NUCL 1

Leonard Mausner's leadership and accomplishments within the Department of Energy Isotope Program

Marc Garland*, Marc.Garland@science.doe.gov. Office of Science, Dept. of Energy, Washington DC, District of Columbia, United States*

Leonard Mausner earned a PhD in nuclear chemistry from Princeton in 1975, was a post-doc at Los Alamos National Laboratory, a scientist at Argonne National Laboratory, and for 36 years was a scientist and program manager at Brookhaven National Laboratory (BNL). During that time, Leonard made significant contributions to the science of accelerator and reactor isotope production. His outstanding leadership and creativity were responsible for development of isotope production methods at the High Flux Beam Reactor (HFBR) and the Brookhaven Linac Isotope Producer (BLIP) at BNL, providing isotope production technology to the community through the publication of more than 150 articles, and a wide range of isotopes through the DOE Isotope Program. He conceived several major upgrades of the BLIP facility thereby increasing the availability of isotopes used in research and applications. In particular, his leadership and technical skills have significantly contributed to the development of production of several medical radionuclides used globally for therapy and diagnosis of life-threatening diseases. Among these are actinium-225 (cancer therapy), xenon-127 (lung imaging), tin-117m ("theranostic" isotope for therapy and diagnostic imaging, and bone pain palliation), Sr-82/Rb-82 (cardiac imaging), Cu-67 (cancer therapy), and scandium-47 ("theranostic" applications). His contributions to isotope production technology include BLIP target facility designs (e.g., stacked targets to simultaneously produce multiple isotopes and the use of a single beryllium beam window in vacuum) that have been incorporated at accelerators around the world, and novel targetry and processing systems for the production of isotopes such as xenon-127 and iodine-131. He has helped educate future generations of scientists through his contributions to textbooks on isotope production and his mentorship of students, post-docs, and early-career researchers, and his participation in nuclear and radiochemistry summer schools at BNL. Leonard's career has had a remarkable impact on Brookhaven National Laboratory, the DOE Isotope Program, and the international isotope community and we are all grateful for his service.

NUCL 2

High power accelerator targets for large scale production of radionuclides at intermediate energies

Francois M. Nortier*, meiring@lanl.gov. Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Targetry for accelerator production of radionuclides varies widely depending on a number of key aspects such as the half-life, quantity and purity of the radionuclide

produced, and the primary beam particle, energy and intensity. For example, low energy accelerator targets (<30 MeV) are distinctly different in design from those used at higher energy facilities (>60 MeV), with each energy presenting unique challenges.
The 100 MeV Isotope Production Facility (IPF) at Los Alamos National Laboratory and the 200 MeV Brookhaven Linac Isotope Producer (BLIP) are two accelerator-based facilities used by the DOE National Isotope Program for radionuclide production, providing large quantities of isotopes to the domestic and international communities for application in science, medicine and industry. They are two of only eight intermediate energy production facilities worldwide and often operate with record breaking beam intensities on target.
Large-scale production requires targets able to consistently withstand extremely high power densities, heat fluxes and peak temperatures. To maintain a reliable supply of a variety of radionuclides, targetry must support the irradiation of diverse target materials. While a few targets can be fabricated from durable metals with suitably high thermal conductivities and melting points, most target materials have non-ideal to very poor thermal performance characteristics, or they react with cooling water, requiring containment in robust capsules.
To meet the diverse needs of the user community, production is supported by dynamic R&D programs and, given their powerful proton beams, IPF and BLIP play a lead role globally in pushing the envelope of high power accelerator targets. Recent focus at both facilities has been on expanding capabilities to further increase Sr-82 production and to develop production of Ac-225, a radionuclide with therapeutic potential. This presentation will provide an overview of the principles of high power targetry with an emphasis on recent developments.

NUCL 3

American Chemical Society's summer schools in nuclear and radiochemistry

Louis Pena[3], *lpena@bnl.gov, Patricia Baisden*[4], *Annalise L. Van Wyngarden*[2], *John D. Robertson*[1]. *(1) Univ of Missouri, Columbia, Missouri, United States (2) Department of Chemistry, San Jose State University, San Jose, California, United States (3) Collider Accelerator, Brookhaven National Laboratory, Upton, New York, United States (4) Lawrence Livermore National Lab, Livermore, California, United States*

In response to the decline in educational opportunities in the field of nuclear and radiochemistry and concomitant lack of student exposure to the field, the American Chemical Society’s Summer Schools in Nuclear and Radiochemistry were initiated to help address the need for an undergraduate pipeline into the field. Since they were first introduced in 1984, the Summer School program has successfully introduced 744 physical science and engineering undergraduates to nuclear and radiochemistry. Of this group, over 20% have chosen careers in nuclear science and many of these individuals are now in a position to influence other young people to enter the field. The Summer Schools are intensive, six-week courses in fundamental principles of nuclear and radiochemistry, held at San Jose State University and at Brookhaven National Laboratory.

NUCL 4

Evaluation of neutron inelastic scattering for radioisotope production

Saed Mirzadeh*, mirzadehs@ornl.gov, Justin Griswold, Marc Garland. Nuclear Security and Isotope Technology Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States*

The production of metastable nuclei such as ^{117m}Sn, ^{195m}Pt (for biomedical applications) and ^{119m}Sn (for mossbäuer spectroscopy) via neutron radiative capture reactions are characterized by small neutron cross-sections and, hence, low production rates. The metastable nuclei typically have excitation energy on the order of 100 keV and a large difference in spin from the ground state (most metastable nuclei have high spin). An alternative route for production of these types of metastable nuclei is through neutron inelastic scattering, where the cross-section of the $^{A}Z[n,n'\gamma]^{Am}Z$ reaction in some cases is substantially higher than that of the $^{(A-1)}Z[n,\gamma]^{Am}Z$ reaction. As has been shown for the case of ^{117m}Sn [Mausner et al, 1985], the magnitude of gain in the cross-section may compensate for the relatively lower fast neutron flux from a well-moderated fission spectrum, $E_n \geqq Q_{[n,n'\gamma]}$ (note that the excitation energy of metastable nuclei will represent the threshold for inelastic scattering). Large research reactors, such as HFIR, with significant fast neutron fluxes are most notably suited for these types of reactions. The results from a systematic study of the production of ^{117m}Sn, ^{119m}Sn, ^{125m}Te, and ^{195m}Pt in the hydraulic tube facility (HT) of the HFIR will be presented in this meeting. In three out of four cases examined, the experimental yields from the [n,n'γ] reactions were higher than that obtained from the [n,γ] reactions. For ^{195m}Pt, ^{117m}Sn, and ^{119m}Sn, the relative gains in the specific activity were 1.4, 1.6, and 8.3, respectively. The larger gain for ^{119m}Sn could be attributed to the relatively lower excitation energy (89.5 keV) of this metastable nucleus.

NUCL 5

Radioisotope research and production for radioimmunotherapy: A multidisciplinary collaborative effort

Kathryn Kolsky*, kolsky.kathy@mayo.edu. Radiation Oncology, Mayo Clinic, Rochester, Minnesota, United States*

Leonard Mausner has devoted his career to research applications and production of radionuclides. During his tenure at Brookhaven National Laboratory (BNL), starting in 1981, he utilized the unique capabilities of the 200 MeV Brookhaven Linac Isotope Producer and the High Flux Beam Reactor to develop a catalogue of radionuclides for a variety of research and production applications. His stewardship provided excellent training for students, collaboration opportunities with on-site and off-site colleagues, and support for the Nuclear Chemistry Summer School. Since 2003 he has lead the isotope production efforts for the Department of Energy (DOE) at BNL. Though primarily a production effort, he generated collaborations with physics and engineering colleagues

at BNL to support target research and design to maximize the isotope production capabilities of the linac. Another research interest of his was using radionuclides developed at BNL for clinical applications in Nuclear Medicine and Oncology. This talk with focus primarily on the contributions of his research and production group in advancing new radionuclides produced at BNL for radioimmunotherapy research. The development of the beta emitters Cu-67 and Au-199 will be highlighted.

NUCL 6

Reactor production of promethium-147 for application in beta voltaic batteries

Kathleen Broderick[1,3], *Kathleen.broderick89@gmail.com, Rita Lusk*[2,3], *Justin Griswold*[3], *Rose A. Boll*[3], *Marc Garland*[3], *Lawrence Heilbronn*[2], *Saed Mirzadeh*[3]. *(1) Chemistry and Biochemistry, Tennessee Technological University, Cookeville, Tennessee, United States (2) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (3) Nuclear Security and Isotope Technology Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States*

In this work, we describe the production yields and level of impurities from several targets consisted of mg quantities of highly enriched ^{146}Nd oxide irradiated at the ORNL-HFIR for durations ranging from 24 to 180 h. A comparison between theoretical and experimental data will also be presented. For a 1-cycle irradiation, ^{147}Pm yield reaches a maximum value of 2.75 mCi/mg at 60 days post EOB. Due to large neutron capture cross-sections of ^{147}Pm, the yield of ^{147}Pm does not significantly increase with longer irradiation. Our estimates of the thermal neutron capture cross-section and resonance integral for ^{146}Nd at 1.46 ± 0.05 b and 3.33 ± 0.25 b, respectively, were consistent with the reported values. The effective neutron capture cross-section of ^{147}Pm to ^{148m}Pm was 53.3 ± 2.7 b -- a factor 2 lower than 122.3 ± 8.2 b calculated from reported cross-sections. The measured σ_{eff} to the ground state (5.37-d ^{148g}Pm) was 82.0 ± 4.1 b; ~34% lower than the value of 115.7 ± 11.7 b derived from reported cross-sections. In this work, we also describe the development of chemical process based on extraction and ion-exchange chromatography for separation of ^{147}Pm from mg quantities of ^{146}Nd targets, and other impurities. Based on these data, we estimated that two round of purification under our experimental conditions can provide a mass separation factor of $>10^4$ between Pm and Nd. Our data indicate that curie quantities of ^{147}Pm can be produced by irradiating gram quantities of highly enriched ^{146}Nd target at the flux trap of ORNL HFIR for one cycle (~24 days) suitable for applications in beta voltaic batteries.

NUCL 7

Impact of inorganic chemistry and Leonard Mausner on radiopharmaceutical development

Cathy S. Cutler, *ccutler@bnl.gov. Collider Accelerator, Brookhaven National Laboratory, Columbia, Missouri, United States*

Brookhaven National Laboratory has been responsible for many innovations that have led to Nuclear Medicine becoming a routine robust application that is now practiced globally. These innovations have been led by leading scientists such as Leonard Mausner who has spent over 30 years developing the production of radioisotopes via both reactor and accelerator routes. This includes developing the targets, the required separation and purification methods as well as the facilities to perform the work. As a graduate student I became interested in evaluating the differences in bone palliation agents particularly how the inorganic chemistry of the radiometal impacted the fate of these bone agents in normal bone uptake. In order to do these studies I required a Technetium isotope that was longer lived than the traditionally used Tc-99m used for imaging but shorter than Tc-99 used for traditional chemistry studies. I was introduced to Dr. Mausner who provided a longer lived Tc isotope, Tc-96 with a 4.3 day half-life that enabled following the fate of Tc bone agents in vivo. Comparative studies of the fate of palliative bone agents comprised of different radiometals and organic ligands were evaluated in normal rats. The results of these studies showed the fundamental inorganic chemistry of the radiometals determined the ultimate in vivo fate of these agents. The results of this work and highlights of Dr. Mauser’s scientific career will be presented.

NUCL 8

Radium targets for the reactor production of alpha-emitting medical radioisotopes

***Roy Copping**, coppingr@ornl.gov, David Denton, Karen Murphy, Eva Hickman, Chris Marcus, Dan Stracener, Saed Mirzadeh. Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

Radium226 can be irradiated in a reactor to produce a variety of important medical radioisotopes. These isotopes can be chemically separated and purified after irradiation, and the radium can be recycled for future use. Since radium is highly radioactive, there are unique challenges with using radium as a target material. Also, the chemical properties of radium are not yet fully explored, so stable surrogate materials, such as barium, are used to develop the process. To irradiate radium at the Oak Ridge National Laboratory (ORNL) High Flux Isotope Reactor, it must be in a stable chemical form and in a safe and thoroughly certified target configuration.

Recent efforts at ORNL have focused on the identification and preparation of several radium compounds to be used as target material for irradiation followed by chemical processing to extract the desired product and recover the radium material. Radium in a stable chemical form can be blended into an aluminum pellet cermet and contained within a welded aluminum capsule. Due to the radioactive properties of radium, the material must be handled in a hot cell, which required design, testing, and construction of in-cell welding and certification capability to seal and certify target capsules. The development of a suitable radium target material, pellet fabrication process, capsule welding, and target dissolution process and subsequent radium irradiation campaigns will be discussed.

NUCL 9

PHITS and MCNP6 Monte Carlo simulations for the ^{232}Th(p, 4n)^{229}Pa reaction cross section at 192 MeV compared with the experimental cross section

Justin Griswold[4,2]*, jgriswo1@vols.utk.edu, Dmitri G. Medvedev*[1]*, Roy Copping*[3]*, Leonard F. Mausner*[1]*, Lawrence Heilbronn*[2]*, Saed Mirzadeh*[3]*. (1) Bldg 801, Brookhaven National Laboratory, Upton, New York, United States (2) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (3) Nuclear Security and Isotope Technology Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (4) Oak Ridge National Laboratory, Knoxville, Tennessee, United States*

High energy proton spallation reactions on ^{232}Th metal targets can be used to produce radioisotopes with promising nuclear medicine applications, such as ^{225}Ac. In addition to ^{225}Ac, many other actinides and fission products are coproduced in these irradiations including Pa isotopes, which are produced in large quantities. To further investigate the experimental cross sections for coproduced ^{229}Pa ($t_{1/2}$ = 1.5 d) and other Pa isotopes, both theoretical and experimental approaches were applied. Monte Carlo radiation transport codes PHITS and MCNP6 were used to simulate the experimental data obtained from a 1-hour irradiation of a Th metal target with ~82 μA proton beam at 192 MeV. The irradiation was conducted at BNL. Target dissolution and processing was carried out at ORNL, where an ion exchange strategy was employed to isolate Pa from dissolved Th, Ac, Ra, and numerous fission products including ^{99}Mo/^{m99}Tc. The PHITS and MCNP6 simulated cross sections for the ^{232}Th(p, 4n)^{229}Pa reaction at 192 MeV are 6.9 mb and 12.5 mb, respectively, while the experimentally measured cross section is 0.44 ± 0.05 mb.

NUCL 10

Challenges and opportunities in radioisotope research and development irradiations at Brookhaven Linac isotope producer

***Dmitri G. Medvedev**, dmedvede@bnl.gov, Anthony DeGraffenreid, Vanessa A. Sanders, Slawko O. Kurczak, Lisa Muench, Steven Bellavia, Christian Cullen, Cathy S. Cutler, Leonard F. Mausner. Collider-Accelerator department, Brookhaven National Laboratory, Upton, New York, United States*

Over the last 15 years, Brookhaven Linac Isotope Producer (BLIP) has been used for the continuous production of radionuclides such as ^{82}Sr, and ^{68}Ge. Its design has been constantly evolving to accommodate larger targets and higher proton currents. Simultaneous irradiation of multiple targets at high energies (up to 200 MeV) and proton current (165 μA) has now become possible at BLIP. For the irradiation, the targets are manufactured by placing the target material into a can which is then hermetically sealed and placed in series to form an array. Each target in the array is placed such that it is spaced apart adequately to accommodate gap for water cooling. The fixed target array and demand for continuous production of ^{82}Sr targets make the irradiation of research

targets highly challenging.
In the last 10 years, Dr. Leonard Mausner has led an effort to overcome these challenges. A number of approaches which facilitated synergetic irradiation of research and production targets have been developed. Specifically, he led the design of a novel target can for the production of a theranostic radioisotope, ^{67}Cu, from electroplated ^{68}Zn disks. The can consisted of two parts that were sealed with eight Allen screws, with target material positioned in a well, machined in one of the parts. This design was further adapted for research irradiations of various target materials both enriched and natural aiming to produce radioisotopes, such as ^{86}Y, ^{225}Ac, ^{72}Se, and many others. The evolution of the target design, along with the results of irradiation experiments will be detailed in the talk.

NUCL 11

Thirty six years of radioisotope research: Some of the fun stuff

Leonard F. Mausner, *lmausner@bnl.gov. Collider Accelerator, Brookhaven Natl Lab, Upton, New York, United States*

In a long career at Brookhaven National Laboratory I was involved in the development of more than two dozen radioisotopes. Some were produced at the High Flux Beam Reactor with both thermal and fast neutrons but most were produced by proton irradiation at our major facility, the Brookhaven Linac Isotope Producer (BLIP). This accelerator now features energy incrementally variable from 66 to 200 MeV and beam intensity of 170µA. The target assembly allows up to eight targets to be simultaneously irradiated enabling both flexibility and high production levels. Most of the radioisotopes developed were for medical application, either basic research, clinical diagnosis or even cancer therapy. All the projects involved chemistry to separate the desired isotope from a large mix of others, nuclear physics to determine the optimum bombardment energy needed to maximize production and minimize unwanted impurities, and mechanical engineering challenges related to target thermal performance. Some of the projects were more interesting, significant, successful or just plain fun. A selection of these highlights, both older and recent, will be reviewed.

NUCL 12

Ligand design for alpha therapy nuclides

Justin J. Wilson[1], *jjw275@cornell.edu, Nikki A. Thiele*[1], *Valery Radchenko*[2]. *(1) Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States (2) Division of Life Science, TRIUMF, Vancouver, British Columbia, Canada*

Targeted alpha therapy employs alpha-emitting radionuclides in conjunction with tumor-targeting vectors to eradicate cancer cells with alpha radiation. A key component of these radiopharmaceutical agents is the bifunctional chelating agent, a ligand that stably retains and attaches the alpha-emitting nuclide to the targeting vector. The development

of bifunctional chelating agents for alpha therapy nuclides is hindered by their unusual coordination chemistry and the limited availability of these elements. In this presentation, we describe our efforts to develop new chelating agents for alpha therapy nuclides. This work highlights the novel ligand design strategies and challenges faced in designing new ligands for these nuclides.

NUCL 13

Pseudo-synthesis-free PET imaging of $\alpha_v\beta_3$ integrin via its pro-ligand

Jing Yang[1]*, jyang37@mgh.harvard.edu, Jian Yang*[1,2]*,* ***Chongzhao Ran***[1]*, cran@nmr.mgh.harvard.edu. (1) Martinos Center for Biomedical Imaging, Massachusetts General Hospital and Harvard Medical School, Boston, Massachusetts, United States (2) School of Pharmacy, China Pharmaceutical University, Nanjing, China*

For constructing a molecular imaging probe, tedious procedures are often needed for synthesis and purification. In this report, we demonstrated that pseudo-synthesis-free PET imaging is feasible via utilizing pro-ligand concept to design PET probes. In this proof-of-concept study, $\alpha_v\beta_3$ integrin in U87 tumors was imaged with a ^{64}Cu-peptidic probe, in which linear peptide GHRGDHG is used as a pro-ligand (conceptually similar to pro-drug), while ^{64}Cu bears three functional roles that include generation of PET signal, coordination with two GHs (Glycine-Histidine) moieties of the pro-ligand, and cyclizing the linear pro-ligand into an active cyclic-RGD form (termed as ^{64}Cu-Cyclo-RGD) for $\alpha_v\beta_3$ integrin. Our pseudo-synthesis-free imaging method is different from "ready-to-use kit" PET imaging. Our design was inspired by the pro-drug concept, in which the linear peptidic pro-ligand is in its inactive form for $\alpha_v\beta_3$, thus it has no "cold compound" effect on occupancy of the imaging target. In vitro and in vivo data indicated that pseudo-synthesis-free PET imaging was feasible, as evidenced by ^{64}Cu-Cyclo-RGD's excellent specificity for $\alpha_v\beta_3$ integrin, fast clearance from the body, and high uptake in U87 tumors. We believe that our design strategy and pseudo-synthesis-free imaging concept could have a broad impact on designing of probes for other imaging targets.

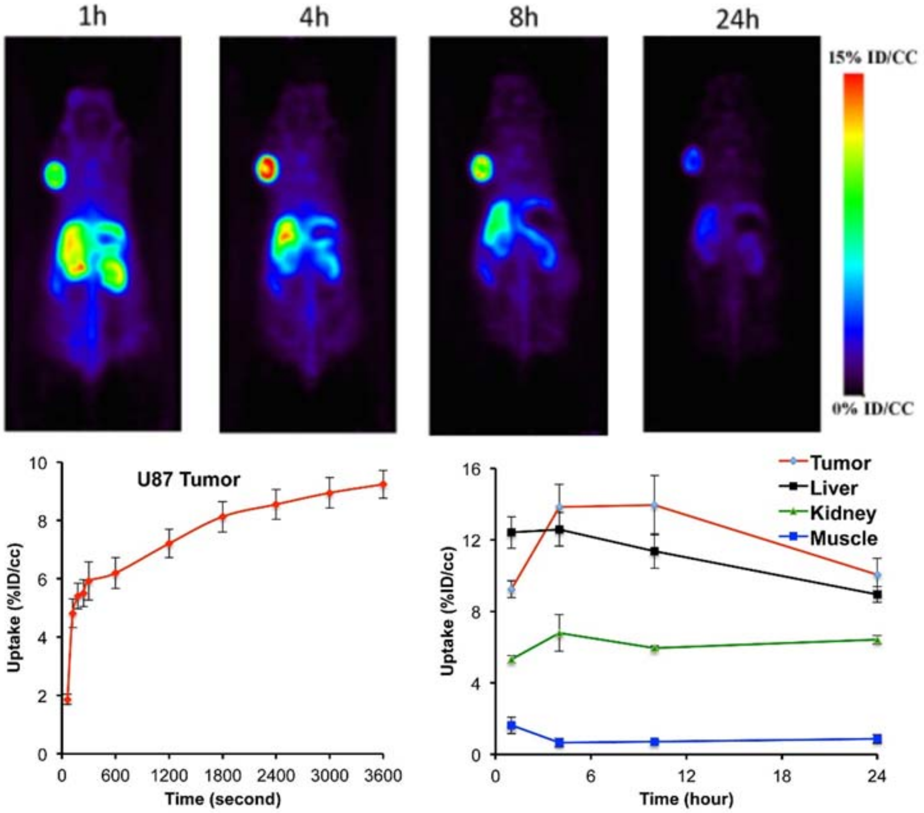


Fig 1. In vivo imaging of U87 tumor mice with ^{64}Cu-Cyclo-RGD. a) Representative images at different time points after tracer injection, b) Time activity curve (TAC) of the tracer in the first 60 minutes, and c) Comparison of uptake in different clearance organs.

NUCL 14

Synthesis of novel Zr-89 bifunctional ligands based on desferrioxamine: Design, eight-coordination, and speciation

Roy P. Planalp*, roy.planalp@unh.edu, Aaron Chung, Brady S. Barron, Mahmoud Abdalrahman. Dept of Chemistry Parsons Hall, University of New Hampshire, Durham, New Hampshire, United States*

With growing interest in Zr-89 as a positron-emitting isotope for diagnostics, several families of bifunctional ligands have been developed for use in vivo. However, there are stability issues which allow Zr(IV) to accumulate in bone. The tris-hydroxamate siderophore DFO has been utilized, but is not completely stable to loss of Zr(IV). We describe the addition of several fragments to DFO to create great stability, syntheses, Zr complexation, and speciation.

NUCL 15

Engineering lanthanide-binding proteins for hepatocellular carcinoma detection and treatment

Michele P. Takacs, Zsofia Lengyel, Alona Kulesha, ***Ivan V. Korendovych****, ivan.korendovych@gmail.com. Syracuse University, Syracuse, New York, United States*

Hepatocellular carcinoma (HCC) is a common type of cancer that is currently very difficult to diagnose early. The probability of success of HCC cure is highly dependent on early detection. Unfortunately, current Positron Emission Tomography (PET) methods for imaging HCC using common radiotracers are not very effective. We have developed HollEE, a 74-amino acid derivative of calmodulin that can tightly bind lanthanides in the presence of physiologically relevant concentrations of calcium. Fusing of HollEE to single chain variable fragment (scFv) of an antibody capable of recognizing glypican-3, a glycoprotein overexpressed on the surface of HCC cells does not interfere with lanthanide binding. Potential applications of HollEE-scFv in yttrium and lutetium based diagnostic and theragnostic applications for HCC treatment will be presented.

NUCL 16

Mn-52 radiolabelling for quantitative characterization of Mn-based MRI contrast agents

Huan Wang[1,2], Ian Ramsay[1,2], Peter Caravan[1,2], ***Eric Gale****[2], egale@nmr.mgh.harvard.edu. (1) Radiology, MGH/ Harvard Medical School, Hingham, Massachusetts, United States (2) Martinos Center for Biomedical Imaging, Massachusetts General Hospital/Harvard Medical School, Malden, Massachusetts, United States*

There is a growing interest in Mn based MRI contrast agents. This is driven largely by concerns over established and potential toxicity related to the Gd present in commercially available MRI contrast agents. Rationally designed Mn complexes provide an attractive Gd-free MRI contrast alternative. The Mn(2+) ion is capable of generating MRI contrast that is comparable to Gd(3+) but unlike Gd, Mn is an essential nutritional element that can be incorporated or eliminated by the human body. In this regard, we invented the complex Mn-PyC3A which provides equivalent MRI contrast and pharmacokinetics to Gd-based standard of care – Mn-PyC3A is thus a potentially direct replacement for commercial Gd-based agents in any contrast-enhanced MRI indication. Mn complexes also hold tremendous promise as “activatable” MRI contrast agents. Mn has many physiologically tenable oxidation states and each is magnetically distinct, thus enabling modulation of the MRI signal in response to biochemical stimuli. We have developed redox active Mn complexes that provide biochemically responsive MR signal modulation that is greater than is possible with Gd at any field strength.

Mn-52 is positron emitting isotope ($t_{1/2}$ = 5.6 days) that is ideally suited for quantitative MR-PET characterization of Mn-based MRI contrast agents. Our group recently began Mn-52 radiolabeling studies in order to better characterize the in vivo behavior and fate of our complexes. Here, we will discuss the critical role that Mn-52 has played in developing our Mn-based MRI contrast agent technology.

NUCL 17

Development of synthetic nuclear melt glass representative of an urban post detonation environment for forensic analysis

Nathaniel Kaminski[1], *nathaniel.kaminski@usma.edu, Geoffrey Bull*[1], *Dawn E. Riegner*[2], *Robert Gilbreath*[1], *Justin Alexander*[1], *Michael James*[1], *Daniel Zheng*[1]. *(1) United States Military Academy, West Point, New York, United States (2) US Military Academy, West Point, New York, United States*

A method to produce surrogate melt glass representative of a nuclear detonation in New York City and Houston has been conducted at the University of Tennessee. Using the same planning process, beads of synthetic melt glass representative of a nuclear detonation in an urban city will be produced, irradiated, and characterized. The purpose of creating a synthetic melt glass representative of an urban environment is to examine to the interference of elemental and isotopic differences between major cities that stem from infrastructure and geographical differences with the isotopic differences compared against a generic nuclear weapon fission fragment yield curve. The chemical composition for each urban debris sample is determined through averaging the chemical element composition obtained from U.S. Geological Survey data of three major cities consisting of New York City, Seattle, and Los Angeles. Samples are then produced through melting powdered oxide compounds in a furnace capable of heating material to 1450 ^{o}C with post production sample composition characterized with X-Ray Fluorescence (XRF). Each sample is then exposed to a 1 MeV equivalent neutron spectrum with a total fluence of 5.7E15 neutrons/cm^2 using a 500kW research reactor located at Ohio State University. Finally gamma spectroscopy of each sample is taken using a HPGe detector to assess isotopic inventory with experimental results compared to isotope inventory computational calculations obtained from SCALE and the Fallout Analysis Tool (FAT) developed by ORNL.

NUCL 18

Mass transport in glassy fallout particles from a near surface nuclear explosion

David Weisz, *weisz3@llnl.gov. Lawrence Livermore National Laboratory, Livermore, California, United States*

In near-surface nuclear explosions, device materials mix with vaporized and melted soil in the resultant fireball, forming aerodynamic glassy particles upon solidification. The analysis of device signatures in this fallout glass has been the subject of study for the

purposes of post-detonation nuclear forensics. The interpretation of the compositional variations observed in such glasses remains a challenge, however, and the physical processes that control this type of fallout formation are not well understood. Fallout particles having spherical, sub-millimeter glassy particles fused to their surfaces, were obtained from a historical US test for analysis. It was the goal of this study to constrain the time and temperature ranges that control mass transport in these fallout glasses by studying apparent diffusion profiles that have been observed in them. Backscatter electron images of carbon-coated polished sections of the glassy particles were acquired by scanning electron microscopy (SEM). In these images, the interfaces where small particles and large particles have fused show an enrichment of relatively higher-Z composition. Further study revealed that these interfaces exhibit what appear to be chemical diffusion profiles of Fe, Ca, and Mg. Concentration profiles across the interfaces were measured using energy dispersive x-ray spectroscopy (EDS), wavelength dispersive x-ray spectroscopy (WDS), and secondary ion mass spectrometry (SIMS). Preliminary approximations of the time scale of mass transport within the studied particles were found to be less than one second, at a fixed temperature of approximately 2000 K. While these values do not take into account the temperature variation of the fallout particles in the fireball or the large uncertainties in literature values of diffusivities, the results provide compelling evidence that the time and temperature ranges of mass transport can be constrained by studying these diffusion profiles.

NUCL 19

Chemical analysis of synthetic nuclear melt glass (urban)

Geoffrey Bull[1], *geoffrey.bull@usma.edu, Dawn E. Riegner*[2], *Nathaniel Kaminski*[3]. *(1) Chemistry and Life Science, United States Military Academy, West Point, New York, United States (2) US Military Academy, West Point, New York, United States (3) United States Military Academy, West Point, New York, United States*

A method for the production of surrogate melt glass representative of a nuclear detonation was previously conducted through research at the University of Tennessee. Using the same process, a synthetic melt glass representative of a nuclear detonation in several urban cities was produced. The synthetic melt glass is produced to examine the challenges to nuclear forensics that elemental and isotopic differences between major cities pose. Infrastructure and geographical differences, including the possible over-representation of rare earth elements due to high densities of electronic devices, may impact post-detonation analysis. The chemical composition for each urban debris sample was determined through averaging the chemical element composition obtained from U.S. Geological Survey data of four major cities consisting of New York City, Houston, Seattle, and Los Angeles. Samples were then produced through melting powdered oxide compounds in a furnace capable of heating material to 1450 ^{o}C. The post-melt samples were analyzed using X-Ray Fluoroscopy and Scanning Electron Microscopy for elemental analysis and Matrix Assisted Laser Desorption/Ionization for isotopic composition. An additional sample that contained higher compositions of rare

earth elements was also analyzed as a proof-of-principle for identifying low quantities of those elements in a melted sample. The resulting chemical analysis was compared to the initial sample compositions and the results will be shown.

NUCL 20

Comparison of microwave dissolution to open vessel fusion methods using ammonium bifluoride for dissolution of post nuclear detonation debris

*Nicholas Hubley[2], Michael Rearick[5], Chris Liebman[5], Wegge Dana[3], Taylor Weilert[4], John D. Robertson[2,1], **John D. Brockman**[1], brockmanjd@missouri.edu. (1) Research Reactor, University of Missouri, Columbia, Missouri, United States (2) Chemistry, University of Missouri, Columbia, Missouri, United States (5) Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Rapid dissolution methods are needed for timely analysis of nuclear debris for attribution analysis. Traditionally digestion of nuclear debris is performed by heating the sample in combinations of highly concentrated mineral acids and requires >24 hours to complete. We have evaluated two methods for sample dissolution using ammonium bifluoride (ABF) as an alternative to concentrated mineral acid digestion. One method is the fusion of samples with ammonium biflouride, demonstrated to dissolve surrogate nuclear debris in less than 3 hours in open PFA or PTFE vessels when heated to 230 ^{o}C. The other method we have investigated uses microwaves for direct heating of the ABF and reaction products. The heating facilitates evaporation of a viscous diffusion layer that forms around sample particles, allowing for an increase in the rate of reaction and thereby decreasing the total time of dissolution to approximately 1.5 hours. Previous fusion methods have used hot plates and/or ovens to accelerate dissolution and evaporation but a microwave only method has not yet been explored. In this work, a rapid open vessel microwave dissolution procedure was developed and evaluated using geological reference materials so that elemental recovery could be compared to recoveries obtained from ABF fusions.

NUCL 21

Measuring key isotope ratios in two irradiated UO_2 fuel samples for the attribution forensics of separated Pu

***Kevin J. Glennon**[1,2], kglennon@tamu.edu, Jeremy M. Osborn[3], Jonathan D. Burns[4], Evans D. Kitcher[4], Sunil S. Chirayath[3,4], Charles M. Folden[1,2]. (1) Department of Chemistry, Texas A&M University, College Station, Texas, United States (2) Cyclotron Institute, Texas A&M University, College Station, Texas, United States (3) Department of Nuclear Engineering, Texas A&M University, College Station, Texas, United States (4) Center for Nuclear Security Science & Policy Initiatives, Texas A&M University, College Station, Texas, United States*

Destructive and nondestructive analyses have been performed on two irradiated UO_2 fuel samples with different irradiation histories to further develop attribution methods which may be applied to separated Pu. The first fuel sample was irradiated to a burnup of 4.4 ± 0.3 GWd/MTU in a pseudo-fast spectrum of neutrons in the High Flux Isotope Reactor (HFIR) reactor at Oak Ridge National Laboratory, and the second fuel sample was irradiated to a burnup of 0.97 ± 0.03 GWd/MTU under a thermal spectrum of neutrons in the University of Missouri Research Reactor (MURR). Analyses have focused on measuring key actinide and fission product isotope ratios within each fuel sample which may be used with a maximum likelihood approach to determine the most likely irradiation history of each fuel. The use of isotope ratios makes this approach agnostic to the separation history of the fuel. The analytical techniques employed to measure these ratios include nondestructive gamma spectrometry, as well as destructive analysis via ICP-MS after a chemical separation by cation exchange chromatography employing α-hydroxyisobutyrate as an eluent. The resulting chromatogram allows each isotope ratio of interest to be measured without experiencing isobaric interference from other elements sharing the same mass to charge ratio. Each isotope ratio measured is compared to simulated values produced by modelling both sample irradiations using state-of-the-art Monte Carlo radiation transport code, MCNP6. In general, there is good agreement (within 20%) between the measured and simulated ratios. These ratios will be used to determine the most likely irradiation history of each fuel sample, which will then be compared to the known history.

NUCL 22

BET surface analysis of ADU materials

Jacquelyn Dorhout[1], *dorhoutj@lanl.gov, Gregory Wagner*[1], *Nicholas Wozniak*[1], *Marianne P. Wilkerson*[2]. *(1) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Chemistry-Nuclear and Radiochemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Surface area and morphological characterizations of nuclear materials may aid in the identification of interdicted materials for nuclear forensic purposes. Variability in the synthetic method used, including fluctuations in temperature, reaction stirring rate, rate of addition of reagents, and concentration of uranium starting materials may lead to differences in the morphology of the products. Ammonium diuranate (ADU) and a series of uranium oxides were synthesized using a variety of routes and characterized using powder X-ray diffraction (pXRD), scanning electron microscope (SEM) imaging, image analysis using Morphological Analysis for Material Attribution (MAMA) software, and surface area analysis using the BET method. These characterization methods identified differences in morphology, which were then correlated to the synthetic method.

NUCL 23

Experimental and theoretical analysis of selective binding of lanthanides and actinides

***Deborah A. Penchoff**[8,1], dpenchof@utk.edu, Charles C. Peterson[2], Mark S. Quint[3,4], Justin R. Powers-Luhn[5], John D. Auxier[3], George K. Schweitzer[6], David M. Jenkins[6], Robert J. Harrison[7,9], Howard L. Hall[5,8]. (1) Joint Institute for Computational Sciences, Oak Ridge, Tennessee, United States (2) Research Information Tehcnology, University of North Texas, Denton, Texas, United States (3) Nuclear Engineering, The University of Tennessee, Knoxville, Tennessee, United States (4) US Army Nuclear and Countering Weapons of Mass Destruction Agency, Ft. Jackson, South Carolina, United States (5) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (6) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (7) Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York, United States (8) Institute for Nuclear Security, Knoxville, Tennessee, United States (9) Computational Sciences Center, Brookhaven National Laboratory, Upton, New York, United States*

Knowledge-based design of selective binding agents is essential to optimize separations of lanthanides and actinides. There are various needs that benefit from predictive capabilities for separations of elements in the f-block, including the shortage of rare earth elements, nuclear fuel cycle, military applications, and neutron radiography, amongst others. Furthermore, radioactivity, short half-lives, and cost often present constraints in laboratory settings, which makes computational predictions indispensable to advance knowledge at the frontiers of the periodic table.
An in-depth complexation study of lanthanides and actinides with carboxylic acids, beta diketones, nitrates, and cyclic imide dioximes will be presented, with focus on thermochemical, structural, and population analysis.

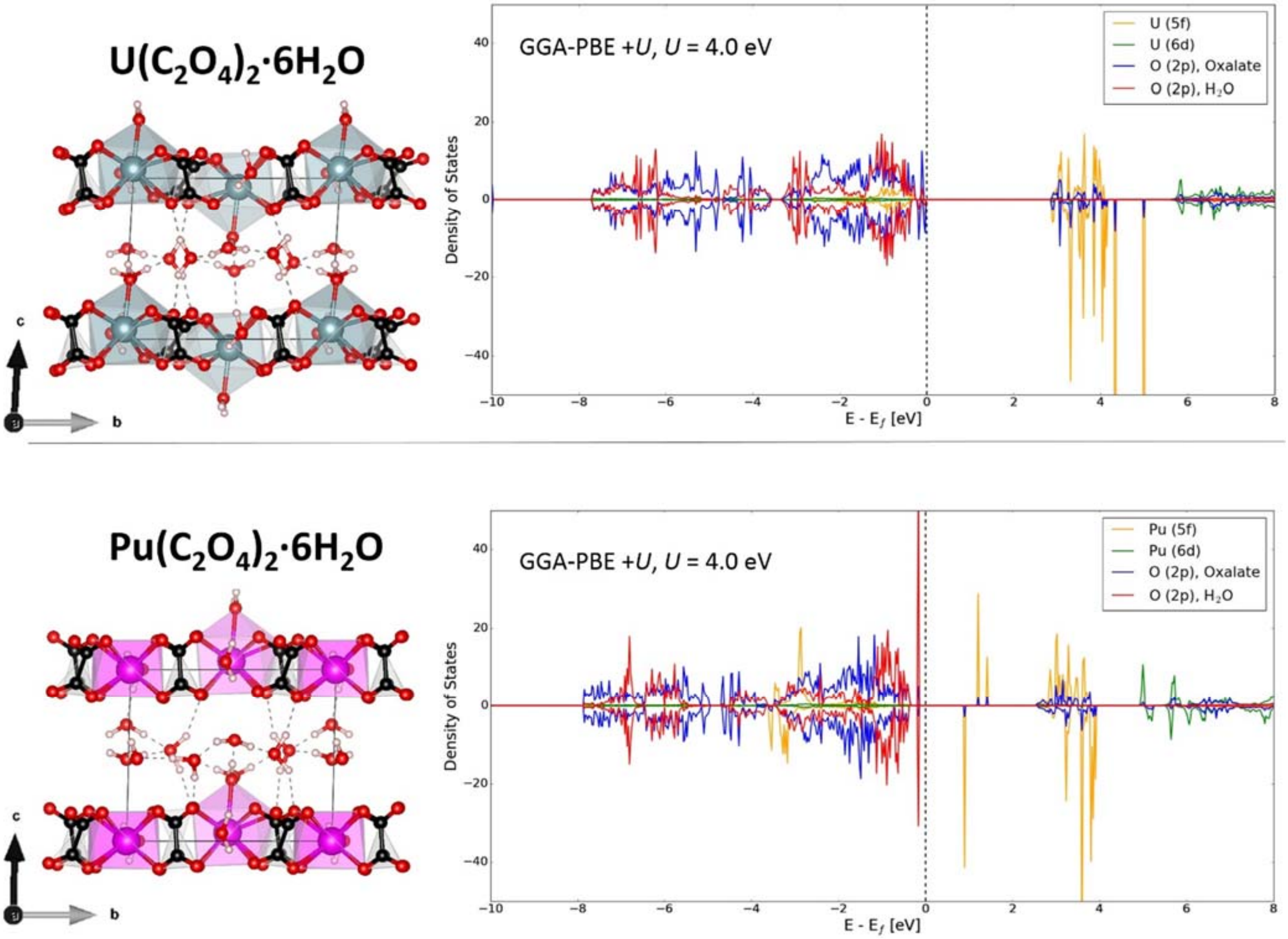
NUCL 24

First principles investigation of the structural and bonding properties of hydrated actinide (IV) oxalates, $An(C_2O_4)_2•6H_2O$ (An = U, Pu)

***Kerry E. Garrett**[1], kerry.garrett@pnnl.gov, Andrew Ritzmann[1], Frances N. Smith[3], Sean H. Kessler[2], Neil Henson[1], David G. Abrecht[1]. (1) National Security Directorate, Pacific Nortwest National Laboratory, Richland, Washington, United States (2) National Security Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States (3) Pacific Northwest National Laboratory, Richland, Washington, United States*

The structural and bonding properties of actinide (IV) oxalates, $U(C_2O_4)_2•6H_2O$ and $Pu(C_2O_4)_2•6H_2O$, are investigated using the generalized gradient approximation (GGA) to spin-polarized density functional theory (DFT) with van der Waals corrections. The GGA optimized structures, ground state magnetic moments, site-projected density of states, and Bader charges are reported. We calculate the energy differences between ferromagnetic (FM) and antiferromagnetic (AFM) spin configurations on the Pu or U sites to determine the preferred magnetic structure of these materials. The relaxed AFM-spin structure of $Pu(C_2O_4)_2•6H_2O$ was found to be considerably lower in energy than the corresponding relaxed FM-spin structure; whereas, there was negligible energy

difference in the relaxed AFM and FM-spin structures of $U(C_2O_4)_2{\bullet}6H_2O$. Weak hybridization between the actinide (Pu or U) 5*f* and O (2*p*) states in the site-projected density of states suggests that these systems are ionic. Furthermore, Bader charge analysis reveals charges on the actinide and oxalate oxygen sites in both $U(C_2O_4)_2{\bullet}6H_2O$ and $Pu(C_2O_4)_2{\bullet}6H_2O$ that are similar to literature data on other actinide species which are ionic, e.g. actinide dioxides. Calculating the density of states using a Hubbard correction parameter of $U = 4.0$ eV based on the GGA+U method shows band gaps of approximately 1 eV for $Pu(C_2O_4)_2{\bullet}6H_2O$ and 3 eV for $U(C_2O_4)_2{\bullet}6H_2O$. Both systems are predicted to be charge-transfer insulators.



Site-projected density of states (PDOS) of An (IV) Oxalates (An = U, Pu) based on GGA-PBE+U with *U* = 4.0 eV. The calculations used AFM-spin configuration for each system. The GGA-PBE ($U = 0.0$ eV) relaxed structures of $U(C_2O_4)_2{\bullet}6H_2O$ and $Pu(C_2O_4)_2{\bullet}6H_2O$ along [100] direction are shown. In the PDOS plots, the Fermi level is set to zero.

NUCL 25

Application of a silicon drift detector to actinide L X-rays

***Robert S. Rundberg**[1], rundberg@lanl.gov, Audrey Roman[2], Katherine Shield[3], Katherine Thornock[4]. (1) Nuclear and Radiochemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (3) Nuclear Engineering, University of California Berkeley, Berkeley, California, United States (4) University of Nevada Las Vegas, Las Vegas, Nevada, United States*

The Silicon Drift Detector, SDD, is an emerging category of semiconductor detectors capable of measuring x-ray photons. They are uniquely capable of measuring x-rays in the fingerprint region below 18 keV. The resolution and capabilities of a silicon drift detector was calibrated using a variety of radioactive elements. The high resolution of silicon drift detector made it possible to distinguish between 235U, 238U, and 239Pu, providing potential applications in nuclear forensics. These isotopes had unique x-ray patterns because the daughter chains are different. Further analysis of data from the silicon drift detector may provide methods to determine isotopic ratios of these elements and additional special nuclear material.

NUCL 26

Thermodynamic data selection. Filling the gap between NEA-TDB and performance assessment needs

***Lara Duro**[1,2], lara.duro@amphos21.com, Mireia Grivé[2], Elisenda Colàs[2]. (1) Amphos 21 Group S.L., Barcelona, Barcelona, Spain (2) Amphos 21 Consulting S.L., Barcelona, Spain*

Thermodynamic data quality is of main concerns in every solubility and speciation calculation needed for Performance Assessment (PA) of radioactive wastes. Great efforts have been done in the last decades to improve thermodynamic databases as well as to assess the associated uncertainties and how they translate into the calculations feeding PA. The NEA-TDB is an example of a high quality database in which very demanding quality criteria are defined for inclusion of thermodynamic data. Quality is, nevertheless, not the only characteristic that a thermodynamic database must fulfil. Excluding poor quality data from TDB has several times resulted in erroneous (or not sufficiently good) calculations, as the error associated with neglecting a given species or solid phase overcomes that associated with the consideration of low quality data. It is better recognising a bounding value for a species stability than neglecting the formation of the species. Including poor quality data in a database requires relevant criteria as well as traceability to identify the origin and the need to revise these data in the light of new experimental/modelling evidences. Performance Assessment needs complete databases and this is one of the reasons why several initiatives have been set in several national programmes for developing exhaustive databases, complementary and even alternative to the NEA-TDB. In this work, we present several examples of data not included in qualified databases, but needed to obtain a complete and reliable description of the system. Comparisons between calculations obtained by using a complete database with those undertaken with a very high quality but incomplete

database are shown. We pinpoint the implications of the results for PA, highlight the need of a sufficiently sound criteria for poor data inclusion and show some of the uncertainties associated with the whole calculation process. Examples are also given of thermodynamic data not considered in the past qualified enough to be included in the NEA-TDB, but included in further updates for the sake of completeness.

NUCL 27

Reference thermodynamic data for modelling of deep geological repositories: The NEA Thermochemical Database (TDB) Project

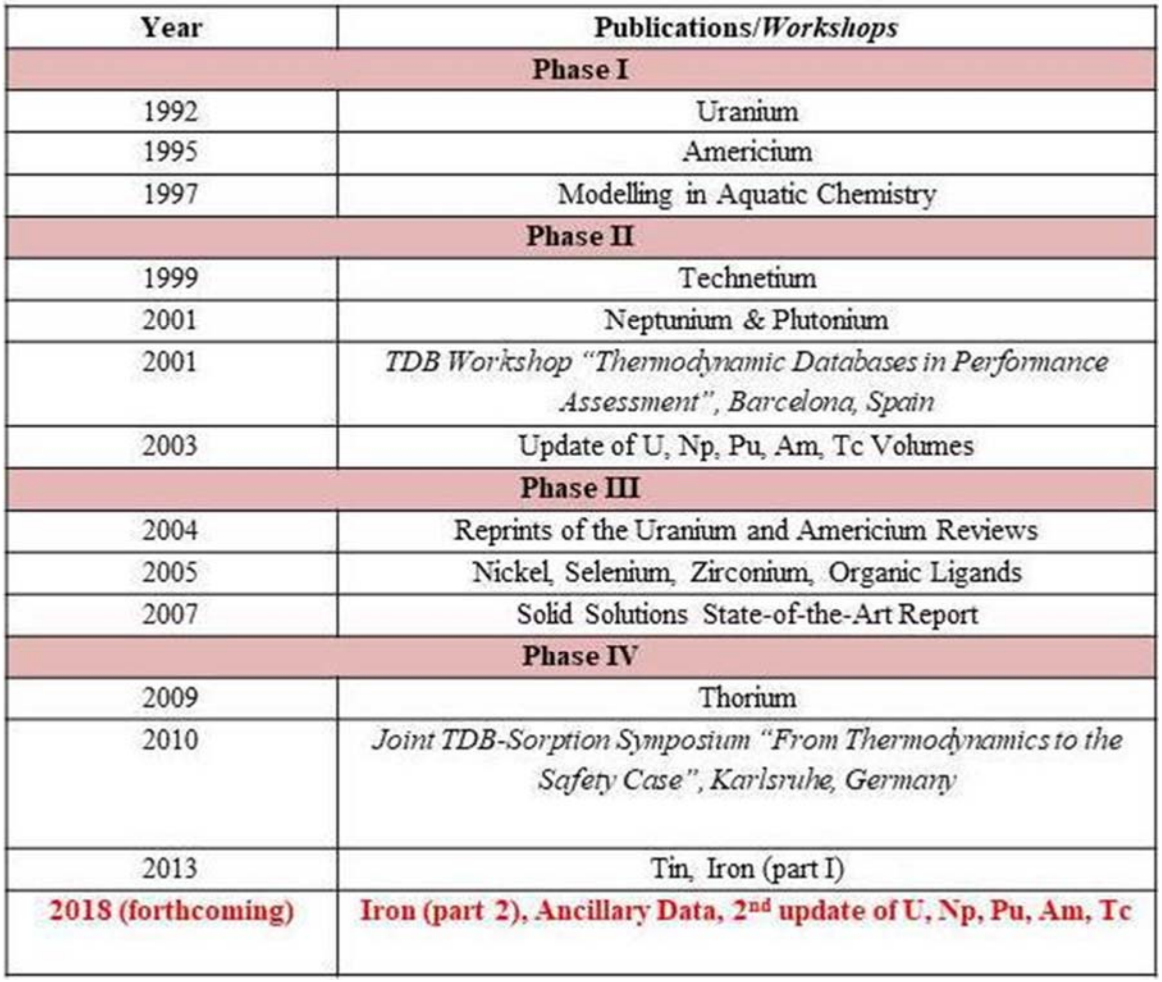
Maria-Eleni Ragoussi*, maria-eleni.ragoussi@oecd.org, Jesus Martinez. OECD Nuclear Energy Agency, Paris, France*

The Thermochemical Database (TDB) Project emerged 30 years ago, under the auspices of the OECD Nuclear Energy Agency (NEA), with the aim of defining an internationally recognized set of reference thermochemical data to support the geochemical modelling of high-level radioactive waste disposal. A chemical thermodynamic database for elements relevant to the safety of deep geological repositories has since been under continuous development.

The data that populate the TDB database are selected on the basis of a well-defined review procedure, under a common frame of requirements and evaluation criteria approved by performance assessors, that tackle the discrepancies arising from the great number of databases worldwide. The Project is coordinated by the NEA and all reference thermodynamic data become freely available. The efforts of the last three decades have resulted in the publication of thirteen major reviews (Table 1) containing selected values for around 1500 species, out of which more than 700 aqueous species, 650 solids and 150 gases, for the most significant radioelements and their compounds related to high-level radioactive waste. Additionally, in the last years, state-of-the-art reports, that present current knowledge on how to deal with issues related to deep geological disposal, have become part of the Project’s programme of work.

The NEA also makes available the data to external third parties in an electronic format. A new software meeting the technological standards of modern thermochemical databases was built during 2017 and will be released in mid-2018. A wealth of advantages characterize this new tool, including consistency checks for the integrity of the data, flexibility for advanced searches and tailored parameter files for PHREEQC.

The key aspects of the Project and the significant forthcoming publications in 2018, the newly designed electronic database and the future programme of work are going to be discussed in this talk.



Year	Publications/*Workshops*
Phase I	
1992	Uranium
1995	Americium
1997	Modelling in Aquatic Chemistry
Phase II	
1999	Technetium
2001	Neptunium & Plutonium
2001	*TDB Workshop "Thermodynamic Databases in Performance Assessment", Barcelona, Spain*
2003	Update of U, Np, Pu, Am, Tc Volumes
Phase III	
2004	Reprints of the Uranium and Americium Reviews
2005	Nickel, Selenium, Zirconium, Organic Ligands
2007	Solid Solutions State-of-the-Art Report
Phase IV	
2009	Thorium
2010	*Joint TDB-Sorption Symposium "From Thermodynamics to the Safety Case", Karlsruhe, Germany*
2013	Tin, Iron (part I)
2018 (forthcoming)	**Iron (part 2), Ancillary Data, 2nd update of U, Np, Pu, Am, Tc**

List of publications of the TDB Project

NUCL 28

Thermodynamic modelling of Selenium in environmental conditions: Traps, pitfalls and perspectives

Frank Bok[3], *f.bok@hzdr.de, Norbert Jordan*[2], *Vinzenz Brendler*[1]*. (1) Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf e.V., Dresden, Germany (2) Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany (3) HZDR, Dresden, Germany*

Any safety assessment of nuclear waste disposal concepts requires comprehensive and consistent thermodynamic data for the respective reactive transport modelling. This includes sorption, ion exchange or surface precipitation as major retardation processes, as well as a correct description of the aqueous chemistry including redox processes. Selenium (with the isotope Se-79 being an important fission product) can occur in oxidation states varying between +VI and –II, the latter also including several polynuclear species. Most often negatively charged species are formed rendering them

extraordinarily mobile in groundwater systems. Namely for Se solubility in highly saline solutions and for Se sorption onto minerals several competing thermodynamic datasets are published to predict the behavior of selenium under environmental conditions. However, there are still critical data gaps. For example, recent findings like the selenite dimerization have to be parameterized and included into thermodynamic data collections. Also, for the selenide chemistry, solubility data are missing as well as ion-ion interaction parameters for the calculation in brines.

Another aspect of the reactive transport of selenium is the retardation of mainly selenate and selenite via sorption onto mineral phases. For these processes, recent spectroscopic investigations in combination with batch experiments have enabled deeper insights into the sorption chemistry of selenium. Here, the various data received must be processed into a consistent data sets.

Several approaches to close critical selenium data gaps will be presented. These are essential steps towards a consistent and quality approved thermodynamic data set that can be included into databases needed for the geochemical and reactive transport calculations, namely THEREDA (http://www.thereda.de) and RES^{3}T (http://www.hzdr.de/res3t).

NUCL 29

Keggin POMs as metal oxide models to understand the binding and stability of Tc-99

***Shejla Pollozi**[1,2], spollozi@gradcenter.cuny.edu, Lynn C. Francesconi[3,2], Donna M. McGregor[1,2], Gustavo E. Lopez[1,2]. (1) Chemistry, Lehman College of the City University of New York , Bronx, New York, United States (2) Chemistry, Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, New York, United States (3) Chemistry, Hunter College of the City University of New York, New York, New York, United States*

Technetium-99 (^{99}Tc) is a long-lived ($T_{1/2}$ = 2.13 x 10^5 years) b-emitting (E_{max} = 294 KeV) radionuclide found throughout the complex, multi-component radioactive waste tanks at national lab sites. 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 both waste characterization and long-term storage. A better understanding of the parameters that affect the speciation, coordination environment and oxidation states of Tc will promote the development of more appropriate methods for the separation of Tc from nuclear waste tanks as well as more fitting mediums for storage. Polyoxometalates (POMs) are a class of inorganic and chemically robust metal oxide clusters with unique and tunable sizes, acidities and redox properties. These properties make them excellent metal oxide model systems and they can thus be used to examine the redox stability and binding requirements for Tc. In this presentation we discuss the use of Keggin POMs, with the general formula $[XM_{12}O_{40}]^{n-}$, to investigate the redox properties of Tc using a combination of experimental and computational techniques.

NUCL 30

Solution chemistry of Pu in alkaline reducing systems: Redox, solubility and complexation with organic ligands

Xavier Gaona[1]*, xavier.gaona@kit.edu, Agost Tasi*[1]*, David Fellhauer*[1]*, Thomas Rabung*[1]*, Jörg Rothe*[1]*, Robert Polly*[1]*, Mireia Grivé*[2]*, Elisenda Colàs*[2]*, Jordi Bruno*[2]*, Klas Källström*[3]*, Marcus Altmaier*[1]*, Horst Geckeis*[1]*. (1) Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany (2) Amphos 21 Consulting SL, Barcelona, Spain (3) SKB, Stockholm, Sweden*

Plutonium-239 ($t½$ = 2.41x10^4 a) can potentially contribute to the long-term risk in underground repositories for the disposal of radioactive waste. In reducing aqueous environment as foreseen after the closure of a repository, the formation of Pu(III) and Pu(IV) is expected. Uncertainties in the thermodynamic data available for both oxidation states lead to a rather ill-defined redox transition border, especially under alkaline to hyperalkaline pH conditions as those defined by cementitious systems. Isosaccharinic acid (ISA) is the main degradation product of cellulose, which may be disposed of in large quantities along with low- and intermediate-level waste (L/ILW). The strong complexation of ISA with An(III) and An(IV) together with the large inventory of this organic ligand requires dedicated research efforts with focus on the Ca(II)–Pu(III/IV)–ISA system, for which virtually no experimental studies are available in the literature.

This contribution summarizes recent and on-going research activities on the solution chemistry of Pu: (i) solubility and redox chemistry of Pu(III)/Pu(IV) in alkaline reducing systems, with focus on the definition of the redox boundary between both oxidation states; (ii) solubility, complexation and redox chemistry of Pu(III)/Pu(IV) in alkaline reducing systems in the presence of ISA and Ca(II); (iii) aqueous speciation of Cm(III) (as analogue of Pu(III)) in the presence of ISA by TRLFS. The results obtained in our study provide quantitative tools for the assessment of solubility and redox processes involving Pu(III) and Pu(IV) in the absence and presence of organic ligands. These studies benefit from the combination of systematic solubility experiments, advanced spectroscopic techniques available at KIT–INE and theoretical density functional theory calculations.

This work contributes also to an improved thermodynamic description of Pu in alkaline reducing systems relevant in repositories for L/ILW, which can be implemented in geochemical models/calculations providing further confidence in the safety analysis of such repositories.

NUCL 31

Plutonium redox interactions in ternary iron-EDTA systems

Nicole Moore[1]*, nmoore2@nd.edu, Ezgi Yalcintas*[2]*, Donald T. Reed*[4]*, Amy E. Hixon*[3]*. (1) University of Notre Dame, Niles, Michigan, United States (2) Los Alamos National Laboratory, Carlsbad, New Mexico, United States (3) Civil & Environmental*

Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States (4) Cemrc, Carlsbad, New Mexico, United States

The Waste Isolation Pilot Plant (WIPP) in Carlsbad, NM is central to the U.S. Department of Energy's (DOE) nuclear waste management effort. Further research on the interactions between plutonium and various components of the WIPP, including EDTA and iron solids, is necessary to determine long-term plutonium speciation in the repository. EDTA is known to be a strong complexant for transuranic actinides in the aqueous phase, stabilizing plutonium as aqueous Pu(IV) in abiotic systems and is present in the WIPP waste. Interactions between plutonium and iron solids are important for the WIPP due to the large quantities of iron metal present from iron corrosion products, waste, and steel waste drums. Interactions between plutonium and iron-containing minerals have been previously investigated, and the literature indicates plutonium interacts with these minerals through sorption and surface-mediated reduction processes resulting in stable Pu(III/IV) surface complexes. However, these two different types of interactions have not been investigated in a single system. This work strives to understand the competition between solid-state and aqueous interactions in order to determine whether EDTA or iron-containing minerals control the speciation, mobility, and redox chemistry of plutonium in a ternary system. Key variables include EDTA concentration, the oxidation state of iron in the mineral phase, ionic strength, and pH.

NUCL 32

NpO_2(s) dissolution under vadose zone conditions

Kathryn M. Peruski[1], *kperusk@clemson.edu, Melody Maloubier*[1], *Daniel Kaplan*[2], *Brian A. Powell*[3]. *(1) Clemson University, Anderson, South Carolina, United States (2) Room 215, Savannah River National Laboratory, Aiken, South Carolina, United States*

Observed transport of neptunium from an initially NpO_2(s) source in 5-L field lysimeter experiments at the Radionuclide Field Lysimeter Experiment (RadFLEx), an ongoing field scale test of radionuclide transport at the U. S. Department of Energy Savannah River Site, has prompted further laboratory studies of NpO_2(s). Field data indicated that downward migration of Np from a NpO_2(s) source was due to transport of 1) soluble neptunyl, NpO_2^+ ions and 2) eigen colloids of NpO_2(s). Both mobile species were proposed to be formed during oxidative dissolution of NpO_2(s). Based on these observations, a hypothesis for new experiments was developed wherein dissolution of polycrystalline phases occurs via alteration of phases along grain boundaries and formation of mobile colloids or polynuclear aqueous species. New NpO_2(s) sources were placed in lysimeters at three depths and exposed to vadose zone field conditions for one year. Electron microscopy verified alteration of NpO_2(s) through formation of granules along grain boundaries. Complimentary laboratory-based dissolution studies were initiated under vadose zone conditions (~pH 5, oxic conditions) were used to mimic environmental conditions the source was exposed to in field lysimeters. Both aqueous and solid phases were monitored to identify the rate and mechanisms involved

in NpO_2(s) dissolution. This work is motivated by a lack of rate constants or dissolution studies of NpO_2(s), particularly non-hydrated or amorphous phases, at environmentally relevant conditions. Overall, these efforts seek to validate observed field data and bridge understanding of NpO_2(s) dissolution from field to nano scale.

NUCL 33

Effect of EDTA on An(IV) chemistry under repository relevant conditions

Ezgi Yalcintas[1], *ezgi.yalcintas@kit.edu, Xavier Gaona*[2], *Michael K. Richmann*[1], *Marcus Altmaier*[2], *Donald T. Reed*[1]. *(1) Los Alamos National Laboratory, Carlsbad, New Mexico, United States (2) Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*

EDTA is a strong complexing ligand used for decontamination purposes in nuclear reactors and clean-up operations that is eventually co-disposed together with radioactive waste and often exists as a subsurface co-contaminant. Complexation of actinides(An) with strong organic ligands like EDTA forms stable aqueous species which can significantly affect the potential retention/mobilization processes in geochemical environments by enhancing the solubility limit and altering the sorption behavior on mineral surfaces. An accurate knowledge of this aquatic chemistry and, more generally, the thermodynamics of actinides are fundamental needs that support nuclear waste disposal concepts. The availability of complete and correct chemical and thermodynamic models helps provide reliable geochemical model calculations and source-term estimations for the safety assessment of nuclear waste repositories. The present work focusses on An(IV) complexation with EDTA and the effect of these complexes on the long-term solubility and the redox distribution of actinides under repository relevant environments. The solubility of An(IV) in the presence of EDTA was investigated from both undersaturation and oversaturation conditions. Experiments were performed in an inert gas atmosphere with < 2 ppm O_2 at T= (22 ± 2) °C. Oversaturation solubility experiments were conducted with $[An]_0 = 10^{-3}$ M, whereas undersaturation solubility experiments were performed with approximately 3 mg of AnO_2(am,hyd). Strongly reducing conditions (pH + pe < 2) were fixed in each independent solubility sample with $SnCl_2$. Background electrolyte solutions were prepared with [EDTA] = 0.01 M, constant ionic strength I = 0.5 and 5.0 M Na_4EDTA–NaCl–HCl–NaOH, and covering the pH_m range 0–13 (with $pH_m = -\log [H^+]$). An concentration, $pH_m$and E_h values were monitored at regular time intervals. The results obtained on the impact of EDTA on the aqueous speciation and long-term solubility of An(IV) will be presented in this contribution and discussed in the context of the presence/absence of ternary An(IV)-EDTA-OH species.

NUCL 34

Reductive removal of Tc and Cr from a waste stream using zero valent iron

Hilary P. Palmer Emerson[1], *hemerson@fiu.edu, Daria Boglaienko*[2], *Abraham Gebru*[1], *Jonathon Williams*[1], *Antony Maria*[1], *Tatiana G. Levitskaia*[3], *Yelena Katsenovich*[1]. *(1) Applied Research Center, Florida International University, Doral, Florida, United States (2) Applied Research Center, Florida International University, Miami, Florida, United States (3) Battelle Pacif N West Natl Lab, Richland, Washington, United States*

Zero valent iron (ZVI) is currently under consideration for treatment of volatile contaminants recovered in off-gas condensate from vitrification of radioactive waste at the Hanford site. It is a commonly used reactive agent for reductive removal of contaminants, including reducible metal ions. However, there has not been a systematic study of the reductive capacity of ZVI with variable synthesis methods and particle sizes. Moreover, although Tc is the major risk driver, significantly greater concentrations of Cr(VI) in the waste stream may lead to competition for reductive capacity. The objective of this research is to quantify the kinetics of reductive removal of both Cr(VI) and 99Tc using ZVI.
Batch experiments and solid phase characterization studies have been conducted to quantify the reductive removal of Tc and Cr in the presence of a suite of different ZVI materials (100 nm to 1-2 mm in diameter). In addition, dissolution of Fe(II/III) was monitored and solid phases were analyzed to measure oxidation of the materials over time. Both variable pH and isotherm experiments were conducted in order to estimate the kinetics of reductive removal and potential loading capacity for Tc and Cr. Contrary to theory, ZVI with relatively large particle size ranges (2 to 0.075 mm diameter) synthesized by an electrolytic process exhibited distinctively better reductive behavior than ZVI of smaller particle sizes ranges including nano ZVI (0.1 to 3 µm). Dissolution of Fe(II) was also higher for the iron materials of larger size ranges and is correlated with reductive removal of Tc(VII). These data suggest that removal is dependent on synthesis process as well as available surface area of ZVI. Moreover, although the theoretical redox potential for reduction of Cr(VI) is above Tc(VII), reduction and removal kinetics are significantly faster for Tc than Cr.

NUCL 35

Studies on An(IV)-hydroxo-carbonate complex formation along the An(IV) = Th, U, Np, Pu series

Marcus Altmaier[2], *marcus.altmaier@kit.edu, Julian Schepperle*[2], *Ezgi Yalcintas*[2,1], *Nese Cevirim*[2], *David Fellhauer*[2], *Xavier Gaona*[2], *Horst Geckeis*[2]. *(1) Los Alamos National Laboratory, Carlsbad, New Mexico, United States (2) Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*

This work provides new experimental studies and improved thermodynamic descriptions of U(IV), Np(IV) and Pu(IV) solubility and speciation in alkaline to hyperalkaline carbonate containing solutions. The new experimental data derived for U(IV), Np(IV) and Pu(IV) obtained in the present work are compared to the comprehensive solubility study and thermodynamic model derived by Altmaier et al. (2004, 2005) on the Th(IV)–OH–CO_3 system.

Undersaturation solubility batch experiments were performed with UO_2(am,hyd), NpO_2(am,hyd) and PuO_2(am,hyd). Independent batch samples were prepared in 0.1 mol $L^{-1} \leqq$ [NaCl] $\leqq$ 5.0 mol L^{-1} solutions in the presence of 0.1 mol L^{-1} and 0.04 mol $L^{-1}$$Na_2CO_3/NaHCO_3$ at $8 \leqq pH_m \leqq 12.5$ ($pH_m = -\log [H^+]$). Redox conditions in the investigated systems were fixed by the addition of reducing chemicals. Measurements of pH_m, redox potential and An concentration were performed on a regular basis until attaining equilibrium conditions.
Slope analyses and systematic evaluation of the solubility data at different carbonate concentrations and ionic strengths result in consistent chemical models for U(IV), Np(IV) and Pu(IV), where the enhanced solubility can be properly explained by the formation of the complex $An(OH)_2(CO_3)_3^{4-}$ as main An(IV) aqueous species in the investigated pH-range. The chemical model derived for U(IV), Np(IV) and Pu(IV) in the present work is significantly different from the one previously reported for Th(IV), where the predominant role of $Th(OH)(CO_3)_4^{5-}$ as well as a greater impact of ionic strength and carbonate concentration on ThO_2(am,hyd) solubility were observed. Based upon our new experimental studies and thermodynamic evaluation, we propose a new comprehensive thermodynamic model for the investigated systems based upon the SIT approach favored by NEA-TDB.

NUCL 36

Different iron (hydr) oxide modified cementitious material for uranium (VI) immobilization

Bo Cao[1], *bocaouh@gmail.com, Shuai Fan*[4], *Mo Li*[2], *Yandi Hu*[3]. *(1) University of Houston, Houston, Texas, United States (2) Civil and Environmental Engineering, University of California, Irvine, Irvine, California, United States (3) Civil Environmental Engineering, University of Houston, Houston, Texas, United States (4) Civil and Environmental Engineering, University of California, Irvine, Irvine, Texas, United States*

Uranium contaminations, both originated from anthropogenic and natural sources, have brought major safety concerns globally. Solidifying in a cementitious material is a prevalent disposal method for low and intermediate-level radioactive waste. However, it may fail to immobilize uranium waste permanently due to the material’s porous structure, low thermal stability, and poor corrosion resistance. In this study, different iron (hyd) oxides, including hematite, ferrihydrite nanoparticles were added into cementitious materials, and the effect on improving uranium encapsulation capability was studied. In the first group, 1.0, 3.0 and 5.0 wt% of hematite nanoparticles were added into cementitious materials, while in the second group, 0.65, 1.30, 3.90, and 6.50 wt % ferrihydrite nanoparticles were added into cementitious materials. After curing the specimens for 28 days, leaching experiments were carried out at 90 °C for up to 170 days. The experimental results revealed that the addition of hematite nanoparticles and ferrihydrite nanoparticles all significantly reduced uranium leaching, which can be mainly attributed to uranium adsorption onto hematite and ferrihydrite nanoparticles. In the first group, the slowest uranium leaching was found in the specimens with 1.0% hematite nanoparticles. The leaching results were complemented by isothermal

calorimetry measurements, mercury intrusion porosimetry, chemical analysis, and compression tests, which showed that hematite nanoparticles promoted the cement hydration rate and degree, reduced the porosity and pore size, decreased leachability, and increased compressive strength. These effects were found to be the strongest in specimens containing 1.0% hematite nanoparticles. In the second group, no significant difference between the different addition of ferrihydrite nanoparticles. However, ferrihydrite showed better encapsulation effects for uranium than hematite nanoparticles, which may be due to that ferrihydrite transform into hematite nanoparticles and U could be incorporated into the structure of formed hematite nanoparticles. This study provides new insights into the modification of cementitious materials with iron (hydr)oxide for enhanced cement hydration and uranium immobilization. It suggests an economical strategy for the long-term disposal of low and intermediate level radioactive wastes.

NUCL 37

Technetium sulfide as a potential immobilization form for Tc-99 in the environment: Stability and dissolution studies

*Ravi K. Gudavalli[1], Nikolla P. Qafoku[3], **Vasileios Anagnostopoulos**[2], vasileios.anagnostopoulos@ucf.edu. (1) Applied Research Center, Florida International University, Miami, Florida, United States (2) Chemistry, University of Central Florida, Orlando, Florida, United States (3) Geosciences Group, PNNL, Richland, Washington, United States*

Past activities related to the chemical separations for plutonium extraction at the Hanford Site (WA) resulted in the production of hazardous liquid and radioactive solid wastes stored in underground storage tanks. Leaks of waste streams containing a variety of contaminants from some of these tanks have caused widespread subsurface contamination. ^{99}Tc, a major contaminant of concern at the Hanford Site, is present as highly soluble pertechnetate (+7 oxidation state) under the predominant oxidizing conditions at Hanford.

Pertechnetate is mobile in the vadose zone and *in situ* vadose zone remediation approaches are being considered to immobilize ^{99}Tc in the vadose zone and decrease its mobility to the groundwater. A combined NH_3-H_2S treatment has been proposed for the immobilization of U and ^{99}Tc in the vadose zone: H_2S reduces mobile Tc(VII) to immobile Tc(IV) sulfide phases; the NH_3 treatment increases the aqueous phase pH promoting mineral dissolution and subsequent neo-phase formation when pH decreases back to natural values after NH_3 gas treatment. The newly formed secondary minerals have the potential of covering Tc(IV) sulfide phases, physically protecting Tc(IV) from re-oxidation and mobilization.

The objective of the current work is to investigate the stability of Tc sulfide phases under conditions similar to those at the Hanford subsurface. Specifically, we are conducting a series of macroscopic dissolution batch studies at various pH values, and under oxidizing and reducing conditions, to measure Tc release rate into the aqueous phase. We are also investigating the role of bicarbonate concentration on Tc release rate and

bicarbonate-facilitated Tc sulfide dissolution. The data will be used to develop the first of its kind database on Tc sulfide stability under Hanford site conditions. The liquid and solid samples from these experiments will be analyzed with a variety of techniques.

NUCL 38

Observation and characterization of Pd-Te compounds within noble metal inclusions in spent nuclear fuel

Sean H. Kessler, *sean.kessler@pnnl.gov, Timothy Lach, Edgar Buck, Jon Schwantes, Richard Clark. Pacific Northwest National Laboratory, Richland, Washington, United States*

The so-called five-metal phase, consisting of Mo-Tc-Ru-Rh-Pd, has been known to exist as nanoparticles in spent nuclear fuel for more than half a century, but the driving forces and chemical mechanisms governing their formation and physical properties remain difficult to fully characterize, in part due to the high-radiation, chemically complex environment in which they are found. We present new evidence for the presence of a Te-containing nonmetallic phase associated with these particles, into which a significant part of the Pd fractionates. This Pd-Te phase presents the potential for better understanding the nucleation mechanism of nascent particles and the means by which Pd migrates through the uranium dioxide fuel matrix. We also consider how the interplay of different crystalline phases may have consequences for the possible catalytic activity of nanoparticles in medium- and long-term storage conditions.

NUCL 39

Competitive metal and REE coprecipitation with ferrihydrite nano-particles

Chen Zhu, *chenzhu@indiana.edu. Earth and Atmospheric Science, Indiana Univ, Bloomington, Indiana, United States*

Competitive coprecipitation of divalent and trivalent metals and REE with ferric iron as a function of pH was studied with titration experiment at ambient temperature and pressure. X-ray diffraction patterns of the Fe precipitates indicated two broad peaks at 0.153 and 0.256 nm, suggesting that the dominant phase is 2-line ferrihydrite. High-resolution transmission electron microscopy analysis showed that Fe precipitates were single crystallites with 2-5 nm in size. No segregated phases were observed in the clusters or at their edges. Solution chemistry analysis demonstrated that Fe^{3+} precipitated at pH ~ 4. The uptake of Cr^{3+}, Al^{3+}, Ga^{3+}, and In^{3+} took place over a narrow pH range (0.1-0.3 pH unit) near pH 4. The sorption edges for Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} , and Mn^{2+} occurred in a wider pH range of 4.0-7.5, with a preferential partitioning order of $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$, which basically follows the Irving-Williams sequence. The uptake of alkaline earth metals (Mg^{2+}, Sr^{2+}, and Ba^{2+}) occurred at pH > 7. No obvious sorption onto ferrihydrite was found for alkali metals (Li^+ and Na^+). The competitive sorption effects were examined for both low and high

sorbate/sorbent scenarios (Fe : metals = 560 : 1 and 56 : 1, respectively). The sorption edges for trivalent metals (Cr^{3+}, Al^{3+}, Ga^{3+}, and In^{3+}) and Pb^{2+} were less influenced by the competing metals than other divalent metals. In addition, for the examined transition metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+}), the competitive coprecipitation effects are more evident for the metals low in the Irving-Williams series. The coprecipitation process was simulated with the generalized diffuse layer model. However, higher surface site densities and larger complexation constants for surface species than those retrieved in adsorption experiments were required to fit the coprecipitation data, indicating a higher efficiency of the trace metal uptake with coprecipitation process. log K values for REE adsorption onto ferrihydrite generally increase with increasing atomic number across the REE series, indicating that the affinity for REE adsorption generally increase from LREEs to HREEs.

NUCL 40

Kinetics of the uranyl peroxide nanocluster U60 sorption to goethite and magnetite

Luke R. Sadergaski, *lsaderga@nd.edu, Amy E. Hixon. Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

The mobility of uranium in the subsurface environment is highly dependent on redox state and has been studied by batch sorption experiments of the uranyl ion (UO_2^{2+}) with various minerals in diverse geochemical systems. However, there has been little research regarding the behavior of U-based nanoclusters, such as $[(UO_2)(O_2)(OH)]_{60}^{60-}$ (U_{60}), in the environment. The presence of these nanoclusters in the environment may significantly impact our current understanding of the fate and transport of U(VI) given their high solubility and persistence when dissolved in solution. Batch sorption experiments were used to examine the kinetics of U_{60} sorption to goethite (α-FeOOH) and magnetite (Fe_3O_4) as a function of U_{60} concentration, mineral concentration, and pH. Powder X-ray diffraction (pXRD) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) were used to analyze the mineral phases before and after reaction with U_{60} and X-ray photoelectron spectroscopy (XPS) was used to monitor changes in oxidation state. The results from this research will enhance our understanding of the interactions between polyoxometalate oxyanions, such as U_{60}, and iron oxide surfaces and allow scientists to make even better predictions of the fate and transport of uranium in the geosphere.

NUCL 41

Isotopic signature and nano-texture of cesium-rich micro-particles: Release of uranium and fission products from the Fukushima Daiichi Nuclear Power Plant

Junpei Imoto[1], Asumi Ochiai[1], Mizuki Suetake[1], Ryohei Ikehara[1], Kenji Horie[2], Mami Takehara[2], Shinya Yamasaki[4], Toshihiko Ohnuki[3], Gareth T. Law[5], Bernd Grambow[6], *Rodney C. Ewing[7], **Satoshi Utsunomiya**[1], utsunomiya.satoshi.998@m.kyushu-u.ac.jp. (1) Chemistry, Kyushu University, Fukuoka, Japan (2) National Institute of Polar Research, Tachikawa, Japan (3) Tokyo Institute of Technology, Tokyo, Japan (4) University of Tsukuba, Tsukuba, Japan (5) University of Manchester, Manchester, United Kingdom (6) University of Nantes, Nantes, France (7) Stanford University, Stanford, California, United States*

Highly radioactive cesium-rich microparticles (CsMPs) released from the Fukushima Daiichi Nuclear Power Plant (FDNPP) provide nano-scale chemical fingerprints of the 2011 tragedy. U, Cs, Ba, Rb, K, and Ca isotopic ratios were determined on three CsMPs (3.79–780 Bq) collected within ~10 km from the FDNPP to determine the CsMPs' origin and mechanism of formation. Apart from crystalline Fe-pollucite, $CsFeSi_2O_6$ nH_2O, CsMPs are comprised mainly of Zn–Fe-oxide nanoparticles in a SiO_2 glass matrix (up to ~30 w% of Cs and ~1 wt% of U mainly associated with Zn–Fe-oxide). The $^{235}U/^{238}U$ values in two CsMPs: 0.030 (±0.005) and 0.029 (±0.003), are consistent with that of enriched nuclear fuel. The values are higher than the average burnup estimated by the ORIGEN code and lower than non-irradiated fuel, suggesting non-uniform volatilization of U from melted fuels with different levels of burnup, followed by sorption onto Zn–Fe-oxides. The nano-scale texture and isotopic analyses provide a partial record of the chemical reactions that occurred in the fuel during meltdown. Also, the CsMPs were an important medium of transport for the released radionuclides in a respirable form.

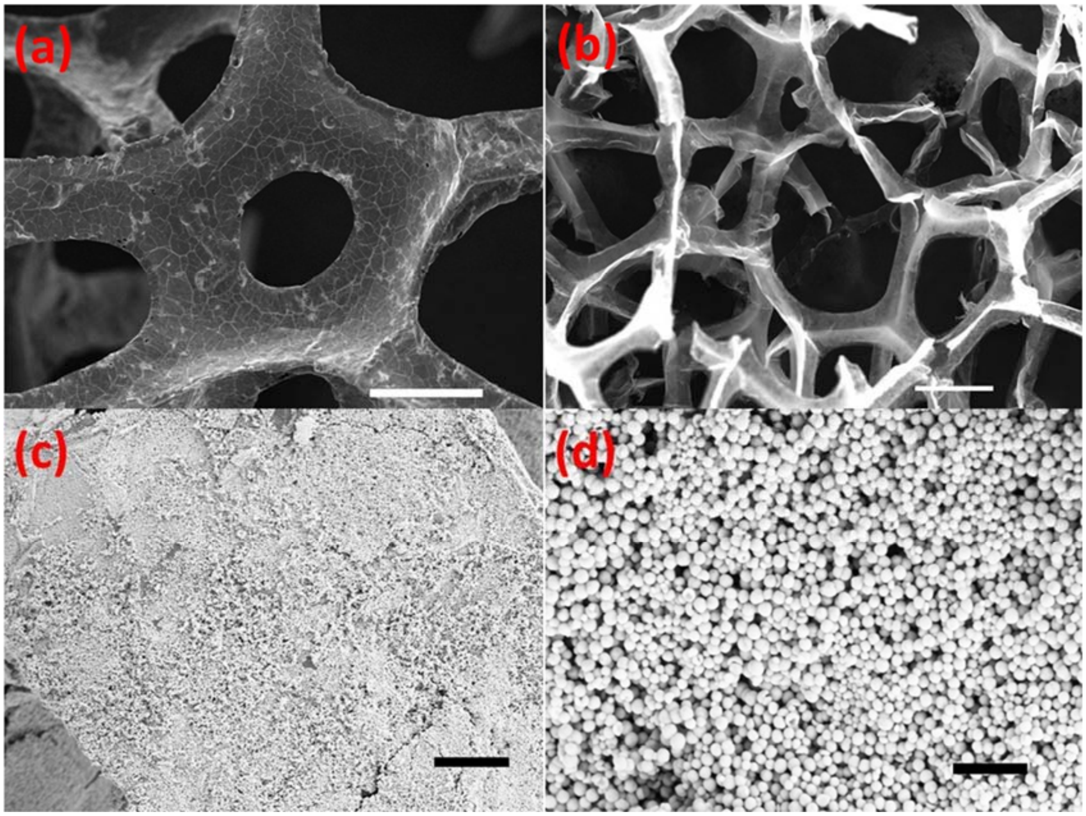
NUCL 42

Investigation of magnetic nanoparticles (Fe_3O_4) anchored 3D-Graphene Foam (3D-MGF) as an adsorbent for strontium adsorption using Central Composite Design (CCD) method

***Sibel Kasap**, skasap@sabanciuniv.edu. SUNUM, Sabanci University, Istanbul, Turkey*

Strontium-90 is the one of the dangerous fission product which is generated during producing electricity in nuclear reactor. Therefore, separation of this radionuclide from contaminated water is an important step to safeguard human health and minimise the impact on the environment. In this research, adsorption behaviour of strontium ions onto magnetic nanoparticle decorated three-dimensional graphene foam (3D-MGF) was investigated. Three-dimensional graphene foam was prepared by CVD method, then it was doped with Fe_3O_4 nanoparticles by hydrothermal method. The characterization of 3D-MGF was investigated by using different characterization techniques. Raman, XRD and FT-IR results revealed chemical and structural characterization of 3D-MGF. The effect of adsorption parameters on adsorption process were evaluated by response surface methodology (RSM) approach based on central composite design (CCD). The analysis of variance (ANOVA) results showed that the applied model was statistical importance owing to large F value (88,45) and very low P value (<0.0001). Adsorption equilibrium isotherms were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich models. According to Langmuir isotherm analysis, a maximum

adsorption capacity of strontium ions on 3D-MGF was calculated 53.48 mg/g. Mean adsorption free energy (E) was found 7.07kj/mol from D-R model and the result indicated that the adsorption process was physi-sorption. Finally, Thermodynamic parameters such as Gibbs free energy (ΔGº), the enthalpy (ΔHº) and the entropy change of adsorption (ΔSº) have also been evaluated and it has been found that the adsorption process was non-spontaneous and endothermic in nature.



Fe3O4 doped 3D-Graphene Foam

NUCL 43

Soil organic matter and plutonium interactions

Daniel Kaplan[1], *daniel.kaplan@srnl.doe.gov, Chen Xu*[2], *Peng Lin*[2], *Kathleen Schwehr*[2], *Nobuhide Fujitake*[3], *Chris Yeager*[4], *Peter H. Santschi*[5]. *(1) Environmental Science and Biotechnology, Savannah River National Laboratory, Aiken, South Carolina, United States (2) Texas A&M University - Galveston, Galveston, Texas, United States (3) Kobe University, Kobe, Japan (4) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (5) Texas A&M University , Galveston, Texas, United States*

Among the key environmental factors influencing the fate and transport of Pu in the environment is natural organic matter (NOM). While this has been well-known for decades, there still remains great uncertainty in predicting NOM-Pu interactions due to lack of understanding of Pu interactions with the specific organic moieties within NOM. A series of studies at multiple field sites were undertaken to describe NOM-Pu interactions, with particular attention directed at the practical problem of identifying conditions when NOM is an aqueous ligand promoting Pu mobility versus when it is a soil-bound ligand reducing mobility. At the field scale, Pu concentrations in wetland surface sediments collected 700m downstream of a former nuclear processing facility in the Savannah River Site (SRS), South Carolina were ~2.5 times greater than those measured in aquifer sediments recovered only 30m upstream from the facility. Sediment Pu concentrations were correlated to total organic C and total N concentrations and even more strongly to hydroxamate siderophore (a hydroxamic acid chelate) concentrations. The importance of hydroxamates within NOM on Pu binding was demonstrated in soils from SRS and Rocky Flats, Colorado. Isoelectric focusing experiments isolated most of the Pu in a single NOM fraction. Hydroxamates in that fraction were then identified using ESI-FTICR-MS and hydroxamate standards. From a survey of 14 well-characterized humic acid (HA) collected from different soils around the world, it was shown that even though colloidal NOM (>3kDa to <0.45µm) accounted for a small fraction of the total HA, it had a much greater tendency to bind Pu than particulate HA. Finally, 55% of the bomb-derived Pu detected in a sediment core from Nagasaki, Japan was enriched in NOM (>3kDa) associated with Fe-oxides and 31% was associated with a NaOH-extractable OM fraction, suggesting that NOM may ultimately be the long-term sink of Pu in surface soils.

NUCL 44

Biogeochemistry of plutonium in subsurface environments

***Donald T. Reed**, dreed@lanl.gov, Juliet Swanson. Los Alamos National Laboratory, Carlsbad, New Mexico, United States*

Microbial processes have the potential to significantly impact the speciation and migration of plutonium in the subsurface. This subsurface biogeochemistry is inherently complex due, in part, to the complexity of the environmental chemistry of plutonium. An update on specific and key interactions with plutonium is provided in the areas of bioreduction, bioassociation, toxicity and general environmental impacts. Although there are relatively few data on plutonium, much of what is understood is based on our general understanding of microbial interactions with metals and actinides and, in some cases, redox-stable analogs can be used to establish the plutonium speciation effects and trends. As is the case with the environmental chemistry of plutonium, its biogeochemistry needs to be interpreted in terms of oxidation-specific interactions. Microbial processes impact plutonium aggregation, oxidation state distribution, complexation, and sorption are identified as the key interactions that impact plutonium speciation. Alternatively, plutonium is radiotoxic towards microorganisms and can impact their viability and nature of the indigenous microbial communities. An accounting of the effects of microbial processes is needed to address natural attenuation issues for near-surface contaminated sites and define the source term in deep repository applications to establish the overall fate and mobility of plutonium in the subsurface.

NUCL 45

Examining radionuclide uptake by flora surrounding the Olympic Dam Cu-U-Au-Ag Mine in South Australia

Samantha Pandelus, *pand0047@flinders.edu.au, Allan Pring, Claire E. Lenehan, Rachel S. Popelka-Filcoff. Science and Engineering, Flinders University, Adelaide, South Australia, Australia*

Naturally occurring radionuclides are ubiquitous in the environment, however mining, processing and other applications are associated with outcomes of radiological importance. Olympic Dam (BHP, South Australia) is the largest mine in the state with an ore deposit containing copper, uranium, silver and gold, where the ore is processed on site. The various stages of both mining and ore processing, such as calcination stack emissions and ventilation gases from the underground mine may release radioactive emissions into the environment. The impacts on the environment from radiological effects have been documented in Europe and North America, and internationally accepted methods are available for non-human biota such as the Environmental Risk from Ionising Contaminants: Assessment and Management (ERICA) tool. Concentration ratios are the essential input for these models. A concentration ratio is a measure of the ratio of an element (or radionuclide) in a target species and the selected media (for example soil or water). However there is a limited amount of data for these models for Australia, in particular for native species in arid environments. Samples from the mine representing the areas of greatest radiological emissions along with flora from Olympic Dam have been studied. Passive sampling using diffusive gradients in thin films (DGT) membranes was used to determine metals and radionuclides in soils from the roots of native flora. This method provides a more accurate representation of the events that occur seasonally that may otherwise be missed from grab samples. Analytical methods including high resolution gamma spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), scanning electron microscopy energy dispersive spectroscopy (SEM/EDS) and X-ray diffraction (XRD) are used for the identification of radionuclides, rare earth elements (REEs), isotope ratios and provide information on the distribution of radionuclides in samples. This research will provide a better understanding of the behavior of radionuclides in an arid environment and provide data on the mechanisms of radionuclide uptake in flora. It will provide a more comprehensive data set and model for Australia and other localities with similar arid environments.

NUCL 46

Potential for transport of cesium and lanthanides as biocolloids in a high ionic strength system

Frances Zengotita[1], *fzeng002@fiu.edu, Hilary P. Palmer Emerson*[2], *Timothy M. Dittrich*[3], *Juliet Swanson*[4,3], *Michael K. Richmann*[3,4], *Donald T. Reed*[4]. *(1) Applied Research Center-FIU, Florida International University, Miami, Florida, United States (2) Applied Research Center, Florida International University, Doral, Florida, United States*

(3) Los Alamos National Laboratory, Boulder, Colorado, United States (4) Cemrc, Carlsbad, New Mexico, United States

The development of nuclear weapons during the Cold War and World War II produced an overwhelming amount of radioactive waste that is currently being disposed of at the Waste Isolation Pilot Plant (WIPP). The WIPP is a deep geologic salt repository for long-term disposal of radioactive waste. The chemical behavior of actinide series elements (the most long-lived byproduct of the waste) and fission products is a major concern for the WIPP due to their long half-lives and unknown mobility in the halite environment. However, experimental data describing the potential mobility of these contaminants under repository conditions is vital to create evidence-based risk assessment models.

The objective of this research is to better understand the potential for transport of radioactive elements with biocolloids. A halophilic bacterium, Chromohalobacter, was isolated from near the WIPP site and identified to thrive in high salt concentrations. Thus, it was utilized to quantify the mobility of risk-driving contaminants under conditions that were relevant to the WIPP in miniature laboratory columns packed with dolomite from the near field of the repository. Non-radioactive lanthanides are used as chemical analogues, elements that have similar properties, for the trivalent oxidation state of the actinides. Transport of non-radioactive Cs is also investigated to consider short term release and transport potential.

Results show that Chromohalobacter is mobile in the dolomite mineral system. Further, there is potential for Nd co-transport with Chromohalobacter; however, under the conditions of these experiments, Nd cannot be removed from the dolomite surface by the bacterium. Cs transported unretarded through the columns without interaction with dolomite or Chromohalobacter in the stationary phase. However, future work will consider uptake in actively growing bacterium as a potential transport vector.

NUCL 47

Plutonium phases in Hanford-derived wastes

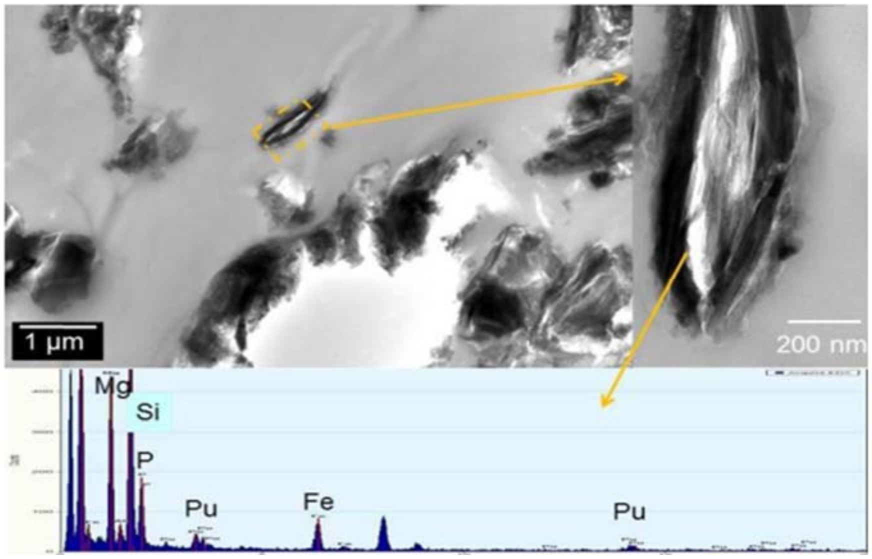
***Edgar Buck**, edgar.buck@pnnl.gov, Dallas R. Reilly. Pacific Northwest National Laboratory, Richland, Washington, United States*

Many sophisticated technologies are available that provide nano-scale information, including; speciation, morphology, trace element, and isotopic distribution in plutonium contaminated sediments and soils. Such information can be used to develop environmental risk assessments and for potential remediation strategies.
Studies to determine the chemical form of plutonium in wastes from the Hanford site have used X-Ray absorption spectroscopy (XAS), transmission electron microscopy (TEM) and NanoSIMS analysis. XAS results clearly demonstrate that the chemical form of the Pu is quite different between the different sites, being primarily monomeric Pu at the Z-12 site and present as PuO_2 like or Pu phosphate particles at the Z-9 trench. The

phosphate required to precipitate the Pu compounds apparently originated from the co-disposal of organics at the site (Figure 1).

At this time, the environmental importance of this phase is unknown. It is unclear whether the phase will undergo extensive migration or will contribute to the attenuation of Pu in the environment. It is possible that this phase has little or no impact on the long-term behavior of Pu. The presence of phosphate phases is significant since past research efforts into the environmental behavior of Pu particles have focused on the formation of PuO_2 or PuO_{2+x} owing to the stability of these phase in environmental systems.

The complexity in the natural environment may lead to the formation of phases that may not be predicted in simple laboratory set-ups. Increasingly, studies point to the complexity of Pu chemistry in complex media and the need to probe these environments with tools that can distinguish the micro-environments.



Thin-Sectioned 216-Z-9 Crib Sediment Showing the Occurrence of a Pu-Phosphate Region Within a Clay-Like Phase. The higher magnification image shows the strands of clay fibers. The composition is consistent with mica with Mg, Si, and Fe as the major components.

NUCL 48

Desorption kinetics of plutonium from altered nuclear melt glass colloids

Claudia Joseph[1], *claudia.joseph@kit.edu, Enrica Balboni*[3], *Teresa Baumer*[2], *Kerri Treinen*[3], *Annie Kersting*[3], *Mavrik Zavarin*[3]. *(1) Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany (2) University of Notre Dame, Notre Dame, Indiana, United States (3) Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, Livermore, California, United States*

Highly radiotoxic plutonium has been introduced into the environment and transported by ground- and surface water at sites of nuclear weapons' production (e.g., Hanford, USA), nuclear weapons' testing (e.g., Nevada National Security Site, NNSS, USA), and nuclear waste disposal (e.g., Little Forest Burial Ground, Australia). In the case of underground nuclear weapons' testing, the released high temperatures led to the volatilization of silicate phases, which eventually condensed, and solidified to glass. In this so-called nuclear melt glass, plutonium is embedded. At NNSS, for tests located below the water table, the displaced water began to return to the original water level within days to years. Under such conditions, hydrothermal alteration processes take place. As a result, the plutonium migration in water is controlled by the rate of glass alteration, the leaching of plutonium, and colloid-facilitated transport. In particular, the nature of plutonium association with the colloids formed in the alteration process and consequently, the desorption kinetics of plutonium are not known, but have a significant impact on the transport behavior of plutonium.

In the present study, nuclear melt glass from NNSS was hydrothermally altered at 25 to 200 °C for about 994 days. During this time, the colloidal load of the suspension increased, and secondary solid phases were formed: plutonium-containing smectite and zeolite minerals. In a subsequent experiment, flow-cell desorption studies with nuclear melt glass colloids formed at 140 (mainly clay) and 200 °C (clay and zeolite) were conducted under NNSS-specific conditions. The desorption behavior was simulated by our recently developed numerical model for plutonium-montmorillonite adsorption/desorption. The results show that the model is able to describe successfully the desorption of plutonium from colloids formed at 140 °C. The desorption of plutonium from colloids formed at 200 °C shows a slower desorption rate than predicted by the model. These experiments indicate that such complex systems can have a different kinetic than simple one solid systems the numerical model was based on. A fraction of plutonium may be permanently associated with the colloids' crystal structure and may, as a result, have much greater migration potential.

NUCL 49

Equilibrium and kinetic studies of lanthanide and actinide sorption to aluminum (hydr)oxide minerals

*Teresa Baumer, **Amy E. Hixon**, ahixon@nd.edu. Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States*

Anthropogenic sources of neptunium, plutonium, and americium have been introduced into the environment through nuclear weapons testing and disposal at legacy waste sites. The long half-lives of these radionuclides mean that once they are released into the environment, they will persist for millions of years. Therefore, it is essential to predict the mobility of these radionuclides in the subsurface environment. We studied europium (as an analog for Am) and neptunium sorption to a suite of aluminum (hydr)oxide minerals – gibbsite, bayerite, corundum, and γ-alumina – under equilibrium conditions. Batch experiments and detailed solid-phase characterization (e.g., powder X-ray diffraction, scanning electron microscopy, and infrared spectroscopy) were used to determine the effect of surface acidity on the sorption of each metal. While the composition of the mineral phase had no apparent effect on europium sorption,

preferential sorption of neptunium followed the trend bayerite > corundum > γ -alumina. In addition to this gap in basic understanding of equilibrium thermodynamics, the kinetics of europium, neptunium, and plutonium sorption have been largely overlooked. Batch sorption experiments conducted as a function of pH, mineral concentration, and metal concentration were used to determine rate laws for Eu(III) and Np(V) sorption and Pu(V) sorption and reduction in the presence of aluminum (hydr)oxide minerals. In each case, pseudo-first-order expressions were used. Neptunium and plutonium interactions were characterized by a two-step reaction with a fast initial sorption step followed by a slow equilibrium process. Future work is focused on determining sorption mechanisms and developing surface-complexation models to describe these systems.

NUCL 50

Batch sorption of Eu, U, Np, and Pu to the iron oxide mineral hematite was examined at variable temperatures and ionic strengths

***Brian A. Powell**, bpowell@clemson.edu, Jeremiah Mangold, Andreas Schnurr. Clemson University, Anderson, South Carolina, United States*

This proposed work seeks to characterize actinide sorption to mineral surfaces under the elevated temperature and ionic strength conditions to allow for more accurate prediction of actinide behavior in geologic waste repositories where such conditions may persist. Batch sorption of Eu, U, Np, and Pu to the iron oxide mineral hematite was examined at variable temperatures and ionic strengths. The primary focus was the development of quantitative thermochemically based models describing the speciation of the actinides in aqueous and solid phases. The models are used to determine the enthalpy and entropy contributions to the overall free energy of actinide sorption to minerals. When possible, surface complexation models were constrained using speciation at solid:water interfaces determined using x-ray absorption spectroscopy and quantum mechanical modeling. A more detailed level of characterization of the surface speciation is required given variability in observed surface reactions of actinides including formation of monomeric surface complexes, surface mediated redox reactions, aging or hysteretic sorption, or surface induced precipitation. Differentiation of enthalpy and entropy contributions can help to evaluate the dominant interfacial reactions as well as provide a more rigorous and technically defendable model of actinide sorption. All systems exhibit positive sorption entropies which are hypothesized to be mechanistically driven by displacement of solvating water molecules from the actinide ion and the mineral surface during sorption. Preliminary data using isothermal titration calorimetry has confirmed these measurements.

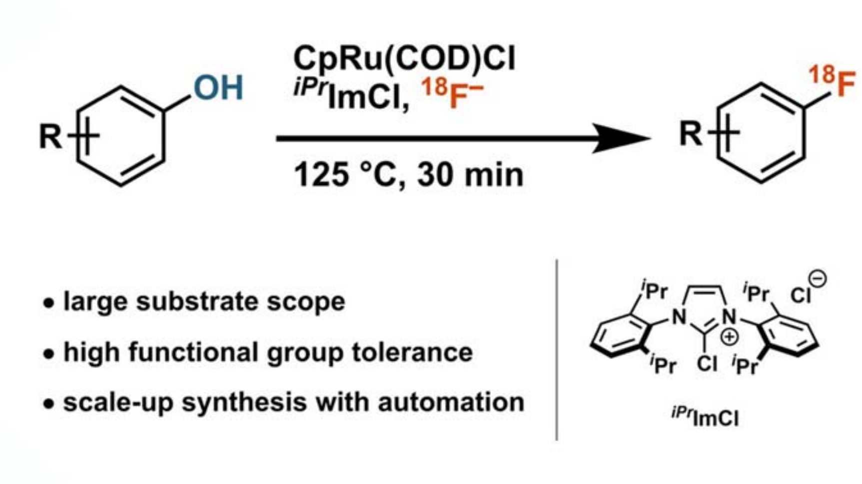
NUCL 51

^{18}F-deoxyfluorination of phenols via Ru *π*-complexes

***M Hassan Beyzavi**[1,2], beyzavi@uark.edu, Debashis Mandal[2], Martin Strebl[2,3], Constanze Neumann[2], Erica D’Amato[2], Junting Chen[4], Jacob M. Hooker[5], Tobias*

Ritter[4]. (1) Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas, United States (2) Chemistry and Chemical Biology, Havard University, Cambridge, Massachusetts, United States (3) Massachusetts General Hospital and Harvard Medical School, Athinoula A. Martinos Center for Biomedical Imaging, Charlestown, Massachusetts, United States (4) Max-Planck-Institut fuer Kohlenforschung, Muelheim an der Ruhr, Germany (5) Room 2301, Massachusetts Gen Hospital Radiology, Charlestown, Massachusetts, United States

The deficiency of robust and practical methods for ^{18}F-radiofluorination is a bottleneck for positron emission tomography (PET) tracer development. The first transition-metal-assisted ^{18}F-deoxyfluorination of phenols will be presented. The transformation benefits from readily available phenols as starting materials, tolerance of moisture and ambient atmosphere, large substrate scope, and translatability to generate doses appropriate for PET imaging.



NUCL 52

Gas-phase complexes of lanthanides and americium with bis-triazynl pyridine

***Tian Jian**[1], tjian@lbl.gov, David Dan[2], Thomas E. Albrecht-Schmitt[2], John K. Gibson[1]. (1) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States (2) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States*

Bis-triazynl pyridines (BTPs) exhibit chelation selectivity for trivalent americium, Am(III), over lanthanides, Ln(III). To elucidate this selectivity, electrospray ionization mass spectrometry (ESI-MS) was used to generate gas-phase complexes $[M^{III}L_3]^{3+}$ and $[M^{III}L_2(NO_3)_2]^{+}$ (M=Ln, Am; L=BTP), which were then characterized by collision induced dissociation (CID). For most $[M^{III}L_3]^{3+}$, CID results in $[HL]^{+}$ and $[M^{III}L_2(L\text{-}H)]^{2+}$, the latter of which rapidly associates with water to yield $[M^{III}(L\text{-}H)(H_2O)]^{2+}/[M^{III}L_2(OH)]^{2+}$ where these isomers are experimentally undifferentiated. CID of $[Eu^{III}L_3]^{3+}$ distinctively results in reductive elimination of L^{+} to yield $[Eu^{II}L_2]^{2+}$, which reflects the more favorable

Eu(III/II) reduction potential. Dissociation of gas-phase $[Am^{III}L_3]^{3+}$ is more facile than of $[Ln^{III}L_3]^{3+}$, this in apparent contrast to solution selectivity of BTP for Am(III) over Ln(III). The $[M^{III}L_2(NO_3)_2]^+$ complexes exhibit the following CID pathways: predominantly $[M^{III}L(NO_3)_2]^+$ from L-elimination; $[M^{III}L(L\text{-}H)(NO_3)]^+$ and $[M^{III}(L\text{-}H)_2]^+$ from 1 or 2 HNO_3-elimination(s). For M = Ce, Pr, Nd and Am, CID of $[M^{III}L_2(NO_3)_2]^+$ additionally results in NO_2-elimination to yield $[MO_2L]^+$ with indeterminate M oxidation states. Computations will be pursued to understand the experimental observations.

NUCL 53

Synthesis and characterization of gas-phase uranyl peroxide dimer complexes

Jiwen Jian[1]*, jianjiwen2006@gmail.com, Qunyan Wu*[2]*, Santa Jansone-Popova*[3]*, Amanda Bubas*[4]*, Irena Tatosian*[4]*, Michael J. Van Stipdonk*[5]*, Jonathan Martens*[6]*, Giel Berden*[6]*, Jos Oomens*[6,7]*, Weiqun Shi*[2]*, John K. Gibson*[1]*. (1) Chemical Science Division, Lawrence Berkeley National Laboratory, BERKELEY, California, United States (2) Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China (3) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (4) Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, Pennsylvania, United States (6) Institute for Molecules and Materials, FELIX Laboratory, Radboud University, Nijmegen, Netherlands (7) Institute for Molecular Sciences, University of Amsterdam, Amsterdam, Netherlands*

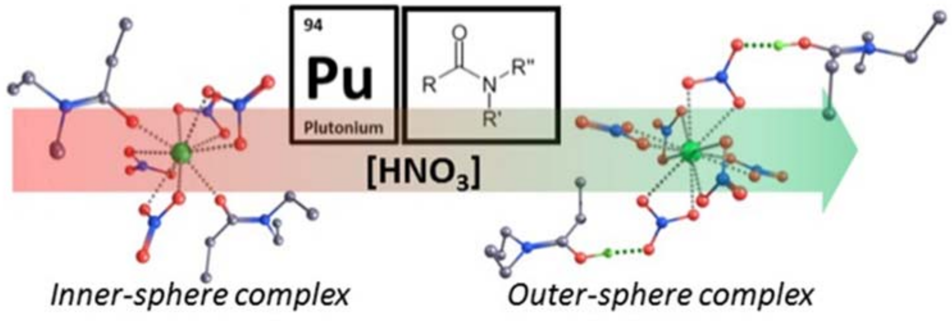
Gas-phase uranyl peroxide dimers $[(U^{VI}O_2)_2(O_2)(L)_2]^{2+}$ are produced in remarkably high abundance by electrospray ionization (ESI) of uranyl and tetradentate hard-soft (2O-2N) donor ligands L. The three such ligands employed in this work are a 2,9-diamide-1,10-phenanthroline (DAPhen) and two bis-lactam-1,10-phenanthrolines (BLPhen). The dimer assignments were confirmed by mass spectrometric mass shifts using isotopically substituted $U^{18}O_2^{2+}$, by collision induced dissociation (CID), and by infrared multiple photon dissociation (IRMPD) spectroscopy. CID of $[(U^{VI}O_2)_2(O_2)(L)_2]^{2+}$ results in peroxide bond cleavage to give $[U^VO_2L]^+$, which chemisorbs O_2 to yield $[U^{VI}O_2(O_2)L]^+$, and in O atom elimination to give $[(U^{VI}O_2)_2(O)(L)_2]^{2+}$, which chemisorbs H_2O to yield $[(U^{VI}O_2)_2(OH)_2(L)_2]^{2+}$. Agreement of the measured and density functional theory (DFT) computed IR spectra confirm the assignments as $[(U^{VI}O_2)_2(O_2)(L)_2]^{2+}$ peroxides. IRMPD spectra for $[(U^{VI}O_2)_2(O_2)(L)(L')]^{2+}$, where L and L′ are the same or different DAPhen/BLPhen ligands, reveal a nearly constant uranyl asymmetric stretch frequency, v_3, as is also predicted by DFT. The near invariance of v_3 suggests similar uranyl-ligand bonding interactions, which appears as inconsistent with the disparate solution affinities of the three ligands for metal ions. The underlying basis for the near-constant v_3, including differences between gas and solution complexation, is being further assessed.

NUCL 54

How x-ray absorption spectroscopy merge with theoretical models to solve actinides and technetium structure in solvent extraction

***Thomas Dumas**[1], thomas.dumas@cea.fr, Marie-Christine Charbonnel[2], Nathalie Boubals[1], Eleonor Acher[1], Dominique Guillaumont[1], Christelle Tamain[1]. (1) DMRC, CEA, Bagnols sur Ceze, France (2) CEA Marcoule, Bagnols-Sur-Ceze, France*

Understanding the structure of actinide ions in organic solution is of particular interest in the development of effective solvent extraction separations for waste remediation in nuclear fuel cycles. In complex organic phases, in which actinide-ligand bonds are diverse and versatile, several complexes can coexist and quantitative structural information is often lacking because of the difficulty to interpret experimental data. Quantum chemistry associated with experimental data can improve this analysis and more particularly help in the EXAFS measurement interpretation. In the present study, we have combined extended EXAFS with XRD, infrared spectroscopy and theoretical calculations to develop an efficient method to solve polydispersity in organic solvent. The crystal data are used as reference structural models. EXAFS spectra were measured in the solid state and in solution. To help EXAFS analysis, ab initio EXAFS spectra were computed from structural parameters and Debye-Waller factors derived from quantum chemistry without using fitting parameters. It was then applied to elucidate the structures of plutonium(IV) and uranium(VI) ions with a series of *N*,*N*-dialkyl amide, as well as co-extracted uranium/technetium by the same *N*,*N*-dialkyl amide ligands. For U(VI), EXAFS analysis combined with XRD shows that the uranyl structure is identical in the solution and in the solid state and is independent of the *N*,*N*-dialkyl amide alkyl chains. For plutonium(IV) complexes, it was not possible to resolve unambiguously plutonium coordination structures in solution from EXAFS measurements and the coordination structure was established from the comparison between experimental and *ab initio* EXAFS spectra. With linear alkyl chain amides, Pu(IV) adopts identical structures in the solid state and in solution while a different coordination structure is found in solution with branched alkyl chain-amides.
Finally, it is shown that EXAFS spectra can be reproduced from *ab initio* calculations without using fitting parameters and support structural characterization in complex solvent extraction systems.



NUCL 55

Experimental and computational investigation of the separation mechanism of ALSEP

***Brian D. Etz**, etz@mines.edu, Gabriela Picayo, An T. Ta, Mark P. Jensen, Shubham Vyas. Chemistry, Colorado School of Mines, Golden, Colorado, United States*

Nuclear waste contains transuranic actinides such as americium (Am) and curium (Cm), that make the handling and storage of used nuclear fuel costly and environmentally harmful. Considerable effort has been dedicated to developing solvent extraction processes to separate the transuranic actinides from the lanthanide fission products to alleviate the burden of used nuclear fuel. One such process, ASLEP (**A**ctinide **L**anthanide **SEP**aration), has shown great recovery and selectivity of trivalent actinides, however suffers from slow stripping kinetics. Therefore, investigation into the separation mechanism and coordination environment of the heavy rare earth metals can help determine what chemical properties affect the separation and how the kinetics can be improved for large-scale nuclear waste processing. The complexation behavior at each stage of the ALSEP process was determined through a combined experimental and computational investigation. Quantum mechanical calculations paired with time-resolved fluorescence spectroscopy provided insights into thermodynamically favorable metal-ligand interactions and helped to confirm the coordination environment around the metal. This talk will focus on investigating the underlying mechanism of coordination and extraction of europium, neodymium, and americium in the ALSEP process to improve the kinetics of actinide/lanthanide separation.

NUCL 56

Ligand dynamics at the liquid-liquid interface in ALSEP process

*An T. Ta, Govind A. Hegde, **Shubham Vyas**, svyas@mines.edu. Colorado School of Mines, Golden, Colorado, United States*

Actinide Lanthanide Separation (ALSEP) has been a topic of interest within recent years as it has been shown to selectively extract problematic actinides (e.g. americium and curium) from spent nuclear fuel more efficiently than previously developed processes. Although successful, the process suffers slow kinetics that prevents ALSEP from being implemented at an industrial scale. In an effort to improve this process, many fundamental studies have been performed on ALSEP, however, most of these studies have focused on the thermodynamics of separation. Within this talk, a different approach utilizing theoretical methods such as Molecular Dynamics (MD) simulations will be discussed along with the progression of MD application to further understand the mechanics of ALSEP. Approaches towards system design, analysis tools, chemical properties, as well as effects of parameters will be presented. Through a series of MD simulations, the unknown dynamical behaviors of participating molecular species were quantified/analyzed as this approach allows one to be able to observe changes to the ALSEP system at a molecular level.

NUCL 57

Educational outreach using nuclear science and fiction in *Star Trek*

***Jeffrey C. Bryan**, jbryan@uwlax.edu. Chemistry/Biochemistry, University of Wisconsin-La Crosse, La Crosse, Wisconsin, United States*

Much of the Star Trek universe can be understood or disputed based on our current understanding of nuclear chemistry and physics. This presentation will explore using Star Trek as a way to make sense of apparently complex topics in contemporary nuclear chemistry for high-school students and the generally geeky public. Topics such as matter/energy conversions, antimatter, medical imaging, and the effects of ionizing radiation on living systems can be examined using clips from the various Star Trek television series and movies. Nuclear chemistry outreach can boldly go where few have gone before to engage critical thought of science fiction and understanding of nuclear science.

NUCL 58

Teaching nuclear science in the general education curriculum

***Alice C. Mignerey**, mignerey@umd.edu. Chemistry and Biochemistry, University of Maryland, College Park, Maryland, United States*

The paper describes an Honors course taught at the University of Maryland within the University Honors Program. Titled "The History of the Manhattan Project", it uses the Pulitzer Prize winning book by Richard Rhodes "The Making of the Atomic Bomb" as the primary source of material. The class starts with the discovery of the electron by J. J. Thomson and moves through the advances made in nuclear physics and radiochemistry - culminating with the discovery of fission in the first half of the semester. Along the way the important experimental techniques used and the science behind them are discussed. The second half of the course is really the development of the Manhattan Project. The historical context of the science serves as a backdrop upon which the discoveries are made. The students in the class come from diverse academic backgrounds, but few have any knowledge of radiochemistry prior to the course.

NUCL 59

Video-based approach to incorporating radiochemistry into the general chemistry curriculum and as an upper level elective for undergraduate chemistry majors

***Shejla Pollozi**[1,2], spollozi@gradcenter.cuny.edu, Donna M. McGregor[3,2]. (1) Chemistry, Lehman College of the City University of New York , Bronx, New York, United States (2) Chemistry, Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, New York, United States (3) Chemistry, Lehman College CUNY, Bronx, New York, United States*

Over decades, radiochemistry has answered questions about the structure of the nucleus, the origin of elements, the relationship between matter and energy, rate equations, and many more processes. Today, all these answers can be easily

understood and explained in a general chemistry undergraduate course. Moreover, laboratory experiments can be designed to include analyses with real-life applications in medical imaging and targeted therapy, environmental protection and forensics. Despite these potentially profound applications the fundamentals of radiochemistry have not been routinely embraced as a component of General Chemistry courses, and more often than not radiochemistry is excluded from the curriculum. Even advanced radiochemistry courses are offered in only a limited number of institutions across the country.

At Lehman and Hunter Colleges of City University of New York, our chemical education and radiochemistry teams are designing video modules in radiochemistry that can be used in any chemistry courses. Specifically, we are interested in material applicable to introductory courses with the intent to expand students' understanding of basic radiochemical concepts and their applications to life in the 21st century. Simultaneously we hope to design one or two key laboratory experiments that help demystify the danger associated with radioactive sources. In this talk we will discuss our perspectives and introduce some of our materials.

NUCL 60

Nuclear workforce development: The University of Missouri experience

Silvia S. Jurisson*, jurissons@missouri.edu. Chemistry, University of Missouri, Columbia, Missouri, United States*

The education of trained professionals in nuclear chemistry, radiochemistry and related disciplines has been a matter of concern for many years. Reports in 1988, 1998 and 2002 all related the same findings that there was a serious shortage of chemists with a background in nuclear and radiochemistry and that no improvements were observed from the previous studies. The Nuclear Chemistry Summer Schools (NCSS) that have been held each year since 1984 have successfully developed a pipeline of students for graduate programs in nuclear and radiochemistry with about 50% of the attendees entering a graduate program in the field. Several institutions in the US, including the University of Missouri, have graduate programs in nuclear and/or radiochemistry, and additional training at the postdoctoral level occurs at universities, medical institutions and national laboratories. Several institutions also have research programs targeting undergraduates as well. As an example, the Department of Chemistry at the University of Missouri in Columbia currently has five radiochemistry faculty members. Each brings a different perspective (inorganic, organic, analytical) for the applications of radioactivity. This provides a "critical mass" for addressing multi-disciplinary projects and gives students the opportunity to be exposed to many facets of radiochemistry and nuclear chemistry research. Current applications include radiopharmaceutical chemistry, radioanalytical chemistry, radioenvironmental chemistry, actinide chemistry, and radiotracer applications to plant biology. An overview or the research and education programs in nuclear and radiochemistry at the University of Missouri will be presented.

NUCL 61

Interdisciplinary approach to radiochemistry education at Colorado State University

***Ralf Sudowe**, ralf.sudowe@gmail.com. Environmental & Radiological Health Sciences, Colorado State University, Fort Collins, Colorado, United States*

Radiochemistry is a specialization within the Radiological Health Sciences Degree M.S. and Ph.D. programs at Colorado State University. These programs attracts students from a variety of scientific backgrounds, such as physics, chemistry, engineering, biology and toxicology. Consequently, the curriculum has to account for these different backgrounds and ensure that all students achieve a similar knowledge base in nuclear science. This requires careful consideration of the appropriate electives and extensive communication and coordination between the faculty members teaching the core courses. This presentation will provide an overview of the Radiochemistry Program at Colorado State University and its teaching & laboratory facilities.

NUCL 62

Radiochemistry at the Colorado School of Mines: Golden opportunities

***Jenifer C. Shafer**[1], jshafer@mines.edu, Mark P. Jensen[2]. (1) Chemistry, Colorado School of Mines, Golden, Colorado, United States (2) Colorado School of Mines, Golden, Colorado, United States*

Radiochemistry efforts at the Colorado School of Mines in Golden, CO were reinvigorated in 2012 courtesy a collaboration between the Chemistry Department and the interdisciplinary Nuclear Science & Engineering Program. The Radiochemistry Program at Mines is supported by Professors Mark Jensen and Jenifer Shafer and has active research in areas related to the back end of the nuclear fuel cycle, fundamental actinide science and nuclear forensics. Infrastructure at Mines enables the consistent work with a variety of radiotracers, including transuranics, and periodic operations with macroscopic amounts of neptunium and plutonium. Two labs are available for wet chemistry work with radioactive materials: the on-campus facilities and off-campus facilities housed at Building 15 in the Denver Federal Center (DFC, fifteen minutes from Mines campus). Building 15 houses a low-enriched uranium-fueled 1 MW TRIGA reactor operated by the US Geological Survey. A Memorandum of Understanding (MOU) exists between the USGS and the Colorado School of Mines, and the collaborative research benefits both organizations in academic and basic research efforts. This presentation will focus on the trajectory and current research capabilities of the radiochemistry program.

NUCL 63

Returning the radio to chemistry: Integrating radiochemistry into a Ph.D. program at Hunter College catalyzed by the NSF-IGERT program

Lynn C. Francesconi[1,2], *lfrances@hunter.cuny.edu. (1) Chemistry, Hunter College of the City University of New York, Bridgewater, New Jersey, United States (2) Chemistry, Graduate Center of the City University of New York, New York City, New York, United States*

Hunter College of the City University of New York (CUNY) started a Radiochemistry concentration in the Ph.D. program that is housed in the Graduate Center of CUNY in Fall, 2010. This program was initially funded and catalyzed by the NSF-IGERT program and started with one graduate student. Presently, we have 32 individuals who are current Radiochemistry graduate students and a number who have graduated. At the onset of the program, we established collaborations with medical institutions on the Upper East Side of Manhattan, notably Memorial Sloan Kettering Cancer Center (MSK) and Weill Cornell Medical College, wherein students are co-mentored by Hunter College faculty and faculty at collaborating institutions. These co-mentorships and collaborations illustrate value added. Hunter faculty and graduate students have the opportunity to work on high impact, interdisciplinary projects with distinct medical and clinical relevance. Hunter faculty who engage in the co-mentorship model use their considerable skills, experience and talent to solve new and important problems in a field, perhaps a new field for the Hunter faculty. Opportunities for student networking abound in these collaborations and students have assumed highly regarded and prestigious post-doctoral, industrial and academic positions upon graduation. The collaborations and co-mentorships have grown over the years to include National Laboratories and other institutions. As a result of the successful Radiochemistry program, Hunter College has hired two new faculty members in Radiochemistry and a senior staff Radiochemist. Also, the program spawned a Radiochemistry program at Lehman College of CUNY. The challenges and benefits will be discussed.

NUCL 64

Physicochemical properties of defect laden uranium

Daniel Pope[1], *daniel.j.pope@wsu.edu, Aurora E. Clark*[2]. *(1) Chemistry, Washington State University, Pullman, Washington, United States (2) Washington State Univ, Pullman, Washington, United States*

Addition of elements to pure uranium may change its properties in beneficial or deleterious ways. In metal uranium fuel the accumulation of fission poisons decreases or kills nuclear reaction efficiency. Formation of uranium alloys, however, can lead to many physical enhancements desirable for reactor operation. The study of the energetics involved in the formation of defects would be useful in the design of addition or removal of these elements. The goal of this research is the computational study of

the energies of defect formation in the bulk system of the high temperature phase of metal uranium with a variety of these possible defects.

The crystal properties of this high temperature phase of uranium were successfully modeled in periodic boundary conditions using plane wave calculations within density functional formalism. Energy of formation of point defects in body-centered cubic γ-uranium crystal were studied with respect to a variety of possible metal substituents. Substitutional energies of molybdenum, rhodium, zinc, niobium, lanthanum, europium, and lutetium are compared. Due to the wide range of elements calculated for comparison, a general, widely applicable GGA-PBE exchange-correlation functional was used. The results of these studies show the likely energetically favorable ordering of possible defects and which may be more likely to diffuse to the uranium surface.

As γ-uranium is a semi-metal, thermal smearing has often been used in previous computational calculations as to improve SCF convergence. It may be possible that the change in energy on application of this method is on the order of the energy of substitution. Calculating energies across a range of thermal smearing values provides a quantitative measure of this effect and informs the degree to which the substitutional energy across different impurities are affected.

NUCL 65

Software and analysis methods for the determination of americium in plutonium via alpha spectrometry

Donivan R. Porterfield[1], *dporterfield@lanl.gov, Michael D. Yoho*[1]*, Jung Rim*[1]*, Sheldon Landsberger*[2]*. (1) Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Nuclear Engineering Teaching Laboratory, The University of Texas at Austin, Austin, Texas, United States*

The in-growth of ^{241}Am from the decay of ^{241}Pu is a well-regarded chronometer for the determination of the time since last chemical-separation in plutonium-based nuclear forensics samples. Alpha-spectrometry software will be presented that determines the relative amount of ^{241}Am in plutonium special nuclear material with about a 1% ($k = 2$) total uncertainty. This is achieved by incorporating Pu isotopics determined by thermal ionization mass-spectrometry into the analysis and by utilizing accurate conversion-electron and tailing functions. Due to the lack of a consensus americium in bulk plutonium standard, it is difficult to determine overall measurement bias. Therefore, a total measurement uncertainty is determined by a GUM (Guide to the Expression of Uncertainty in Measurement) bottom-up methodology. Sources of uncertainty include Poisson statistics, nuclear data, deconvolution, interferences and sample inhomogeneities.

NUCL 66

Making americium-241 great again

***Donivan R. Porterfield**, dporterfield@lanl.gov, Jung Rim, Michael D. Yoho. Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Given strong domestic commercial demand for americium-241, Los Alamos National Laboratory (LANL) at the request of the U.S. Department of Energy - Office of Science has re-constituted the capability for providing high-purity americium-241 oxide in gram quantities. Providing a domestic source of this nuclear material eliminates the need for domestic users to procure it from foreign sources.

The source of americium-241 available to LANL results from the decay of plutonium-241 (14.33 year half-life), a small abundance component in all grades of plutonium. By recovering this in-growing impurity and purifying it up to customer required specifications, we can divert this TRU waste component from current long term disposition at the Waste Isolation Pilot Plant (WIPP), reduce potential worker external dose from current on-site inventory, and satisfy a domestic commercial need for this nuclear material.

In implementing the methodologies necessary for insuring that the produced americium-241 oxide meets customer specifications we evaluated the application of a non-destructive analysis (NDA) methodology, i.e. gamma-ray spectrometry. Gamma-ray spectrometry can provide timely and cost-effective results to the LANL production capability but also be mindful of managing the external dose to our analytical personnel, i.e. applying the principle of As Low As Reasonably Achievable (ALARA).

Some specific radionuclide impurities in americium-241 we evaluated the application of gamma-ray spectrometry to were americium-243, neptunium-237, and plutonium-239. This presentation will address the factors that influenced our success or not in meeting the needed impurity specification for these radionuclides.

NUCL 67

Radiochemistry education through controlled remote instrumentation

***Donivan R. Porterfield**, dporterfield@lanl.gov. Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

There are a number of constraints on reasonable access to the instrumentation and radioactive sources that many would view as a necessary part of a quality educational program in radiochemistry / nuclear physics.

As we approach an era in which our vehicles will drive themselves, our packages will be delivered by drone, and robots will care for our households should we also give reasonable consideration to the value of conducting educational experiments via controlled remote instrumentation? It is important to distinguish between experiments conducted in an entirely virtual environment from those that are physically conducted using controlled instrumentation in a remote location. The former may be cheaply and

easily accomplished but would it be as satisfying or of appropriate value to the student? Over the last decade or more there have been a number of controlled remote instruments developed for educational purposes. However none of those have transitioned to N much greater than 1 that would allow realistically broad access to such an educational resource. This presentation will take a look at what it may take to allow for such a transition.

NUCL 68

Solubility, complexation and redox behaviour of Tc(IV): Effect of carbonate, sulfate and nitrate

Xavier Gaona[1]*, xavier.gaona@kit.edu, Alexander Baumann*[1]*, Sarah Duckworth*[1]*, Ezgi Yalcintas*[2,1]*, Robert Polly*[1]*, Marcus Altmaier*[1]*, Horst Geckeis*[1]*. (1) Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany (2) Los Alamos National Laboratory, Carlsbad, New Mexico, United States*

^{99}Tc is one of the main fission products of ^{235}U and ^{239}Pu in nuclear reactors. Due to its long half-life (2.1×10^5 a) and redox-sensitive character, ^{99}Tc is a very relevant radionuclide in the safety assessment of repositories for radioactive waste disposal. Tc(VII) is the prevailing oxidation state under oxidizing and redox-neutral conditions and exists as soluble and mobile TcO_4^-. Tc(IV) forms sparingly soluble hydrous oxides ($TcO_2.xH_2O$(am)) under reducing conditions as those expected in deep underground repositories. An appropriate knowledge of the stability fields of Tc redox states, solubility, hydrolysis and complexation behaviour of Tc(IV) in dilute to concentrated saline systems is required for a correct assessment of Tc source term in repositories for radioactive waste disposal. Studies developed within this framework can also provide relevant insights for understanding Tc chemistry in legacy sites such as Hanford nuclear tank wastes.

This contribution summarizes recent and on-going research activities at KIT–INE, Germany, on the solution chemistry of Tc: (i) solubility and complexation of Tc(IV) in dilute to concentrated $NaCl–NaHCO_3–Na_2CO_3–NaOH$ systems; (ii) solubility and complexation of Tc(IV) in dilute to concentrated $NaCl–Na_2SO_4–NaOH$ systems; (iii) solubility and redox behaviour of Tc(IV) in dilute to concentrated $NaCl–NaNO_3–NaOH$ systems. This systematic work contributes to an improved thermodynamic description of Tc(IV) in dilute aqueous solutions to concentrated brine systems, which can be implemented in geochemical models/calculations, thus providing further confidence in the safety analysis of repositories for the disposal of radioactive waste.

NUCL 69

Studies on actinide chemistry at elevated temperatures at KIT-INE within the German collaborative ThermAc project

***Marcus Altmaier**, marcus.altmaier@kit.edu, Francesco Endrizzi, Jun-Yeop Lee, David Fellhauer, Xavier Gaona. Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany*

This contribution highlights recent studies at KIT-INE on actinide chemistry at elevated temperatures performed within the German ThermAc project. ThermAc project is extending the chemical understanding and available thermodynamic database for actinides, long-lived fission products and relevant matrix elements in aquatic systems at elevated temperatures. To this end, a systematic use of estimation methods, new experimental investigations and quantum-chemistry based information is used. Work is developed with the aim of improving the scientific basis for assessing nuclear waste disposal scenarios at elevated temperature conditions.

The focus of KIT-INE within ThermAc is presently on long-lived actinides in oxidation states III, V and V. The temperature range from ~20°C up to ~90°C is studied, with a focus on systems at low or intermediate ionic strength. Chemical analogs for the actinide elements are used, especially in order to gain information on solid phase transformation processes. As examples from the studies of KIT-INE at elevated temperature conditions four examples will be shown, addressing (i) solubility and speciation of U(VI) in NaCl solution, (ii) effect of T on the Ca-U(VI)-CO_3 system, (iii) Np(V) solid phase transformation processes, and (iv) hydrolysis and solubility of trivalent actinides.

NUCL 70

Actinide solubility and speciation in the WIPP

***Donald T. Reed**[1], dreed@lanl.gov, Michael K. Richmann[2], Juliet Swanson[2], Ezgi Yalcintas[2]. (1) Cemrc, Carlsbad, New Mexico, United States (2) Los Alamos National Laboratory, Carlsbad, New Mexico, United States*

The Waste Isolation Pilot Plant (WIPP) transuranic repository remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. The EPA recertified the WIPP for the third time in July 2017 (designated CRA-2014). Full recovery from the February 2014 operational incidents will not be complete until a second shaft is installed to allow for additional panels in the WIPP underground (tentatively planned for ~ 2021) but the WIPP has re-opened and shipments to the WIPP resumed in January 2017. These operational issues did not affect the long-term safety case for the permanent disposal of transuranic (TRU) waste and the use of a salt repository concept for the permanent disposal of nuclear waste remains intact. The operational issues, however, did lead to a higher focus on the scientific basis of the overall safety case and, in particular, the underlying brine and actinide chemistry models. This understanding is needed to address the low-probability scenario that brine inundation and release could occur due to human intrusions and is driven by regulatory requirements for the repository license case.

For these reasons, research to strengthen and assess the degree of conservatism in the WIPP-relevant actinide/brine chemistry models continues. The overall ranking of

actinides, from the perspective of potential contribution to release from the WIPP, is: Pu ~ Am > U >> Th and Np and remains unchallenged from past recertification. Research emphasis in the past couple of years has focused on issues raised during the regulatory review process of the 2014 recertification application. The most important of these are: 1) oxidation state distribution of plutonium and the overall redox conditions expected; 2) role and importance of site-specific solubility studies in assessing the overall source term modeling in PA; and 3) effects of organic complexation on the An(III) and An(IV) oxidation states; and 4) further progress in understanding microbial effects. A status of ongoing research in these four areas will be provided.

NUCL 71

Fate of actinides in the presence of EDTA and dolomite at variable ionic strength

Hilary P. Palmer Emerson[1], *hemerson@fiu.edu, Frances Zengotita*[2], *Donald T. Reed*[3]. *(1) Applied Research Center, Florida International University, Doral, Florida, United States (2) Applied Research Center-FIU, Florida International University, Miami, Florida, United States (3) Los Alamos National Laboratory, Carlsbad, New Mexico, United States*

The development of nuclear weapons produced an overwhelming amount of radioactive waste that is currently being disposed of at the Waste Isolation Pilot Plant (WIPP). The WIPP is a deep geologic salt repository for long-term disposal of transuranic waste. The chemical behavior of actinide series elements (the most long-lived byproduct of the waste) and fission products is a major concern for the WIPP due to their long half-lives and unknown mobility in the halite environment. Moreover, experimental data describing the potential mobility of these contaminants under repository conditions is vital to create evidence-based risk assessment models.

The objective of this research is to better understand the potential for transport of actinide elements in the +3, +4, and +6 oxidation states under high ionic strength conditions relevant to the WIPP repository including the presence of ethylenediaminetetraacetic acid (EDTA). EDTA was previously identified as the ligand that potentially poses the greatest threat due to its strong complexation of metals. Batch experiments were conducted in 0.01 to 1.0 M ionic strength brines consisting of NaCl, $CaCl_2$, or $MgCl_2$ with 5 mg/L of EDTA in the presence and absence of dolomite [CaMg(CO3)2] from near the WIPP repository with Nd^{+3}, Th^{+4}, and UO_2^{2+} up to 1000 µg/L. Although Nd is a lanthanide and not an actinide, it has been shown previously to exhibit similar chemistry to the trivalent actinide elements.

Results show that the sorption affinity of EDTA-An complexes follows the trend Th > Nd > U with steady state reached by 30 days. Furthermore, filtration suggests that the EDTA may stabilize precipitated Th and Nd in the aqueous phase leading to potential for enhanced colloid-facilitated transport. Additional data is currently being analyzed in order to compare the effect of ionic strength and background electrolyte on the fate of these contaminants in the presence of EDTA.

NUCL 72

Role of methods from voluntary consensus standards development organizations

***Donivan R. Porterfield**, dporterfield@lanl.gov. Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

ASTM International is one of a number of standards development organizations (SDOs) that develops voluntary consensus standards (VCS) in the area of environmental radiochemistry.Other SDOs providing similar standards includes Standard Methods (www.standardmethods.org)
and the International Organization for Standardization (ISO). The standards published by these organizations provide detailed and validated methodologies for the analysis of radioactive constituents in a range of environmental media. Such standards can be of value to both the
experienced and new practitioner. Some of these standards are referenced by governmental agencies as part of a regulatory structure (e.g. U.S. EPA Safe Drinking Water Act) to help assure the generation of quality data.

Organized in 1898, ASTM International is one of the world's largest international standards developing organizations and ASTM standards improve the lives of millions every day. ASTM is driven by the expertise and commitment of its 30,000 members, who hail from more than 140 countries. The efforts of those ASTM members organized in 150 technical committees provides over 12,000 ASTM standards that can be found in the 80+-volume Annual Book of ASTM Standards or on the ASTM website. The ASTM standards development process is available and open to all interested parties at any time and membership in ASTM is quite economical. The U.S. National Technology Transfer and Advancement Act (NTTAA) directs U.S. Federal agencies to adopt voluntary consensus standards wherever possible (avoiding development of unique government standards) and establishes reporting requirements for federal agencies.

NUCL 73

Nuclear and Radiochemistry at the University of Alabama at Birmingham

***Suzanne E. Lapi**, suzannelapi@live.com. Radiology, University of Alabama at Birmingham, Birmingham, Alabama, United States*

The University of Alabama at Birmingham has a newly established vibrant nuclear and radiochemistry group which involves students and faculty from the Departments of Radiology, Chemistry and Biomedical Engineering. Students have access to state of the art infrastructure including a TR-24 variable energy cyclotron with 4 beamlines, small animal PET scanners and other nuclear and radio-analytical equipment including HPGe, radio-HPLC, radio-TLC and associated space for nuclear and radiochemistry experiments. Students have the opportunity to be involved with projects ranging from new isotope production techniques through to preclinical and clinical imaging studies. A recently established course “Radiochemistry for the Life Sciences” is also available through the Chemistry department for senior undergraduate and new graduate students.

NUCL 74

Environmental radiochemistry at the University of Central Florida: Biogeochemical transformations of radionuclides in the environment

***Vasileios Anagnostopoulos**, vasileios.anagnostopoulos@ucf.edu. Chemistry, University of Central Florida, Orlando, Florida, United States*

The Environmental Radiochemistry research component at the Department of Chemistry at the University of Central Florida aims to provide students and researchers with the opportunity to study the biogeochemical transformations of radionuclides in the environment. Researchers will learn basic radiochemistry principles in combination with fundamental radioanalytical techniques and their applications to environmental samples. Experimental work will focus on the binding properties and the redox chemistry of radionuclides (Tc-99, I-125, actinides) with different environmental matrices, such as Natural Organic Matter (NOM), clays and iron minerals and will elucidate the mechanism by thermodynamic and speciation studies. Furthermore, researchers will have the opportunity to receive training in speciation modelling, as well as surface characterization techniques. The departmental and the core facilities capabilities (e.g. analytical techniques and surface characterization techniques) will be discussed briefly, as well as the infrastructure to handle radio-iodine samples and research opportunities for students will be presented.

NUCL 75

Training students within the Actinide Center of Excellence

***Amy E. Hixon**[1], ahixon@nd.edu, Jennifer E. Szymanowski[1], Ginger Sigmon[2], Peter C. Burns[3]. (1) Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana, United States (2) University of Notre Dame, South Bend, Indiana, United States (3) Univ of Notre Dame, Notre Dame, Indiana, United States*

The actinide science program at the University of Notre Dame is an informal program housed within the Department of Civil & Environmental Engineering & Earth Sciences. Although our main focus is on graduate education in actinide chemistry and mineralogy, high school students, undergraduate students, and postdoctoral scholars are also an important part of our program. This presentation will discuss the procedures that we follow which allow minors to work in the lab in addition to highlighting our recently expanded transuranic capabilities and the associated additional procedures we have put in place to ensure that graduate students, postdoctoral scholars, faculty, and staff can work safely while manipulating milligram to gram quantities of neptunium and plutonium.

NUCL 76

Radiochemistry education opportunities at Lawrence Livermore National Laboratory

***Mavrik Zavarin**, zavarin1@llnl.gov. Lawrence Livermore National Laboratory, Oakland, California, United States*

Established in 1991, the LLNL branch of the Glenn T. Seaborg Institute conducts collaborative research between LLNL and the academic community in radiochemistry and nuclear forensics. The Seaborg Institute serves as a national center for the education and training of undergraduate and graduate students, postdocs and faculty in transactinium science. In this presentation, we will summarize the various radiochemistry education programs, research areas, and state-of-the-art facilities that make LLNL a thriving institution of radiochemistry research and education. Our education programs include an 8-week Nuclear Forensics Summer Internship Program in which graduate and undergraduate students work directly with researchers on projects ranging from nuclear physics to environmental radiochemistry. Throughout the year, the Seaborg Institute invites graduate students and faculty to conduct research with staff scientists through a variety of sponsored programs. This includes DOE and NNSA-sponsored university consortia. For example, the Seaborg Institute is a partner in the DOE Traineeship in Nuclear and Radiochemistry led by Washington State University and the Colorado School of Mines. Additional competitive fellowship and internship opportunities are available for students and postdocs throughout the LLNL campus. This includes the National Nuclear Security Administration Graduate Fellowship Program, the Office of Science Graduate Student Research program, and many others. These programs are intended to prepare graduate students for science, technology, engineering, or mathematics careers critically important to the DOE mission by providing graduate thesis research opportunities at DOE laboratories.

NUCL 77

Making radiochemistry meaningful to high school students through engagement at a national laboratory

***Aleida Perez**[1], pereza@bnl.gov, Bernadette Uzzi[1], Cathy S. Cutler[2]. (1) Office of Educational Programs, Brookhaven National Laboratory, Upton, New York, United States (2) Collider Accelerator, Brookhaven National Laboratory, Columbia, Missouri, United States*

The U.S. Department of Energy’s Brookhaven National Laboratory (BNL) has a long and rich history in the development and production of radioisotopes for medical applications. One of these, technetium-99m (Tc-99m), is today’s most commonly used isotope for medical imaging. In order to share Brookhaven’s story in a way that was meaningful, the Office of Educational Programs together with members of Brookhaven’s Medical Isotope Research and Production Program, designed a program to do just that.

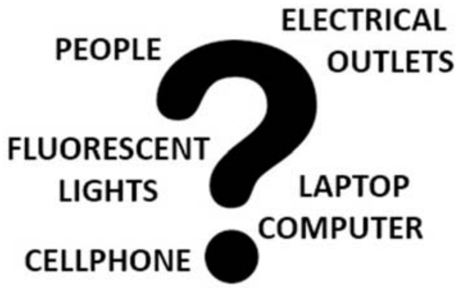
During the summer of 2017, high school students from the New York State Science and Technology Entry Program (STEP) were invited to spend four days at the Laboratory to engage in a series of hands-on activities mediated by scientists and educators. In addition, students met experts in the field and visited the Brookhaven Linear Isotope Producer (BLIP) facility. Through the activities, participants modeled the generation of radioisotopes and detection of charged particles. A series of lectures gave participants an overview of the field and introductions to the production process and to medical applications. During the visit to BLIP, students were exposed to the process of radioisotope manufacturing and general principles of particle accelerators. Additionally, students were introduced to NaI detectors and their function. These experiences create public awareness of nuclear science and radiochemistry. In addition, these hands-on activities and engagement with scientists expose students, particularly women, underrepresented and underserved students, to careers in this important field.

NUCL 78

What is radioactive in this room?

***Catherine H. Middlecamp**, chmiddle@wisc.edu. Nelson Inst for Environmental Studies, Univ of Wisconsin-Madison, Madison, Wisconsin, United States*

In some general chemistry courses, topics in nuclear chemistry occupy several lectures in the curriuclum. As one who taught such general chemistry courses for years, who observed how students readily engage in learning about radioactive substances, and who served as the lead author on the nuclear chapter in the ACS undergraduate textbook, "Chemistry in Context," the thought occurred to me that a few lectures could not do justice to the topic. Rather, teaching a entire semester centered on nuclear-related topics would be worth both my time and that of my students. With this thought in mind, my course "Radioactivity, People, and The Planet" was born. But where to start a conversation that could last an entire semester. By asking a single question: What is radioactive in this room? This presentation reports the ways that students (also the general public) tend to answer this question, offering a revealing look at which items people suspect to be radioactive and what they know about radioactive elements. The question can be adapted for use with almost any audience, engages science and non-science majors alike, and can generate questions that last an entire semester, if not a lifetime.



NUCL 79

Development of a nuclear forensics chemistry coursework

***John D. Auxier**, jdauxier2@yahoo.com, Matthew T. Cook. Department of Nuclear Engineering , Institute for Nuclear Security , Jefferson City, Tennessee, United States*

In recent years, there has been a significant increase in undergraduate nuclear forensics education and training opportunities that provide an overview of nuclear and radiochemical education efforts. However, there are unique challenges to nuclear forensics that rely heavily on established chemical techniques that can't be practiced due to the safety restrictions, lack of technical expertise in the existing personnel, or other factors. Furthermore, if the experiments can be done, many academic institutions do not have the correct measurement equipment (e.g. advanced mass spectrometry) that allows for students to learn to perform data interpretation. This gap in knowledge is crucial to fill as many graduate students have been focused on advanced the science of forensics analysis without an appreciable sense of the technology that they are trying to replace. The focus of this talk will be to highlight some of these challenges and hopefully open the discussion how to develop a curriculum that can be deployed to undergraduate and graduate programs help to fill this increasing gap in this crucial field.

NUCL 80

Role of electronic excitation and the effect of structural and composition changes in ion-irradiated $La_2Ti_{2-x}Zr_xO_7$ pyrochlores

***Michel Sassi**[1], michel.sassi@pnnl.gov, Steven Spurgeon[2], Tiffany Kaspar[1], Vaithiyalingam Shutthanandan[3]. (1) Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States (2) Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States (3) Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, United States*

Pyrochlores with the general formula $A_2B_2O_7$ are complex ceramics that exhibit a range of physical, chemical and electric properties, which make them useful for a wide range of applications. For example, chemically stable pyrochlores can be considered as host materials for the immobilization of actinides. Much scientific effort has been devoted to investigate the response of pyrochlores to irradiation and to understand the mechanisms driving defect creation and phase transformation. In that context, it has been observed that some pyrochlores undergo structural phase transition from ordered to amorphous structure due to internal irradiation, as caused by the decay of incorporated actinides, or external ion-irradiation. While several mechanisms, mainly based on atomic collision processes, have been proposed to explain the origins of irradiation-induced amorphization, here we present the results of *ab initio* molecular dynamic simulations investigating the role of electronic excitations in the formation of amorphous phase of $La_2Ti_2O_7$ and $La_2Zr_2O_7$pyrochlores. Particularly, the effect of *B*-site

cation substitutions on the irradiation behavior, about which little is known, has been investigated by considering $La_2Ti_{2-x}Zr_xO_7$ compounds. The results highlight how changes in structure and composition affects electronic excitation induced amorphization in lanthanide-based pyrochlores.

NUCL 81

Importance of the unprecedented δ back-donation in An^{IV} metallacycles

Ivan A. Popov, *vanekpopov@gmail.com, Morgan P. Kelley, Enrique R. Batista, Ping Yang. Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States*

Whereas the strength of metal-ligand (M–L) bonding interactions is primarily dependent on the strength of the M–L σ-bonding, π contributions are of no less importance. In general, both σ and π interactions are necessary to correctly describe the electronic and geometric structures of most molecular systems. In actinide organometallic compounds, δ bonds can play as much a role as π bonds, however, the participation of the 5f and 6d orbitals in the formation of δ bonds has not yet been fully addressed in the literature. In my talk, I will describe the chemistry of actinide metallacycles with various ring sizes that leads to unusually complicated chemical bonding motifs. By means of electron localization techniques, I will show the importance of δ bonding interactions in An^{IV} metallacycles and will demonstrate a unique type of δ-bonding, which is crucial for the understanding the M–L bonding in the actinide series from Th to Pu. These fundamental findings underline the significance of δ back-donation in actinide complexes in general, with a particular emphasis on the 5f unpaired electrons of Pa and U complexes.

NUCL 82

Relativistic *ab initio* accurate minimal basis sets for the heavy elements

George Schoendorff, *gschoend@gmail.com. Department of Chemistry and Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, Texas, United States*

Relativist *ab initio* accurate minimal basis sets (AAMBS) are computed for the elements Cs – Rn and stored internally in GAMESS. Valence virtual orbitals (VVOs) are formed based on a singular value decomposition (SVD) with respect to the AAMBS for the atoms, providing a basis set independent method for extracting chemically meaningful lowest unoccupied molecular orbitals (LUMOs). Oriented quasi-atomic orbitals are formed for the occupied orbitals together with the VVOs. The OQUAOs are used to provide a description of the bonding characteristics heavy metal complexes.

NUCL 83

Utilizing computational protocols for binding selectivity of lanthanide and actinide compounds

Charles C. Peterson[1], *charliecpeterson@gmail.com, Deborah A. Penchoff*[2], *Howard L. Hall*[3], *Robert J. Harrison*[4]. *(1) Research Information Technology, Univeristy of North Texas, Denton, Texas, United States (2) Institute for Nuclear Security, University of Tennessee , Knoxville, Tennessee, United States (3) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (4) Institute for Advanced Computational Science, Stony Brook , New York, United States*

Better understanding of binding selectivity of the heavy elements is crucial to design selective separation agents. Theoretical predictions from obtained data ranging from the structural, thermochemical, and orbital population analysis are used to understand the behavior of the lanthanide- and actinide-containing systems. Various current computational methodologies including ab initio and DFT are utilized to study the dependence of properties of interest (including thermochemical and structural characteristics). Other effects, such as relativistic considerations including scalar relativity and spin-orbit coupling, high electronic correlation, and core correlation, will be presented to evaluate the dependence of the predicted selectivity on the method of choice.

NUCL 84

Evaluating the performance of electronic structure methods on predictions of Raman and IR spectroscopy of UF_6 and MoF_6

Justin R. Powers-Luhn[1], *jpowersl@vols.utk.edu, Charles C. Peterson*[3], *Jeff Lux*[2], *John D. Auxier*[2,4], *Deborah Penchoff*[5,6], *Howard L. Hall*[1,5]. *(1) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee, United States (2) Department of Nuclear Engineering , Institute for Nuclear Security , Knoxville, Tennessee, United States (3) Research Information Technology, University of North Texas, Denton, TX, Texas, United States (4) Radiochemistry Center of Excellence, University of Tennessee, Knoxville, Tennessee, United States (5) Institute for Nuclear Security, University of Tennessee, Knoxville, Tennessee, United States (6) Joint Institute for Computational Sciences, ORNL/UTK, Knoxville, Tennessee, United States*

Predictive capabilities for detection of hexafluorides are essential for applications in power production, national security, and cancer treatment. Spectroscopic analysis, including Raman and IR can provide critical information for identification of these compounds as well as impurities which could affect efficiency in medical or industrial processes. An exploratory benchmark study was performed on MoF_6 and UF_6 seeking to evaluate the level of theory dependence in the prediction of spectroscopic characteristics. A statistical analysis was performed on a data set of spectroscopic characteristics generated with DFT and *ab initio* methods including various functionals,

basis sets, and relativistic considerations (including scalar and spin-orbit effects). Highlights of the performance of the methods, as well as interpretation from statistical analysis will be presented.

NUCL 85

Towards stability constant prediction in uranium siderophore complexes

Jason L. Sonnenberg[1], *sonnenberg.11@osu.edu, Matthew E. Kirby*[2], *Alexandra Simperler*[3], *Samuel Krevor*[2], *Dominik J. Weiss*[2]. *(1) Gaussian Inc., Wallingford, Connecticut, United States (2) Earth Science and Engineering, Imperial College London, London, United Kingdom (3) Chemistry, Imperial College London, London, United Kingdom*

Siderophores are organic molecules secreted by plants, bacteria or fungi to gather key metal nutrients such as iron. To fully understand the effects of siderophores on uranium speciation, one must know the chemical details of siderophore-uranium complexation reactions. The uranium-siderophore log K values can be used in geochemical modeling to create speciation diagrams along with surface-complexation and reactive-transport models. Unfortunately, experimental log K values for uranium-siderophore complexes are still quite rare in the literature. Density functional theory (DFT) combined with solvation models can provide a cost effective way to predict the stability of uranium complexes. A general stability series based on DFT results is presented for uranium(VI) complexes with environmentally relevant organic ligands and siderophores.

NUCL 86

Dynamic solvation behavior of organic ligands within the ALSEP process

An T. Ta, *anta@mymail.mines.edu, Govind A. Hegde, Shubham Vyas. Colorado School of Mines, Golden, Colorado, United States*

Due to their role as some of the primary contributors to the strain experienced by our waste repositories, transuranic actinides such as americium and curium have been of major concern within the management of spent nuclear fuel. One extraction method capable of selectively recovering these actinides is known as Actinide Lanthanide Separation (ALSEP), however, its slow kinetics prevents ALSEP from being implemented at an industrial scale. Therefore, application of this process within nuclear plants requires an improved extraction mechanism, of which most studies attempted to uncover by focusing on the thermodynamics of separation. Within this talk, attempts to understand the *kinetics* of ALSEP through theoretical investigation of the organic ligands 2-ethylhexylphosphonic acid mono-2ethylhexyl ester (HEHEHP) and N,N,N’,N’-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) will be discussed. Specifically, the solvation dynamics of HEHEHP and T2EHDGA were investigated through a series of Molecular Dynamic (MD) simulations in which different parameters (e.g. concentration) were varied. By utilizing MD, behaviors of the organic ligands involved within ALSEP

were able to be analyzed at the molecular level which will aid in the ultimate goal of identifying kinetic barriers involved with the particular extraction process.