, as well as the synthesis and characterization of hematite.

NUCL 101

Large particle titanate sorbents for treatment of high level waste

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Monosodium titanate (MST) is the baseline material for the removal of strontium and actinides from High Level Waste (HLW) at the Savannah River Site (SRS). MST is a spherical amorphous solid, with a particle size of approximately 1 – 10 microns. The typical process involves a batch contact of the MST with HLW, followed by filtration to remove the loaded MST solids. Filtration is often the rate limiting step in the process, and filtration could be improved with a larger particle size sorbent. In addition, movement from a batch contact method to a column deployment would increase the efficiency of the process; however, the relatively small particle size of MST precludes its use in a column configuration without large presssure drop. This talk will discuss attempts at modifying the MST synthesis to produce larger particle sizes for 1) improved filtration and 2) column deployment of the material. Effects of the increasing particle size on the sorption kinetics will also be discussed.

NUCL 102

Synthesis and characterization of extractive scintillating resin for ultra-trace-level quantification of alpha- and beta-emitting radionuclides in aqueous media

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Traditional methods of quantifying alpha- and beta-emitting radionuclides in environmental water samples involve time-intensive, batch style analytical techniques that utilize bulky instruments. A recent development in environmental sensing is a portable, flow cell detector that utilizes extractive scintillating resin. The extractive scintillating resin serves the dual purpose of (1) concentrating the radionuclide of interest and (2) serving as a radiation transducer by transmitting a photo-signal proportional to the radionuclide's activity. Nowadays, such resins are produced by physically absorbing organic extractants and fluorophores into a polymer matrix. Unfortunately, this approach yields resins with poor stability as the active components leach from the resin over time.

This contribution describes our work to synthesize a new class of extractive scintillating resin in which the fluorophore is incorporated into the polymer matrix during particle formation and the extractive ligand is bound covalently within the matrix. Suspension polymerization was used to prepare porous poly[styrene-*co*-divinylbenzene-*co*-(4-vinylbenzyl chloride)] resin beads with 2-(1-naphthyl)-5-phenyloxazole as the fluorophore. The resin was functionalized with a uranium-selective bisphosphonate ligand through a nucleophilic substitution reaction and then hydrolyzed to its bis(phosphonic acid) form. It was characterized by FTIR, confocal laser scanning microscopy to observe the distribution of the fluorophore, and titrations to quantify the accessible binding sites. The binding capacity and uptake kinetics were investigated for both the bisphosphonate and bis(phosphonic acid) functionalized resins. Uranium uptake experiments were performed for both resins at pH values above and below the pKa1 and pKa2 of the phosphonic acid groups to compare the resin uptake for two binding mechanisms: chelation and cation exchange. Findings from this research provide the foundation for a new class of chemically stable extractive scintillating resin for use in field-deployable environmental sensors.

NUCL 103

Sorption of plutonium and europium to ordered mesoporous carbons

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Two different ordered mesoporous carbons (OMCs) were synthesized to test their application as actinide sorbent materials: 3d-cubic FDU-16-type and 2d-hexagonal C-CS-type. A portion of each OMC was oxidized with acidic ammonium persulfate (APS), to make FDU-COOH and C-CS-COOH. All four OMCs were characterized by nitrogen adsorption, scanning electron microscopy (SEM), transmission electron microscopy

(TEM), small-angle X-ray scattering (SAXS), elemental analysis, thermogravimetric analysis (TGA), infrared spectroscopy (FT-IR), and determination of the point-of-zero-charge (PZC). Based on plutonium (Pu) sorption and desorption tests with FDU-16, oxidized FDU-16-COOH, C-CS, and oxidized C-CS-COOH, the C-CS-COOH was the most effective OMC for sorption of Pu over a wide pH range. Subsequent batch experiments with Pu(VI) and Eu(III) to determine the uptake capacities, sorption kinetics, and effects of ionic strength only included C-CS and C-CS-COOH. The nature of the Pu sorption reaction was also probed via X-ray absorption spectroscopy (XAS) and TEM. The C-CS-COOH has a highly oxidized surface, open pore structure, and fairly high surface area, rendering it an effective general scavenger for actinide and lanthanide cations. Pu and Eu uptake by C-CS-COOH appears to be dictated by chemisorption, and the Langmuir Eu capacity (138 mg/g from pH 4 solution) is higher than those previously reported for several carbon materials. Pristine C-CS has a very high surface area, but a relatively low concentration of surface groups, and thus a low affinity for Eu(III). However, C-CS is an excellent sorbent of PuO_2 nanocrystals, which are formed because the carbon reduces Pu(VI) and Pu(V) to Pu(IV). Plutonium is also reduced by C-CS-COOH, but PuO_2 colloid formation in pH 4 solution is prevented by carboxyl complexation of Pu(IV) at the C-CS-COOH surface. Experiments are underway with Pu(IV), Np(V) and U(VI) to further explore the redox and sorption interactions of actinides with OMCs.

NUCL 104

EXAFS investigations of actinide coordination in engineered and environmental systems

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Effective global stewardship requires scientifically informed policies to effectively minimize negative effects on humans and the environment. The understanding of actinide interactions with barrier materials, both naturally occurring and engineered, is essential to accurately predict actinide fate and transport in nuclear waste repositories and in the environment. Likewise, in engineering materials for actinide sequestration, separation, and sensing, a molecular-level understanding of the coordination environment and the geometry of the sorbed actinide is also required. Extended X-ray Absorption Fine Structure (EXAFS) is an element specific probe of local coordination environment. Here we report on the use of EXAFS to study the bonding of plutonium and neptunium to iron oxide mineral and clay materials under different pH and ionic strength conditions. Additionally, we report on the ability of engineered mesoporous carbon materials, both untreated and chemically oxidized, to reduce and sorb Pu(VI) in solution. Different pH conditions are considered, and the results are compared to commercially available granular activated carbon. EXAFS analysis is combined with other techniques, including electron microscopy and FTIR, to develop an understanding

of sorption behavior in these materials. In doing so we have the ability to differentiate between plutonium associated with the surface without long range order, and that of nanoparticles of plutonium dioxide.

NUCL 105

Study of extraction selectivity for separations of uranium, neptunium, plutonium, and americium

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Improving the understanding of actinide chemistry with respect to different extracting agents can provide critical information for the design and optimization of separation processes. Selective separations of actinides are needed for extraction of uranium from seawater, as well as handling of radioactive waste from nuclear fuel cycles, and waste disposal. Where possible, it is particularly beneficial to combine experimental and computational investigations to elucidate differences in bonding, electronic structure, and thermodynamic properties, such as Gibbs energies of formation.

We present a summary of recent efforts toward the design of new extracting agents. In particular, our studies involve in depth analysis of complexation of uranium, neptunium, plutonium, and americium with cyclic imide dioximes, and other related cyclic extracting agents. Particular emphasis is given to a possible conjugated system due to delocalization of electron density in the ligands' backbone that could play a critical role in future optimization and design of extracting agents.

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NUCL 106

Radiation resistance of novel polymeric encapsulants

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Although cement is the material of choice for encapsulating hazardous nuclear waste, in some scenarios it suffers limitations. For instance, reactive metals corrode causing cracking of the wasteform while polymeric wastes, such as ion exchange resins, do not

bind properly to the concrete causing it to crack. Amine cured epoxy resins have been proposed as an alternative encapsulant, which is not susceptible to these processes and will maintain the integrity of the wasteform for as long as possible in the geological disposal facility environment. Radiolytic and chemical degradation of the epoxy polymer matrix could potentially lead to leaching of small organic products into the groundwater. This leaching is problematic if the organic species are acidic or capable of acting as ligands to mobilise radionuclides.

A group of four resin formulations have been considered; two pure and two commercially available. In order to test their suitability as nuclear waste encapsulants, the polymers were irradiated with cobalt 60 gamma radiation in a number of environments; pure water at pH 7 and saturated $Ca(OH)_2$ solutions, in both aerated and deaerated atmospheres. Samples were also irradiated using accelerated helium ions. The polymers and contacting aqueous phase were analysed to determine chemical and physical changes in the polymer and the identity and quantity of species leached from the resin. There is clear evidence of organic species being leached from the resins including discolouration of the water and a significant increase in total nitrogen and organic carbon contents measured. Investigations into the identity of leached species are ongoing, employing ion chromatography and HPLC-MS.

NUCL 107

Tetravalent metal phosphonate-phosphate hybrids as ion exchange materials for the nuclear fuel cycle

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One problem associated with the recovery of spent nuclear fuel is the separation of lanthanides generated during the fission of ^{235}U from the remaining actinides in the nuclear fuel cycle. The process for treating radioactive spent fuel requires a material that has radiolytic stability, is reusable, and generates little extraneous waste.

The basis for the separation procedures required is through a group of ion exchangers that are composed of phosphonate-phosphates with the general composition of $M(O_3PC_6H_4PO_3)_{0.5}(HPO_4)\bullet nH_2O$ where M is Zr^{4+} or Sn^{4+}. These compounds are porous and exhibit low affinity for ions of 1+ and 2+ charge but are highly selective for ions of higher charges (3+,4+). By utilizing oxidation procedures and solution pH, it is proposed that a clean separation of lanthanides of 3+ charge and actinyl ions of 1+ charge can be effected. These ion exchangers are simple to prepare and may ultimately be recycled for increased efficiency. Early attempts at the separation of lanthanides from actinides

will be shown. This work is in collaboration with Los Alamos National Laboratory – Carlsbad Operations (LANL-CO) and Savannah River National Laboratory (SRNL).

NUCL 108

Investigating the radiation stability of lanthanide-actinide separations ligands used in nuclear waste recycling: Water soluble BTPs and BTBPs

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In order to meet future energy needs without increasing greenhouse gas emissions, nuclear energy remains one of the best available options. However, there are concerns about the long-term disposal of the reactor spent nuclear fuel, as demonstrated in the Fukushima-Daiichi tsunami incident. An alternative practice is to recycle and reprocess spent nuclear fuel. To date, the use of solvent-extraction systems with designer ligands have proven very effective in quantitatively separating out uranium and plutonium from fuel dissolved in nitric acid. However, the removal of the minor actinides, americium and curium, from the more prevalent lanthanides present, is more problematic. In addition, all of these chemicals must be first shown to endure high radiation exposure in order to for the separation to be ultimately successful.

One potentially useful separations approach for the minor actinides is to use an appropriate hydrophilic ligand for the selective complexation of actinides, and extract out the undesired lanthanides into an organic phase. Specific ligands such as water-soluble BTPs or BTBPs have been synthesized for this approach. However, the radiation stability of these compounds has not yet been determined.

Previous work on other extraction ligand systems has shown that their radiation-induced degradation is mostly by indirect means, from the radical species produced in diluent radiolysis. In aqueous solution, the nitrate and hydroxyl radicals have been identified as the most important for ligand degradation at process scale. Therefore in this study we have determined the kinetics and efficacy of these radical reactions, utilizing electron pulse radiolysis and steady-state irradiation techniques.

NUCL 109

Silica-anchored CMPO-modified calix[4]arenes for radionuclide separations

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Within the past two decades, calixarenes have been examined for their properties in effecting the separation of radionuclides for a variety of purposes. The goals of many of these studies have been to separate elements possessing similar chemistry and oxidation states but slightly different radii, such as the lanthanides, americium, and curium. Carbamoylmethylphosphine oxide (CMPO), a ligand that has been shown to be selective for separating trivalent f-block elements, was attached to the upper rim of the calixarene in some of these studies in order to achieve such separations. In the overwhelming majority of these studies, these modified calixarenes have been used in liquid-liquid extraction systems. Recently, we have succeeded in anchoring a CMPO-modified calix[4]arene to porous silica. The synthesis of this new material has allowed us to investigate the radionuclide sorption properties of the anchored CMPO-modified calix[4]arenes, within the context of a solid-supported system, rather than a liquid-extraction system. Preliminary studies have been undertaken to investigate the sorption of europium on the silica-anchored CMPO-modified calix[4]arene system. These initial studies show the effect of ionic strength and pH on the calix[4]arene's ability to effectively sorb europium, and extend to a study of other lanthanides, as well as americium and curium.

NUCL 110

Synthesis of uranium mononitride microspheres via higher uranium nitrides

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Recent interest in using uranium mononitride (UN) as the fission core for accident tolerant nuclear fuels in the form of tristructural isotropic (TRISO) particle fuels has brought forth the importance of investigating different routes in synthesizing UN. Other than synthesizing UN, such investigations should also unveil potential pathways that could lead to the fabrication of high density UN; densities up to 95% theoretical density. Furthermore, the replacement of UO_2 by UN in nuclear fuels has been considered because of UN's desirable chemical and physical properties such as high fissile metal density, high melting point, and high thermal conductivity compared to UO_2. In this presentation, we discuss a synthetic route to UN in the form of microspheres via higher nitrides, especially uranium sesquinitride (U_2N_3). In this process, microspheres of carbon-incorporated UO_2 or UO_3 were first synthesized using an internal gelation process. These oxides were nitridized in N_2 gas environment to form U_2N_3, which was then fully converted into UN. Chemical and physical characteristics such as phase purities, microstructure, and densities of higher nitrides as well as the mononitride will be discussed in this presentation.

NUCL 111

Catalysis: Uranyl monomer to U_{24} nanocapsule

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Self-assembly mechanism of Uranyl nanocapsules has been known for almost a decade. Crystals of monomers and POM capsules have been isolated and well characterized in both solution and solid state by techniques such as X-ray diffraction, X-ray scattering, multi-nuclear NMR, and vibrational spectroscopies. However, further details for the process of capsule self-assembly and to control the capsule geometry, size and monospecificity remains to be elucidated. We are currently investigating this reaction pathway, using as a model system, self-assembly of the $[UO_2(O_2)OH]_{24}^{24-}$ (U_{24}) capsule from the lithium monomer using Raman spectroscopy and Small-angle X-ray Scattering (SAXS). The surprising finding of this study is that we can completely turn this reaction on and off by the presence or absence of a catalyst that serves to decompose the peroxide ligand. While prior calorimetric studies indicated thermodynamic stability of the monomer compared to the capsules, the kinetics of the reaction has not been addressed. This current study suggests that there is indeed an energetic barrier to conversion of the monomer to the nanocapsule.

NUCL 112

Solid solution formation and uptake of Radium in the presence of barite

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The migration of radionuclides in the geosphere is to a large extend controlled by sorption processes onto minerals and colloids. On a molecular level, sorption phenomena involve surface complexation, ion exchange as well as co-precipitation reactions. Co-precipitation leads to the formation of structurally incorporated radionuclides in a host structure. Such solid solutions are ubiquitous in natural systems – most minerals in nature are atomistic mixtures of elements rather than pure compounds. In many cases the formation of solid solutions leads to a thermodynamically more stable situation compared to the formation of pure compounds, due to a negative excess Gibbs energy of mixing. Deriving a thermodynamic model

requires a molecular level concept including information such as the actual substitution mechanism, site occupancies and related ordering phenomena.

In this study we have combined experimental data, atomistic simulations and thermodynamic modeling to study in detail how a Radium containing solution will equilibrate with solid $BaSO_4$ under conditions relevant to the disposal of high level nuclear waste in a deep geological repository. Batch sorption experiments at close to equilibrium conditions and time of flight secondary mass spectrometry (ToF-SIMS) indicate the formation of a $Ra_xBa_{1-x}SO_4$ solid. Our first principles calculations based on the single defect method indicate a value of $W_{BaRa} = 2.50 \pm 1.00$ kJ/mol, implying a non-ideal solid solution. The results of thermodynamic modeling are in good agreement with the final $Ra_{(aq)}$ equilibrium concentration from experimental data at room temperature. A lower limit of the computed W_{BaRa} (1.50 kJ/mol) and a solubility of the $RaSO_4$ endmember of $pK_{RaSO4}= 10.41$ can be proposed based on the combination of the experimental and computational data.

NUCL 113

Influence of temperature and ionic strength on actinyl ion sorption to hematite

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The migration of actinides in the environment is affected considerably by their interactions with the mineral – water interface. In deep geologic repositories used for storing nuclear waste, actinides encounter more extreme environmental conditions than those normally studied in surface and ground water systems. In particular, these nuclear waste repositories have been found to possess elevated ionic strengths (> 1 M) and temperatures (80 ^{o}C). However, the vast majority of aqueous speciation data and sorption data for actinides has been collected for low ionic strength, low temperature conditions. Therefore, sorption experiments conducted at high ionic strengths and elevated temperatures are warranted.

In this work, uranium and neptunium adsorption onto the iron oxide mineral hematite (α-Fe_2O_3) was studied over a range of concentrations (1 – 1000 µg/L), temperatures (25 – 80^{o}C), and ionic strengths (0.01 and 1.0 M). Hematite was selected as a representative degradation product of steel canister corrosion within a spent nuclear fuel repository. While uranium has previously been determined spectroscopically to form inner-sphere surface complexes with hematite, adsorption of uranium in our study was observed to decrease considerably with increasing ionic strength, indicating that changes in double layer thickness, potential formation of outer-sphere complexes, ion competition, and/or ion activity are influencing uranium binding. In contrast, neptunium adsorption to hematite was not found to be affected by increasing ionic strength; which is intriguing given neptunium's weaker affinity for the mineral surface compared with that of uranium. Sorption of uranium at constant ionic strength increased with increasing temperature.

This rise in sorption is hypothesized to be due to an entropy driven reaction in which hydrating waters of uranium and the mineral surface are displaced upon formation of the surface complex.

NUCL 114

Effect of borate on An(III/IV/V and VI) solubility in dilute to concentrated NaCl, $CaCl_2$, and $MgCl_2$ solutions

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The assessment of the long term safety of a nuclear waste repository requires reliable information about the chemistry and migration behavior of actinides. Boron may be present in the repositories for radioactive waste as a component of the emplaced waste. In repositories in rock-salt formations, boron can further be a component of the intruding brine solutions.

In the present work, the interaction of Nd(III) (as chemical analogue of An(III)), Th(IV), Pu(IV), Np(V) and U(VI) with borate in dilute to concentrated alkaline NaCl, $MgCl_2$ and $CaCl_2$ solutions was studied at 22 ± 2°C by a comprehensive series of solubility experiments complemented with XRD and XPS measurements. No significant increase in Nd(III) solubility occurred in any of the investigated salt systems in the presence of $[B]_{tot} \leq 0.4$ M, compared to borate-free systems. On the contrary, a significant decrease in Nd(III) concentration was observed at $pH_c \leq 9$ in NaCl and $MgCl_2$ systems with $[B]_{tot} \geq 0.16$ M. This observation, together with a clear change in the slope of the solubility curve and the further confirmation by XPS analyses indicated the transformation of $Nd(OH)_3(am)$ into a so far unknown Nd(III)-borate solid phase. The solubility of $Th(OH)_4(am)$ remains largely unaffected by borate within $7 < pH_c < 11$ in dilute to concentrated NaCl and $MgCl_2$ solutions. Additional experiments with $PuO_2(am)$ under similar conditions are currently under way. No significant increase in the solubility of $NpO_2OH(am)$ in NaCl and $MgCl_2$ solutions with $0.04 \text{ M} \leq [B]_{tot} \leq 0.16$ M is observed in first scoping experiments although minor effects at present cannot be ruled out. Additional experiments are ongoing to further assess the Np(V) and also U(VI) case (solubility studies with $UO_3{\cdot}2H_2O(am)$ solid phase are being started) in order to establish robust solubility data and analyze possible transformation processes into less soluble borate bearing actinide phases.

NUCL 115

Rapid method for determination of Ra-226 from unconventional (shale) gas flowback water by ICP-MS

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Radium is a common naturally occurring radioactive material (NORM) with high mobility that is found in high salinity shale gas wastewater (flowback and produced water). Ra-226 is the dominant radionuclide encountered in shale gas water at activities exceeding ten thousand picocuries per liter. In comparison, the EPA maximum contaminant level (MCL) for drinking water is 5pCi/L and the maximum radioactivity for disposal in RCRA-D non-hazardous landfill is 25pCi/g. Traditional methods for Ra-226 determination either require long sample holding time to allow radon emanation to reach equilibrium (e.g. EPA method 903.0 and 903.1) or long detection time (e.g. EPA method 901.1). A novel detection method with reduced sample holding and detection time that utilizes Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) in combination with solid-phase extraction to separate radium isotopes from the background matrix in high salinity solution was first developed and validated in this study. This method requires a series of sample preparation steps as outlined on Figure 1 and several minutes of detection time for each sample.

Figure 1. Radium purification protocol utilizes a combination of 50W-X8 and Sr*Spec resins to extract radium from high salinity solutions

NUCL 116

Cs isotopic ratio measurements from environmental samples using thermal ionization mass spectrometry: Applications to ultra-trace environmental analyses and nuclear forensics

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Cs isotopic ratios can provide the age, origin, and history of anthropogenic Cs contamination in the environment. One challenge with Cs analyses is that most environmental samples contain ultra-trace, femtogram quantities of fission product Cs. Thermal Ionization Mass Spectrometry (TIMS) is one method that enables accurate quantification of Cs isotopic ratios at some of the lowest detection limits currently achievable. However, TIMS requires highly purified Cs samples; complete removal of any isobaric and ionization inhibiting interferents becomes increasingly important with decreasing concentration. We report a new chromatographic method for performing Cs isotopic ratio measurements from environmental samples using TIMS. This method utilizes the extremely high selectivity of ammonium molybdophosphate-polyacrylonitrile

resin (AMP-PAN) to extract Cs under a wide variety of environmental matrices (soil, rice, clover, spinach, grass, and others) and mass loads. Application of this method to several case study samples, where the power of Cs isotopic analyses for the determination of environmental Cs contamination, will also be discussed.

NUCL 117

Application of a sequential extraction procedure for analysis of actinides in various soil and sediment samples

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To obtain a better understanding of the mobility of actinide element contaminants in the environment, the association of the contaminants with specific host phases of soils and sediments must be investigated. This investigation is most commonly conducted using sequential extraction techniques that employ the selective dissolution of soil phases with increasingly aggressive chemical treatment. A sequential extraction procedure by Outola et al (2009) is used as the basis for this research. Five operationally defined soil fractions are leached using the procedure: exchangeable, carbonate, Fe/Mn oxides, organic and residual. The procedure is applied to various standard reference materials from the International Atomic Energy Agency (IAEA) and the National Institute of Standards and Technology (NIST) to determine its applicability across a broad range of soil profiles. Analysis of the resulting leachates containing multiple actinide elements requires sample separation and purification prior to alpha spectroscopy and can be very time consuming and labor intensive. An extraction chromatography based procedure by Maxwell et al (2006) is therefore investigated as an alternative separation method due to the quick and efficient separation of actinide elements that can be achieved. Samples are prepared for alpha spectroscopy using cerium fluoride microprecipitation. Results give a better understanding of how the procedure is affected when used with soils and sediments from various environments; i.e. lake sediment vs. sediment from an ocean lagoon. Information on bioavailability, mobility, origin and mode of occurrence can be furnished from this method, which is important for such applications as environmental remediation, fate and transport of radionuclide contaminants in the environment, and nuclear forensics.

NUCL 118

FDG-based prodrugs for imaging chemical microenvironment

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Several molecular imaging modalities have focused on imaging agents that are chemically modified in the tumor microenvironment, for example ^{18}F-FMISO, which is accumulated in hypoxic cells by an O_2-dependent mechanism. Our work has focused on the development of a prodrug scaffold to interrogate tumor microenvironments, for example the low pH found in the extracellular matrix, and increased concentrations of reactive oxygen species (ROS) in particular H_20_2. We have synthesized several 18F hydrazones and oximes as imaging prodrugs from their corresponding hydrazine and hydroxylamine precursors, at high radiochemical yield. These have shown to be responsive to chemical microenvironment *in vitro*.

NUCL 119

Radiosynthesis of H_2O_2- labile ^{18}F prodrugs for ROS sensing

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Reactive oxygen species (ROS) including hydrogen peroxide have been shown to play an important role in the development and progression of cancer. The aim of this project is to develop a PET probe capable of sensing hydrogen peroxide in tumor microenvironments. Toward this goal we have developed new radiochemical methods for incorporation of H_2O_2-labile chemistry into ^{18}F tracers. Here we report the radiosynthesis of ^{18}F H_2O_2-labile prodrugs and their peroxide-dependent uptake in UOK 262 cells *in vitro*.

NUCL 120

Development of nuclear receptor imaging agents

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Estrogen receptor (ER) is expressed on the majority of newly diagnosed breast cancers, and endocrine therapy is superior to standard chemotherapy in these tumors. Although lack of ER expression is predictive of lack of response to endocrine therapy, not all ER

positive tumors are responsive. The progesterone receptor (PR) is a downstream target of estrogen receptor transcription; therefore molecular imaging approaches aimed at detecting either increased PR expression after estrogenic stimuli or decreased PR expression after anti-estrogen therapy offer the potential to determine functional ER status and predict endocrine therapy response a) non-invasively b) rapidly and c) in multifocal disease, offering advantages over current immunohistochemical approaches for patient selection.

Successful imaging of PR status by the steroidal compound [^{18}F]-FFNP was initially carried out in a mouse model and subsequently progressed to clinical trial.[1-2] The lipophilicity of [^{18}F]-FFNP may contribute to non-specific uptake, confounding imaging data. Non-steroidal compounds such as Tanaproget (a high affinity PR ligand developed) have superior physicochemical properties and have been show to express high specificity to PR with little cross-reactivity to other members of the steroid hormone receptor family.

Synthesis of a focused library of non-steroidal Tanaproget derivatives incorporating a fluorine-containing motif has been successfully completed. Biological evaluation in cell-based assays has highlighted some high affinity compounds and a lead candidate has been selected for radiolabeling (Figure 1). Radiolabeling of a lead compound via Suzuki cross-coupling under microwave conditions is currently being investigated.

[illegible]

References:

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NUCL 121

PET/PDT theranostics: Synthesis and biological evaluation of a peptide-targeted Ga-68 porphyrin

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The development of theranostic Positron Emission Tomography (PET)/Photodynamic Therapy (PDT) agents combines two promising areas of cancer research, providing both diagnostic and therapeutic action in a single compound. Incorporation of a PET-appropriate radioisotope allows quantitative evaluation of tumours, while PDT agents can subsequently treat the cancer with minimal damage to healthy tissue. Porphyrins represent excellent synthetic targets for these theranostics; they can be modified to be conjugatable and water-soluble, and the central cavity can act as a metal chelator, allowing radiolabelling without modification of the porphyrin skeleton. Ga-68 is of particular interest as it offers on-demand isotope production at low cost, while allowing retention of the photophysical properties of the porphyrin following complexation.

Conjugation of porphyrins to tumour-targeting biomolecules allows improved uptake into target tissue, with peptides representing ideal targeting moieties due to their ease of modification, binding selectivity and rapid clearance from the body. The TWYKIAFQRNRK dodecapeptide was selected for use in this work as it specifically binds to the $\alpha_6\beta_1$-intergrin, which is upregulated in glioblastoma cells and other cancers. While imaging applications for this peptide are limited due to activation of the intergrin and subsequent increased tumour invasiveness, it is a promising targeting agent for theranostics which allow treatment following imaging.

In this work, the first example of both cold and hot gallium-complexation in a water-soluble, conjugatable porphyrin is demonstrated, with complexation carried out under aqueous conditions with minimal purification required. Optimisation of hot gallium insertion was carried out, with >95 % radiochemical yields obtained. Targeting with the FITC labelled dodecapeptide was demonstrated *in vitro*, and a “click” bioconjugation methodology between the porphyrin and peptide was optimised. Photobiological evaluation of the conjugate was carried out, with future work aiming to assess its suitability as a PET agent in appropriate *in vitro* and *in vivo* models.

NUCL 122

Evaluation of ligand binding groups for improved chelation of zirconium-89

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Zirconium-89 is a valuable nuclide for antibody-based radiotracers for diagnostic positron emission tomography (PET) imaging due to the advantageous match between its physical half-life of 78.41 h and the multi-day biological half-life of IgG antibodies. Within the realm of ^{89}Zr-based PET tracers, the most widely used chelator for $^{89}Zr^{4+}$ is desferrioxamine (DFO); however, the observed uptake of radioactivity in the bones of mice is evidence of *in vivo* release of $^{89}Zr^{4+}$.[1] A more robust chelation system for $^{89}Zr^{4+}$ could eliminate the release of the bone-seeking $^{89}Zr^{4+}$ cation *in vivo* and thus make for a safer PET tracer with reduced dose to non-target tissues. The first step in selecting an improved chelator is to understand the coordination chemistry of the Zr^{4+} cation. Zr^{4+} is a hard, oxophilic metal which requires a hard, oxygen donating ligand. DFO is a natural siderophore containing three hydroxamate groups, which works reasonably well with Zr^{4+}. Other potentially interesting binding groups from natural siderophores include catechols and hydroxypyridinones. Herein, we examine the individual binding functionalities of hydroxamate, catechol, and hydroypyridinone groups as well as evaluate existing chelators containing these groups, namely DFO, 3,4,3-LICAM, and 3,4,3-(LI-1,2-HOPO), respectively. These last two ligands — 3,4,3-(LI-1,2-HOPO) and 3,4,3-LICAM — were selected from a library of published Pu chelators on the basis of the fact that Zr and Pu are known to have similar chemistries.[2] The 3,4,3-(LI-1,2-HOPO) ligand in particular is shown to form a highly stable complex with $^{89}Zr^{4+}$.

NUCL 123

Hunt for the most thermodynamically stable ligand for $^{186/188}$Re(V): A computational and experimental approach

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The clinical utility of technetium-based radiopharmaceuticals for imaging makes designing appropriate therapeutic agents complementing the ^{99m}Tc-imaging pharmaceuticals advantageous. Rhenium, the third-row congener of technetium, has two radioisotopes useful for developing therapeutic radiopharmaceuticals, ^{186}Re and ^{188}Re. Rhenium(V) is the most accessible oxidation state from perrhenate, the chemical form available at the radiotracer level. Forming kinetically stable Re(V) complexes under *in vivo* conditions is much more challenging than for Tc(V) because of the susceptibility for re-oxidation to perrhenate. The successful development of therapeutic $^{186/188}$Re agents hinges on the design of chelators that form kinetically inert complexes with the Re(V) metal center. To better understand which ligands most likely form thermodynamically stable complexes with monooxorhenium(V), a computational search of a series of monoamine-monoamide dithiol (MAMA) and bisaminothiol (BAT) ligands was performed. These studies also compare analogous ligands that replace the N_2S_2 systems of the MAMA and BAT ligands with N_2O_2, N_2Se_2 and P_2S_2 coordinating atoms to determine if changing the heteroatom will improve complex stability. Additionally, NO_3, NS_3, NSe_3, and PS_3 ligands were investigated. Preliminary *in silico* results showed that P_2S_2 complexes are more thermodynamically stable than the other ligands. P_2S_2 ligands, previously prepared for rhodium(III) complexation, have been modified for use with monooxorhenium(V). The computational findings for all of the ligands, experimental preparation of the P_2S_2 ligand and the preliminary complexation of monooxorhenium(V) will be discussed.

NUCL 124

Neutron capture radiography of boron distribution in maize

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Boron (B) plays a critical role in plant reproduction and growth, and thus, has implications for the world's food supply; however, its role is not yet completely understood. A key component of this research area relies on the elucidation of the B distribution and concentration in normal and mutant tissues. Boron distribution and concentration could be measured by neutron capture radiography (NCR), but to date, there have been few published studies in this regard. NCR should be able to provide data in high resolution not easily obtained by other methods of analysis (*e.g.*, azomethine H colorimetric test, ICP-AES). We have validated NCR for its use in maize using the 10-megawatt facility at MU-Research Reactor Center. Calibration standards and leaf tissue were attached to CR-39 detector plastic and irradiated for 1 minute. The detectors were etched in 6.25 N aqueous NaOH at 98 °C for 25 minutes. Regions of detector, 1 x 1 mm in size, were analyzed by a TASL track reader. Reasonable precision of standards from 1 – 200 ppm B-10 (5 – 1000 ppm natural B) was obtained with a limit of detection between 1 – 5 ppm B-10. NCR values were correlated with standard ICP-MS. DOE Project Number: DE-SC0002040 (SS Jurisson, PI) provided partial support of this research.

NUCL 125

Preparation of simulated urban debris samples formed from nuclear weapons explosions

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Following the destruction of the World Trade Center on September 11, 2001 it was discovered that the bulk of particulate samples consisted of conglomerates of concrete and glass. While this attack was not a nuclear incident, it did bring to light that in the event of an attack the majority of samples to be collected and analyzed would consist of a melt-glass material containing urban debris.

The purpose of this research is to prepare melt-glass samples that can be analyzed for isotopic components, allowing researchers to establish methods of analysis prior to the need arising. This research is being conducted as a collaboration between the University of Nevada Las Vegas, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Pacific Northwest National Laboratory.

Four samples were irradiated at the Flattop Critical Assembly at the Nevada National Security Site. The samples consisted of gold, platinum, titanium, and iridium, each containing an aluminum-gold wire as a neutron flux monitor. Following irradiation the samples were shipped to the University of Nevada Las Vegas where they were dissolved and prepared for inclusion in the melt-glass complex. The melt-glass samples consisted of 1 gram pre-treated soda lime glass, 1 gram pre-treated Portland cement, and a combined solution of the irradiation products totaling 1 milliliter. The samples were heated in a tube furnace at 1500°C for one hour under an argon atmosphere. The samples were removed, packaged, and shipped to their respective laboratory.

The sample preparation for this project was successful. However, the melt-glass did fuse to the platinum-gold crucibles that were used. Gamma spectroscopy of the prepared melt-glass and liquid aliquots was completed. Once the melt-glass has been successfully removed from the crucible further analysis can be conducted.

As this collaborative project continues, different isotopes and urban-debris complexes will be utilized for melt-glass preparation.

NUCL 126

Quantification of americium in soil cores from the site of the BOMARC accident

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The Boeing Michigan Aeronautical Research Center (BOMARC) operated as a nuclear missile defense site from 1958-1971. In June of 1960, a missile carrying a nuclear warhead was partially consumed by a fire which resulted in the release of weapons grade plutonium (WGP). The WGP was scattered over a 7-acre area due to turbulent local atmospheric conditions and the water applied as part of the fire extinguishing measures. The WGP hot particles in the BOMARC soil exist in the form of high-fired PuO_2. These refractory particles consist of a matrix containing ^{239}Pu, ^{240}Pu and ^{241}Am. The americium is expected to be trapped in the refractory matrix together with the plutonium; however several studies have found the presence of ^{241}Am outside of this matrix. This research is part of a study that will aid in the investigation of the mechanisms that resulted in the migration of ^{241}Am away from the refractory matrix. Soil samples from the BOMARC missile incident were examined and the amount of ^{241}Am present was quantified. Soil samples were counted for 72 hours each on a planar thin window Canberra Broad Energy Germanium (BEGE) detector. The Canberra Genie 2000 Spectroscopy software was used to identify ^{241}Am and ^{239}Pu by locating the associated full energy peaks. The area under the peak was determined and the amount present in each soil sample was quantified after background and efficiency correction. The activities in each soil sample were compared. The results of this study can be used to model responses for future situations involving the accidental or intentional release of WGP. The isotopics of the WGP matrix can also be used to obtain information about the source material, to identify production processes and provide chronometric information.

NUCL 127

Chromatographic separation of fast neutron activated titanium for post-detonation nuclear forensic analysis

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In Nuclear Forensics, nuclear or radiological materials are characterized by their physical, chemical, isotopic, microstructural, and morphological properties. Techniques and information determined through characterization of materials allow for government and international agencies to correctly trace the origin of nuclear or radiological materials seized, or dispersed into the environment.

Presently, little data exists on the effect of prompt fast-neutron activation on many common metals in the urban environment and detonation device such as titanium. Activated titanium needs to be separated under known conditions so as to provide baseline data of what is present in the urban environment and how the metal may change from activation.

Extraction chromatography is being employed to separate concentrations of scandium (^{46}Sc, ^{47}Sc, and ^{48}Sc) from activated stable titanium (^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti, and ^{50}Ti) enabling determination of n-p cross section values. The retention of scandium (III) and titanium (IV) in ppm quantities was measured in hydrochloric and nitric acid matrices using Eichrom's Ln and DGA resins. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Emission Spectroscopy (ICP-AES) were used to measure concentrations of analytes left in solution after extraction occurred.

Using Eichrom's Ln resin, scandium was found to almost entirely adsorb in both matrices with a k' of ~8000 where k' is the number of free column volumes to peak maximum or resin capacity factor. However, significant titanium quantities adhered as well preventing a pure separation. As the pH of the solutions were lowered from concentrated to 0.1 M, the k' value of titanium decreased to ~10-20 in both acid matrices while scandium's k' stayed constant. A purer separation is needed where titanium has a k' below 1. Further work will be employed using Eichrom's DGA resin in both matrices. Once a high purity separation is completed, the process will be scaled up to gram quantities.

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Nuclear forensics program at Texas A&M University

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Nuclear proliferation is a growing concern worldwide due to the increased availability of nuclear materials, knowledge of sensitive technologies, and the possibility of diverting nuclear materials such as uranium and plutonium away from peaceful uses. Due to the increased risk of nuclear threats, nuclear forensics capabilities are being developed at Texas A&M University with sponsorship from the Department of Homeland Security.

Our objective is to determine the differences in fission products and actinides characteristics for uranium samples irradiated in different type of nuclear reactors. This paper presents the experimental part of the research. The final goal of these experiments is to analyze trace elements and isotopes present in the residual matrix produced by each and every step of industrial PUREX process. This talk will discuss the latest work in this area.

NUCL 129

Impact of electrospray ionization (ESI) on metal: Ligand solution equilibria

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The impact of ionization during electrospray ionization (ESI) on the complexation equilibria between rare-earth cations (Nd^{3+} and Yb^{3+}) and aminocarboxylate ligands is under investigation. Ligands include NTA, EDTA, DTPA, and DOTA, which are used as f-element complexants in applications ranging from nuclear fuel recycling to nuclear medicine. Using a combination of experimental and computational techniques, the influence of ESI on cation:ligand systems involving methanol as a co-solvent demonstrates that careful evaluation of the data allows comparison of gas phase speciation with expected solution phase complexation. ESI-MS may prove to be a valuable supplement to current safeguards techniques within a nuclear reprocessing setting, and it could possibly serve as an effective process control monitoring tool for the production of radiopharmaceuticals.

NUCL 130

Environmental and radiochemistry in the nuclear engineering program at the University of Utah

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The University of Utah Nuclear Engineering Program (UNEP) offers Master of Science, Master of Engineering, and Doctor of Philosophy degrees in nuclear engineering. This program includes students from science and engineering disciplines such as, but not

limited to: chemical, environmental, materials and civil engineering; physics, chemistry, pre-med, and computer science. Collectively, the various backgrounds of our students helps to contribute to the domestic workforce in supporting the design, construction, operation, and regulation of nuclear facilities and the safe handling of nuclear materials. The UNEP houses world-class laboratories and facilities, including a TRIGA research reactor (one out of 35 remaining in the world and one out of 13 remaining in the U.S.), Radiochemistry, Microscopy, Advanced Radiation Simulation, Radiation Measurement, and Neutron Activation Analysis Laboratories. In addition, UNEP recently acquired an additional 2,000 sq. ft. of newly renovated clean laboratories for trace actinide analysis and spectroscopy. The program also offers a senior reactor operator and reactor operator training programs consisting of two consecutive 6000-level (graduate) courses. Ongoing research projects in UNEP will be discussed as relevant to the ACS Division of Nuclear Science and Technology.