American Chemical Society

Division of Nuclear Chemistry and Technology
247th ACS National Meeting, Dallas, TX, March 16-20, 2014

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

SUNDAY MORNING

Glenn T. Seaborg Award for Nuclear Chemistry: Symposium in Honor of Walter D. Loveland

D. Morrissey, Organizer; D. Thomas, Organizer; D. Morrissey, Presiding Papers 1-5

SUNDAY AFTERNOON

Radiation Hardened Materials for Accelerators, Reactors and Spacecraft

R. Devanathan, Organizer; I. Szlufarska, Presiding; R. Devanathan, Presiding Papers 6-11

Glenn T. Seaborg Award for Nuclear Chemistry: Symposium in Honor of Walter D. Loveland

D. Thomas, Organizer; D. Morrissey, Organizer; J. Natowitz, Presiding Papers 12-16

MONDAY MORNING

Glenn T. Seaborg Award for Nuclear Chemistry: Symposium in Honor of Walter D. Loveland

D. Thomas, Organizer; D. Morrissey, Organizer; C. Folden, Presiding Papers 22-26

Radiation Hardened Materials for Accelerators, Reactors and Spacecraft

R. Devanathan, Organizer; K. Nordlund, Presiding Papers 17-21

MONDAY AFTERNOON

Symposium in Honor of Norman Edelstein: A Distinguished and Diverse Scientific Career in Actinide Chemistry

A. Sattelberger, Organizer; D. Clark, Organizer; D. Shuh, Organizer; L. Soderholm, Organizer; D. Clark, Presiding Papers 32-40

Radiation Hardened Materials for Accelerators, Reactors and Spacecraft

R. Devanathan, Organizer; J. Greer, Presiding Papers 27-31

TUESDAY MORNING

Global Status of Nuclear Energy
J. Terry, Organizer; K. Nash, Organizer; J. Terry, Presiding; K. Nash, Presiding Papers 41-48

Symposium in Honor of Norman Edelstein: A Distinguished and Diverse Scientific Career in Actinide Chemistry
A. Sattelberger, Organizer; D. Clark, Organizer; D. Shuh, Organizer; L. Soderholm, Organizer; J. Gibson, Presiding Papers 49-59

TUESDAY AFTERNOON

Global Status of Nuclear Energy
K. Nash, Organizer; J. Terry, Organizer; J. Terry, Presiding; K. Nash, Presiding Papers 60-67

Symposium in Honor of Norman Edelstein: A Distinguished and Diverse Scientific Career in Actinide Chemistry
A. Sattelberger, Organizer; D. Clark, Organizer; D. Shuh, Organizer; L. Soderholm, Organizer; L. Soderholm, Presiding Papers 68-78

WEDNESDAY MORNING

Symposium in Honor of Norman Edelstein: A Distinguished and Diverse Scientific Career in Actinide Chemistry
A. Sattelberger, Organizer; D. Clark, Organizer; D. Shuh, Organizer; L. Soderholm, Organizer; A. Sattelberger, Presiding Papers 85-94

Nuclear Batteries and Radioisotope Micropower Sources
D. E. Meier, Organizer; J. Robertson, Presiding Papers 79-84

WEDNESDAY AFTERNOON

Nuclear Batteries and Radioisotope Micropower Sources
D. E. Meier, Organizer; J. Schwantes, Presiding Papers 95-99

Symposium in Honor of Norman Edelstein: A Distinguished and Diverse Scientific Career in Actinide Chemistry
A. Sattelberger, Organizer; D. Clark, Organizer; D. Shuh, Organizer; L. Soderholm, Organizer; D. Shuh, Presiding Papers 100-107

NUCL 1

Synthesis of Z = 113, 115, 117 super heavy elements

Joseph H. Hamilton[1], *j.h.hamilton@vanderbilt.edu, Yuri T. Oganessian*[2]. *(1) Department of Physics, Vanderbilt University, Nashville, TN 37235, United States (2) Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Dubna, Russia RU-141980, Russian Federation*

Recent studies of the ^{249}Bk + ^{48}Ca and ^{243}Am + ^{48}Ca reactions have yielded definitive evidence for the discoveries of the new elements with Z = 113, 115 and 117. The reactions were studied with the U400 cyclotron and gas filled separator at the Flerov Laboratory of Nuclear Reactions in Dubna. The targets were made in the Oak Ridge National Laboratory High Flux Isotope Reactor, chemically separated and shipped to Russia. The 2010 results and the 2012 results for the synthesis of ^{293,294}117 will be presented. The confirmation of ^{294}117 at GSI will be noted. In the ^{243}Am reaction, 28 measurements of ^{288}115 that alpha decays to ^{284}113 were observed to definitively confirm the three earlier events in Dubna. Also very important were the four new ^{289}115 events found in these studies at lower energies. This is the same isotope into which ^{293}117 alpha decays. Thus, the agreement of the ^{249}Bk ^{293}117 events and ^{243}Am ^{289}115 events on the decay chain of ^{289}115 give definitive cross-bombardment evidence for the discoveries of the new elements with Z = 113, 115 and 117. The ^{294}117 and ^{288}115 have been seen recently in separate experiments at GSI. Prospects for future research will be presented. Of particular importance is the new Super Heavy Element Factory under construction in Dubna which will produce the order of 5000 SHE per year in the new dedicated SHE research facility. The new opportunities this opens up will be discussed.

This work is presented for JINR, ORNL, LLNL, VU Collaboration

NUCL 2

Recent super heavy element experiments

Mark A Stoyer, *mastoyer@llnl.gov.Physics, LLNL, Livermore, CA 94550, United States*

The Dubna/LLNL collaboration has been investigating the nuclear and chemical properties of the heaviest elements since 1989, with ORNL and Vanderbilt University joining in 2008. Elements 113-118 have been synthesized and characterized using fusion-evaporation nuclear reactions of ^{48}Ca beams on actinide targets (^{237}Np, ^{242,244}Pu, ^{243}Am, ^{245,248}Cm, ^{249}Bk, and ^{249}Cf, respectively) at the U400 cyclotron located at the Flerov Laboratory of Nuclear Reactions in Dubna, Russia [1]. This talk will discuss the ramifications of the experimental work during the last 10-15 years on the synthesis of elements 113 – 118, including the recent IUPAC acceptance of element names for 114 (flerovium) and 116 (livermorium), concentrating on the even-Z elements. Prediction of the heaviest element possible is highly uncertain because of the complex interplay of strong nuclear forces, Coulomb forces, surface/volume effects and shell corrections. For

some combination of protons (Z > 118) and neutrons, the strong nuclear force which binds nucleons together will not be able to counter the Coulomb repulsion of the protons in a nucleus, and thus nuclei will cease to exist. Experimental and theoretical efforts to locate and access the next region of doubly-magic spherically-shaped nuclei, the Island of Stability, will be presented.

[1] Yu. Ts. Oganessian, et al., Phys. Rev. Lett. **109** (2012) 162501; Yu. Ts. Oganessian, et al., Phys. Rev. C **87** (2013) 014302; Yu. Ts. Oganessian, J. Phys. G: Nucl. Part. Phys. **34** (2007) R165; and references therein.

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

NUCL 3

Superheavy element research at GSI

***Christoph E Duellmann**, duellman@uni-mainz.de.Institute of Nuclear Chemistry, University of Mainz, Mainz, GermanySHE Chemistry Department, GSI Helmholtzzentrum fuer Schwerionenforschung, Darmstadt, GermanySHE Chemistry Section, Helmholtz Institute Mainz, Mainz, Germany*

At the GSI Darmstadt, a unique combination of experimental facilities is installed that allows addressing key questions in SHE research.

Currently studied topics include:

- synthesis of the heaviest elements
- nuclear reactions
- nuclear structure, with a focus on isomerism in Z~100-110 nuclei
- direct mass measurements beyond fermium
- direct atomic number identification of nuclides from ^{48}Ca on actinide reactions
- chemical properties of the transactinide elements

I will start with a brief introduction to the current status of SHE research and then give an overview on the GSI program and present recent highlights.

The main part of my talk will be devoted to recent experiments performed at the gas-filled separator TASCA, including experiments dedicated to search for new elements beyond the heaviest claimed element with Z=118.

NUCL 4

Heavy element experiments at Berkeley

***Kenneth E Gregorich**, kegregorich@lbl.gov.Nuclear Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

Heavy Element Studies at Berkeley

Walter Loveland has been a collaborator with the Heavy Element Nuclear and Radiochemistry Group at Lawrence Berkeley National Laboratory since (at least) the BEVALAC days (early 1980s). We began working more closely during the first experiments with the Berkeley Gas-filled Separator (BGS), and Walt has been an indispensable contributor to the BGS research program ever since. Walt is the person who asks the simple questions that turn out to be not-so-simple, and searching for the not-so-simple answer usually leads to a new understanding. In this talk, heavy element research from the early days with the BGS until the present time will be reviewed.

NUCL 5

Award Address (Glenn T. Seaborg Award for Nuclear Chemistry sponsored by the ACS Division of Nuclear Chemistry and Technology). Large-scale nuclear collective motion: A retrospective

***Walter Loveland**, lovelanw@onid.orst.edu.Department of Chemistry, Oregon State University, Corvallis, OR 97331, United States*

My scientific career has been spent studying large-scale nuclear collective motion, through observations of heavy ion fusion, other ways of preparing hot heavy nuclei (relativistic and intermediate collisions) and studies of the fission process. I will review what I have learned about the fusion of halo nuclei and neutron-rich radioactive nuclei. I will also discuss my incomplete understanding of fusion hindrance (P_{CN} and inverse fission). The systematics of heavy residue formation in relativistic and intermediate energy collisions will be discussed. Fission studies motivated me in graduate school (ternary fission), the postdoctoral years (transition state spectroscopy) and early faculty years (fragment angular momentum). Recently we have tried to characterize the survival probability of hot heavy nuclei. As a chemist working at a reactor lab, I've used activation analysis to study meteorites, particulate air pollution and stable activable tracers

NUCL 6

Effects of radiation on the hardness of nanowires and nanotubes

***Kai Nordlund**, kai.nordlund@helsinki.fi, Andrey Ilinov, Wei Ren, Antti Kuronen, Arkady V Krasheninnikov, Flyura Djurabekova.Department of Physics, University of Helsinki, Helsinki, Finland*

Although it is well known that radiation can be used to harden many kinds of bulk and thin film materials, the effects of radiation on nanomaterials are much less well understood. Using molecular dynamics computer simulations, we have examined the effects of ion and electron irradiation on the mechanical properties of nanowires and nanotubes. Generally we find that for single wires and tubes, radiation softens both kinds of materials [1,2,3], but the behaviour is sometimes surprising. For instance, we have found that under tensile mechanical strain, the threshold displacement energy may, counterintuitively, increase [1]. On the other hand, in carbon nanotube bundles, multiwalled carbon nanotubes and macroscopic nanotube paper the strength of the material can strongly increase due to irradiation [4,5,6]. In this talk we will discuss the physico-chemical reasons to these effects and experimental results confirming the theoretical predictions.

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[6] J. A. Åström, A. V. Krasheninnikov, and K. Nordlund, Phys. Rev. Lett. 93, 215503 (2004)

NUCL 7

Radiation-induced super-quenching and plasticity in metallic glasses

***Michael J Demkowicz**, demkowicz@mit.edu.Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Metallic glasses respond to radiation in qualitatively different ways than crystalline solids. I will describe two distinctive mechanisms of radiation response in metallic glasses, identified through a series of ½ billion-atom simulations using molecular dynamics. In the first, inter-nuclear scattering causes localized melting and quenching at rates approaching 10^{14} K/s, giving rise to nanoscale “super-quenched zones” (SQZs) with exceptionally high free volume. In the second, rapid volumetric expansion in regions of localized melting generates intense stress pulses that cause polarized plastic deformation in adjacent material. These insights lead to the construction of a parameter for predicting the radiation response of amorphous materials that may be used in the

selection of metallic glasses for applications ranging from nuclear waste storage to ion beam materials modification.

NUCL 8

Effects of helium implantation on tensile properties and microstructure of amorphous nickel phosphorous metallic glasses

Julia R Greer[1]*, jrgreer@caltech.edu, Rachel Liontas*[1]*, Wendy Gu*[1]*, Yongqiang Wang*[2]*, Nan Li*[2]*, Engang Fu*[2]*, Nathan Mara*[2]*. (1) Division of Engineering and Applied Sciences, California Institute of Technology, Pasadena, CA 91125, United States (2) Los Alamos National Laboratory, Los Alamos, NM, United States*

Nuclear reactions generate insoluble helium, which forms nano-sized bubbles that can lead to swelling and embrittlement of irradiated materials. Innovative structural materials must be created and utilized to enable new-generation nuclear reactors to withstand harsh thermomechanical environments and to suppress helium-induced embrittlement. One family of candidate structural materials is metallic glasses, which offer high elastic limit and strength, corrosion resistance, and potential for improved ductility upon irradiation. A significant detriment in their use for structural applications is catastrophic failure under tensile loads

We use templated electron-beam lithography and electro-deposition to fabricate 100 nm-diameter amorphous Ni-P metallic glass cylindrical nano-tensile specimens. Earlier studies in our group demonstrated the emergence of brittle-to-ductile transition in nano-sized metallic glasses upon tension, with useful ductility in excess of 20% in some cases. In this work we explore the effects of Helium implantation into already-ductile nano-sized metallic glasses. Helium was implanted uniformly into each sample at a concentration of 3 at% at 25°C and at 280°C to result in the bubble sizes between 2-3nm and ~10nm. In-situ uniaxial tension experiments revealed that He-ion implantation increased available plastic strain in the nano-metallic glass tensile specimens by a factor of 2 and maintained the high strength of ~2.1 GPa. We discuss these promising results in the framework of microstructural and defect response to ion irradiation in metallic glasses.

NUCL 9

Plastic localization in irradiated fusion steels: New insights from modeling and simulation

Jaime Marian*, marian1@llnl.gov.Lawrence Livermore National Laboratory, United States*

Low temperature irradiation of crystalline materials is known to result in hardening and loss of ductility, which limits the usefulness of candidate materials in harsh nuclear environments. In bcc metals, this mechanical property degradation is caused by the

interaction of in-grown dislocations with irradiation defects, particularly small dislocation loops resulting from the microstructural evolution of displacement cascades. In this work, we present a multi scale model encompassing molecular dynamics (MD), dislocation dynamics (DD), crystal plasticity, and finite element (FE) simulations of bcc Fe containing various concentrations of dislocation loops produced by irradiation at room temperature. The study is motivated and inspired by experimental observation of plastic flow localization and softening in a variety of structure materials for nuclear applications, and the very formulation of the models is guided by observed phenomena. At the macroscopic scale, the simulations reveal a transition from homogenous to highly localized deformation at a critical loop density. Above it, plastic flow proceeds heterogeneously, creating defect-depleted channels as a principal signature of softening. These simulations are then used to calibrate a tensorial crystal plasticity model capable of reaching strains in excess of 10% for linkage with the engineering scale. The calibrated crystal plasticity model is used as the constitutive relation in FE simulations of polycrystalline irradiated Fe systems, and the results compared to experiments.

NUCL 10

Stress and irradiation effects on solute diffusion to dislocations

Dallas R. Trinkle[1], *dtrinkle@illinois.edu, Zebo Li*[1], *Thomas Garnier*[1,2], *Venkateswara R. Manga*[1,3], *Maylise Nastar*[2], *Robert C. Averback*[1], *Pascal Bellon*[1]. *(1) Dept. Materials Science and Engineering, Univ. Illinois, Urbana-Champaign, Urbana, IL 61801, United States (2) Service de Recherches de Métallurgie Physique, CEA Saclay, Gif-sur-Yvette, France (3) Dept. Materials Science and Engineering, University of Arizona, Tuscon, AZ, United States*

Study of creep under irradiation requires a quantitative description of diffusion of point defects such as vacancies, interstitials, and solutes to traps like dislocations. Prediction of dislocation creep rates involves consideration of diffusion under non-uniform, non-hydrostatic stress, the increased point defect density from irradiation, and the interaction of defects. We present calculations of the diffusion of Si in Ni, which has both vacancy- and mixed-dumbbell mediated diffusion under stress at dilute concentrations. First-principles calculations and self-consistent mean field method (SCMF) calculate the fluxes of various species under stress. Stress reduces the symmetry for hops in FCC Ni, and SCMF provides a direct calculation of phenomenological coefficients--including off-diagonal terms--for the lower-symmetry geometry. In particular, stress changes solute drag in particular directions, which affects the diffusion to sinks under irradiation and the resulting microstructure near dislocations. The final results are combined with the dislocation strain field to model these effects.

NUCL 11

Advanced steels as accident tolerant fuel cladding in commercial light water reactors

***Raul B. Rebak**, rebak@ge.com.Corrosion and Electrochemistry, GE Global Research, Schenectady, NY 12309, United States*

After the March 2011 events in north east Japan, the U.S. congress directed the Department of Energy (DOE) to focus efforts on the development of fuels with enhanced accident tolerance. In comparison with the standard UO2–Zircaloy system, the proposed system should better tolerate loss of active cooling in the core for a considerably longer time period while maintaining or improving the fuel performance during normal operations. A GE Global Research led program is investigating the behavior of advanced steels both under normal operation conditions in high temperature water (e.g. 288°C) and under accident conditions for reaction with steam up to 1475°C. In the case of an accident, these advanced steels offer a lower kinetics of reaction with steam, they generate less hydrogen gas when reacting with steam, they have higher mechanical properties at higher temperature and they offer longer retention of fission products when compared with zirconium alloys. Under normal operation conditions, the ferritic steels are highly resistant to stress corrosion cracking in high temperature water and less susceptible to irradiation damage such as void swelling.

NUCL 12

Exploring the coupling to neutron transfer in fusion involving neutron-rich nuclei

***Felix Liang**, liangjf@ornl.gov.Joint Institute for Heavy Ion Research, Oak Ridge National Lab, Oak Ridge, TN 37831, United States*

Fusion induced by neutron-rich radioactive beams may be used for producing isotopes of superheavy elements. Fusion of neutron-rich nuclei in the crust of a neutron star may influence its composition and energy distribution. These reactions take place at energies near and below the Coulomb barrier. Heavy-ion fusion rates have been found to be enhanced at sub-barrier energies. This enhancement is attributed to the coupling of the inelastic excitations of the reactants and nuclear reactions. Neutron transfer has been shown to be a doorway to fusion. In reactions induced by neutron-rich radioactive nuclei, there can be a large number of neutron transfer channels with positive Q-values. These reactions are good candidates for studying the effects of transfer on sub-barrier fusion enhancement. In this talk, fusion excitation functions for reactions involving stable and neutron-rich radioactive nuclei are compared. The influence of neutron transfer on sub-barrier fusion enhancement will be discussed.

This research was supported by the Office of Nuclear Physics, US Department of Energy.

NUCL 13

Super-heavy element synthesis and the role of quasifission

***Birger B Back**, Back@anl.gov.Physics Division, Argonne National Lab, Argonne, IL 60439, United States*

Three decades ago, it was first recognized that the dynamics of heavy-ion reactions diverts a large fraction of the reaction cross section into the quasi-fission channel rather than the formation of a compound system that, via subsequent neutron evaporation, would lead to the synthesis of super-heavy elements. The result is that the cross section for formation of the heaviest elements is strongly suppressed relative to expectations based on simple fusion-evaporation models. In spite of these obstacles, however, the progress of synthesizing ever heavier elements has continued such that the periodic table now extends up to element number 118 thanks to a devoted effort by several groups worldwide.

In this talk I'll review the experimental evidence for the quasi-fission process and discuss some of the theoretical progress in understanding the dynamics of the heavy-ion reactions and the competition between complete fusion and quasifission.

This work was supported the US Department of Energy, Office of Nuclear Physics under contract DE-AC02-06CH11357

NUCL 14

Survival of shell-stabilized, spherical nuclei and prospects for discovery of the next new element

***Charles M. Folden III**, Folden@comp.tamu.edu.Cyclotron Institute, Texas A&M University, College Station, TX 77843-3366, United States*

The production of shell-stabilized, spherical nuclei has received significant attention in recent years due to the discovery of new superheavy elements with these characteristics. Reactions of ^{48}Ca, ^{45}Sc, ^{50}Ti, and ^{54}Cr with lanthanide targets produce shell-stabilized, spherical nuclei near the N = 126 shell, and excitation functions for the *xn* and *pxn* exit channels have been measured using the MARS spectrometer at Texas A&M University. The peak cross sections for the 4n evaporation channels in the ^{48}Ca-induced reactions are substantially larger than for the other projectiles, and in some cases the *p*3*n* cross sections of the ^{45}Sc-induced reactions are larger than the corresponding 4*n* cross sections. The data have been described theoretically by a simple model that incorporates an angular momentum-dependent fission barrier, and that excludes rotational energy from the energy available to emit neutrons. This work demonstrates that the production of nuclei near the N = 126 shell using fusion-evaporation reactions is heavily influenced by the atomic number of the projectile, and that cross sections for evaporation residues formed using projectiles with $Z_p > 20$ may be substantially reduced relative to ^{48}Ca-induced reactions. This talk will summarize the

most recent experimental results, discuss the theoretical model, and give some observations on the likelihood of future new element discoveries.

NUCL 15

Search for high energy alpha particles in the reactions of 7.5AMeV ^{197}Au with ^{232}Th

Sara Wuenschel[1]*, wuenschel@comp.tamu.edu, Joseph B Natowitz*[1,2]*, Kris Hagel*[1]*, Marina Barbui*[1]*, Gianluca Giuliani*[1]*, EunJoo Kim*[1]*, Nicolas Blando*[1]*, Hua Zheng*[1]*, Seweryn Kowalski*[3]*, Katarzyna Schmidt*[1]*, Zbigniew Majka*[4]*, Zbigniew Sosin*[4]*, Andrejz Wieloch*[4]*. (1) Cyclotron Institute, Texas A&M University, College Station, Texas 77845, United States (2) Department of Chemistry, Texas A&M University, College Station, Texas 77845, United States (3) Institute of Physics, University of Silesia, Katowice, Slaskie, Poland (4) Smoluchkowski Institute of Physics, Jagiellonian University, Krakow, Poland*

The search for alternative reaction paths for heavy element production requires a careful experimental investigation of mechanisms other than fusion, e.g., multi-nucleon transfer or very asymmetric fission of even heavier transient systems. Many super heavy elements are expected to decay by alpha particle emission. The heaviest elements are characterized by unusually high alpha particle energies which distinguish them (in general) from the lighter elements. Using ^{197}Au projectiles incident on a ^{232}Th target, we are pursuing survey experiments based upon the implantation of recoiling heavy reaction products in a catcher foil and the detection of alpha particle decays characteristic of these heavy nuclei. The 7.5 MeV/nucleon ^{197}Au beam was pulsed at different intervals in order to be able to identify species of different half-life. A large number of interesting high alpha-energy activities were detected `both in-beam and out of beam. These data will be discussed as will extensions of this program using an active catcher system consisting of a high granularity array of scintillators read by photomultiplier tubes that will allow us to correlate a detected alpha decay with an implantation position and observe multiple decays from the same recoil implantation site.

NUCL 16

Fusion with radioactive ion beams

Zach Kohley*, kohley@nscl.msu.edu.Department of Chemistry and NSCL, Michigan State University, E. Lansing, MICHIGAN 48824, United States*

Low energy radioactive ion beams (RIBs) provide a unique opportunity to explore how exotic properties, such as neutron skins, halos, or changes in shell structure, manifest themselves in fusion reactions. Heavy-ion fusion induced with medium mass RIBs ($9 < Z < 50$) remains almost completely unexplored yet provides the perfect tool to study the isospin dependence of hot and cold fusion reactions.

The new ReA3 reaccelerated beam facility at the National Superconducting Cyclotron Laboratory (NSCL) will provide high quality radioactive ion beams, produced from fast fragmentation reactions, at energies around the Coulomb barrier. The development of a new research program focused on using the RIBs from ReA3 in heavy-ion fusion reactions will be discussed. Additionally, prelimimary results from a stable beam experiment examining the isospin dependence of quasifission at the Australian National University will be presented.

NUCL 17

Materials challenges for inertial fusion energy

Christian Mailhiot, *christian.mailhiot@wsu.edu.College of Arts and Sciences, Washington State University, Pullman, WA 99164-2816, United States*

The development of high-energy laser offers the possibility to replicate the extreme conditions needed to achieve not only fusion ignition and burn in the laboratory, but also energy gain – key milestones in the scientific pursuit of fusion energy as a source of electricity. Specifically, the National Ignition Facility (NIF) at the Department of Energy's Lawrence Livermore National Laboratory can deliver to a target nearly two million joules of ultraviolet laser energy in nanosecond pulses. NIF is designed to produce fusion burn and energy gain using inertial confinement fusion (ICF). NIF's 192 intense laser beams, focused into a gold cylinder called a hohlraum, generate soft x-rays that compress a hollow shell filled with deuterium and tritium.

As a fundamental science platform, the NIF facility can generate conditions similar to those in the stars and the cores of giant planets and allow the possibility to perform laboratory astrophysics experiments and to investigate the properties of extreme states of matter. As an energy system, NIF can provide the basis for evaluating future decisions about inertial fusion energy (IFE) development facilities and programs. In an IFE power plant, 10 to 20 pulses of fusion energy per second would heat a low-activation coolant surrounding the fusion targets. The coolant in turn would transfer the fusion heat to a turbine and generator to produce electricity. A NIF-scale laser operating at this repetition rate would produce more than 1,000 megawatts (MW) of electricity for the grid.

This presentation will highlight the unprecedented materials challenges presented by the design and operation of an IFE power plant as they relate to laser-induced damage to high-value optical components, target fabrication and assembly, and radiation damage to the target chamber. The scientific approach to address these challenges integrates computational materials science simulations and laboratory-scale experiments.

NUCL 18

Tunsten as a nuclear structural material

***Lance Snead**, sneadll@ornl.gov, TS Byun.Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37934, United States*

Refractory materials and tungsten in particular have been considered for fusion and advanced fission power systems for decades. However, much of the fundamental irradiation effects leading to the known embrittlement issues are not well understood. What is known is that the irradiation behavior is a function of the crystal response to irradiation and the stability of the grain boundary which is a strong function of the processing route. To date, much of the irradiation effects studies have been carried out on powder metallurgy materials for which grain boundaries dominate behavior. For these reasons the current database on irradiation effects is both lacking in the fundamental understanding of base material and the materials of interest for next generation devices. This paper will present a brief summary of the current knowledge-base and results of a new collaboration begun to address these limitations.

A recent program to understand the behavior of irradiated tungsten includes polycrystalline tungsten, single crystal W of [100] and [110] orientations in various rolling and anneal conditions, and 0.5 mm thick W/Cu laminates. Specimen types were 0.1×4×16 mm bars and SS-J2 tensile specimens for which tensile testing, ball punch, and microhardness was performed. Fission reactor irradiations were carried out in the 0.02 to 20×10^{25} n/m^2 (E>0.1 MeV) at 90, 300, 500, and 650°C. In addition to contrasting the mechanical properties and microstructural evolution of the single crystal material with the polycrystalline and engineered materials, the present results will be compared with the literature. Moreover, implication of the irradiation response as a function of dose and temperature with the viability of tungsten as a nuclear structural material will be discussed.

NUCL 19

Radiation-induced defect formation and short-term evolution: Computational methods and experimental results

***Roger E. Stoller**[1], rkn@ornl.gov, Haixuan Xu[3], Yuri Osetskiy[1], Donald M. Nicholson[2], Malcolm Stocks[1]. (1) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States (2) Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States (3) Department of Materials Science and Engineering, University of Tennessee, Knoville, TN 37996, United States*

Continuing developments in *ab initio* and atomistic methods increase the probability of making direct comparisons between their predictions and relevant experimental results. The timescale for radiation-induced defect formation in atomic displacement cascades is $\sim$10-20x10^{-12} sec. This is followed by short-term evolution processes ($\sim10^{-3}$ sec), that ultimately lead to defect diffusion and damage accumulation for times up to many years. The longest time scale is associated with significant levels of microstructural evolution and mechanical property changes that limit the service life of these materials in current

and advanced nuclear energy systems. The shortest timescale is amenable to accurate atomistic simulations, but it is challenging to make comparisons with experimental data at such short times. Methods such as mean-field reaction rate theory or object kinetic Monte Carlo are available for simulating long time evolution and making direct comparisons with experimental results. In practice, such methods suffer from the requirement of an extensive set of predetermined, and often poorly defined, material parameters. However, is now possible to improve the parameterization of these models using both *ab initio* calculations and atomistic simulations. New insights into defect formation and evolution obtained in the ORNL Center for Defect Physics will be described with a focus on providing a direct link between computational simulations and experimental measurements; implications for improved radiation resistance of structural materials will also be discussed.

NUCL 20

Radiation tolerance and radiation shielding properties of novel materials for space exploration

Richard Wilkins, *rtwilkins@pvamu.edu.NASA Center for Radiation Engineering and Science for Space Exploration, Prairie View A&M University, Prairie View, TX 77446, United States*

Materials for space exploration ideally must be light weight and muti-functional. One important function, particularly for long-term human exploration, is radiation shielding for solar particle events. In addition, materials for spacecraft and habitat must be structurally strong, radiation tolerant, and cost effective. The Center for Radiation Engineering and Science for Space Exploration (CRESSE) at Prairie View A&M University has developed and utilized planetary surface testbeds designed to simulate habitats constructed both above and below the lunar and Martian surface. The lunar and Martian testbeds are called The Bioastronautics Experimental Research Testbeds for Environmental Radiation Nostrum Investigations and Education (BERT & ERNIE) respectively. Radiation shielding results from experiments performed using High Z and Energy (HZE) ions delivered at the NASA Space Radiation Laboratory (NSRL) at Brookhaven National Laboratory, and high energy protons delivered at the Proton Synchrotron at Loma Linda University Medical Center will be presented. Shielding data is obtained from measuring radiation absorbed dose and dose equivalent using a tissue equivalent proportional counter (TEPC) which is functionally identical to instruments operating on the International Space Station and on-board the shuttle orbiter. Composites designed and fabricated by CRESSE researchers that consist of simulated regolith (for both lunar and Martian environments) and ultra-high molecular weight polyethylene (UHMWPE) were used in the BERT and ERNIE testbed configurations. The shielding ability of these composites, as well as unaltered regolith will be compared with similar thicknesses of aluminum and high density polyethylene. Mechanical strength measurements on irradiated and non-irradiated composites indicate long term radiation tolerance of the composite materials. In addition, radiation characteristics of

complex carbon composites doped with boron for missions that may include a mixed radiation field from space and a nuclear reactor will be presented.

NUCL 21

Radiation tolerance of programmable metallization cell memory devices

Michael N Kozicki[1]*, michael.kozicki@asu.edu, Hugh Barnaby*[1]*, Maria Mitkova*[2]*, Yago Gonzalez Velo*[1]*, Pradeep Dandamudi*[1]*, Mahesh Ailavajhala*[2]*, Keith Holbert*[1]*. (1) School of Electrical, Computer, and Energy Engineering, Arizona State University, Tempe, Arizona 85287-5706, United States (2) Department of Electrical and Computer Engineering, Boise State University, Boise, Idaho 83725-2075, United States*

Programmable metallization cells (PMCs) are metal–ion conductor–metal structures which exhibit resistive switching at low energy. Their operation is based on the formation and dissolution of nanoscale conductive filaments between oxidizable and inert electrodes via electric field dependent ion transport and electrochemical reduction-oxidation (redox) mechanisms. PMC is the technology platform for Conductive Bridging Random Access Memory (CBRAM), a commercial product which is used in a variety of non-volatile memory applications. In this paper, we describe the effects of high dose ^{60}Co irradiation on PMC memory devices. Test element groups containing $Ge_{40}S_{60}$–based PMCs were tested before and after ^{60}Co irradiations. The devices were incrementally exposed to a maximum total ionizing dose (TID) of 10 Mrad(GeS) and electrical characterization was performed at several stress dose levels in order to determine the evolution of the switching characteristics with increasing dose. The PMC structures were irradiated in the OFF-state and five successive voltage double sweeps were performed on elements before and after TID exposures. Figure 1 shows plots of the cumulative distributions of the ON and OFF-state resistances of the devices. The data show that these devices show essentially no change in the ON-state resistance after 10 Mrad and that the OFF-state resistances show little change apart from a slight increase at 10 Mrad.

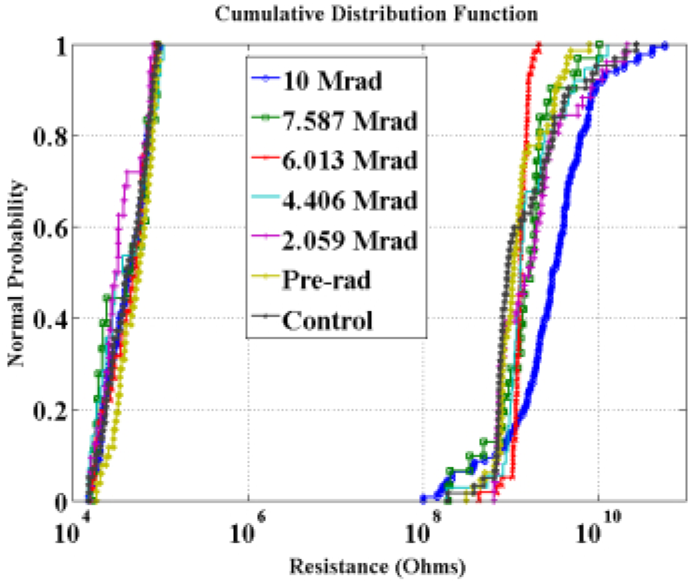

Figure 1. Cumulative distributions of ON and OFF-state resistances of 5 µm diameter PMCs at various total-ionizing doses.

NUCL 22

Functionalized and unaltered mesoporous materials for radionuclide sequestration

Heino Nitsche, *hnitsche@lbl.gov.Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720-1460, United StatesNuclear Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8169, United States*

The separation of actinides and lanthanides on the industrial scale is primarily performed using waste-intensive liquid-liquid extraction. We have undertaken the design, synthesis, and testing of reusable mesoporous materials for actinide and lanthanide separation, sequestration, and sensing. We have identified three materials with high binding capacity for plutonium: organically-modified ("functionalized") mesoporous silica, ordered mesoporous carbon, and oxidized ordered mesoporous carbon. Mesoporous silica and ordered mesoporous carbons (OMCs) are attractive as sorbents because of their extremely high surface areas and large pore volumes. We have explored plutonium as well as selected other actinide and lanthanide ion sorption interactions with several functionalized silica and three different types of OMC materials, both as-synthesized and after chemical oxidation. The chemical and physical properties of the sorbing matrices were characterized by a variety of different physical-chemical methods: ^{13}C (intactness of ligand) and ^{29}Si (binding between ligand and surface) solid-state nuclear magnetic resonance (NMR) spectroscopy; infrared spectroscopy (FT-IR) (ligand intactness); thermogravimetric analysis (TGA) (surface coverage); potentiometric titration (point of zero charge); Scanning electron microscopy (SEM) and

Transmission electron microscopy (TEM) (substrate morphology); X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS) (binding mechanism). We will report the results on the characterization of surface properties, target ion capacity, binding kinetics, stability, and reversibility as a function of pH and other solution conditions.

NUCL 23

Walt Loveland – a modern nuclear chemist

***Alena Paulenova**, alena.paulenova@oregonstate.edu.Chemistry, Oregon State University, Corvallis, OR 97331, United States*

For the last 11 years I have had the unique privilege of working with Walt Loveland, an extraordinary scientist who dedicated his life and career to Oregon State University in Corvallis, a small town in Western Oregon. Unless he is gone for an irradiation experiment at Berkeley or another research accelerator facility, every morning, a few minutes after 7 A.M., he can be seen walking through the back door of the reactor building to his small office that he has occupied for almost five decades. Walt's mentor during his first years in OSU, prof. Roman Schmidt once told me that he never met a better blend of a chemist and physicist in one person. Yes, Walt, an old fashioned professor who still writes his notes with an ink-pen on a yellow paper pad is actually a very modern nuclear chemist. His numerous research publications and several textbooks are a thoughtful attempt to tie nuclear chemistry and physics into a cooperative endeavor called nuclear science. I am honored with opportunity to speak about him.

NUCL 24

Maximum results with minimum resources

***Kjell Aleklett**, kjell.aleklett@geo.uu.se.Department of Earth Sciences, Uppsala University, Uppsala, Sweden*

If you asked Walter Loveland, "Which accelerator laboratories did you use for your research from 1978 to 2004" (the time period we worked together) the answer would be, "In the USA Argon, Berkeley, Brookhaven, Fermi lab, Michigan State, and in Europe CERN - Switzerland, GANIL - France and Uppsala - Sweden. I think it will be hard to find any scientist in the world who has used more facilities than Walter Loveland. The conclusion you might make is that he must have had an enormous research budget. I know that Walter would laugh in his friendly way about that statement and tell you that the grants he received were really minimum resources. How is it that someone with a minimum research budget can use the maximum number of accelerator facilities for his research? That story will be told.

NUCL 25

Transition from heavy-ion induced reactions in the low energy region to those in the intermediate and high energy regions

***Akihiko Yokoyama**, yokoyama@se.kanazawa-u.ac.jp.Institute of Science and Engineering, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan*

I have worked on a project of heavy-ion induced reactions with an aim to investigate the mechanisms of nuclear fission and deep inelastic processes in the 1980s in Japan. After that, I had chance to work with Prof. Loveland, and extended my interest in heavy-ion reaction study to the intermediate and high energy regions which were absolutely unfamiliar to me, then. I was able to continue my work at an office next to the professor's in Radiation Center of the university for about 2 years until I got back to Japan to occupy a permanent position in Osaka University in 1990.

Prof. Loveland and I worked together on the measurement for fragmentation of Au-197 by 21MeV/nucleon Xe-129[1], which may attract one's interest as a collision of heavy nuclei in the intermediate energy, while the combination of the nuclei do not lead to complete fusion even in the low energy. We concluded that the stochastic nucleon exchange model correctly predicts the shape of heavy residue mass distribution, but overestimates the fragment longitudinal velocities as does the dissipative fragmentation model, perhaps due to preequilibrium emission process. The work was published in 1992 [1]and also selected as a paper of late Prof . Glenn T. Seaborg in "Modern Alchemy" published in 1994.[2]

After returning to Japan, I was able to utilize my experience with Prof. Loveland because I had chance to perform several experiments on heavy-ion reactions in the intermediate and high energy regions in Japan.

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NUCL 26

Studying a spectrum of nuclear reaction mechanisms with Walter Loveland

***David J Morrissey**, morrissey@nscl.msu.edu.Chemistry and NSCL, Michigan State Univ., East Lansing, MI 48824, United States*

A brief overview of the wide ranging studies of nuclear reaction mechanisms that Walter Loveland and I have carried out over the years will be presented.

NUCL 27

Interactions of radiation-induced defects with grain boundaries in covalent ceramics

***Izabela Szlufarska**, szlufarska@wisc.edu, Dane Morgan, Ming-Jie Zheng, Chao Jiang.Department of Materials Science & Engineering, University of Wisconsin, Madison, WI 53706-1595, United States*

Compared to polycrystalline materials, nanocrystalline (nc) materials are expected to exhibit superior radiation resistance due to the presence of a large volume fraction of grain boundaries (GB), which can act as sinks for point defects. Although the enhanced radiation resistance of nc materials has been supported by many recent experiments, there also exist reports of contrary observations. Consequently, understanding of the interactions of radiation-induced defects with GBs is essential for designing radiation-tolerant nc ceramics for advanced nuclear applications. Using SiC as a model covalent ceramic we demonstrate that the grain size effects during irradiation are strongly coupled to defect energy landscape. For example, we discovered that the presence of recombination barriers in nc ceramics can lead to the interstitial starvation. In this phenomenon interstitials are prevented from recombining with vacancies due to high recombination high barriers, and instead interstitials migrate to GBs where they are annihilated. As a result, there is a crossover with an increasing temperature from the regime where nc materials are more radiation resistant to the regime where their radiation resistance is inferior as compared to the coarse-grained material. We will also present our results on the effects of GB stresses on the sink strength. Sink strength of GBs is a measure of GB efficiency in annihilating point defects. Most previous models of GB sink strengths have ignored the effects of GB stress on the rate of defect annihilation. We found that while for coarse-grained materials the effects of the stress field are negligible, GB stresses play a significant role in the kinetics of defect annihilation in fine-grained materials. Contrary to what has been established for larger grain size, in nanomaterials small angle GB can annihilate defects faster than large angle GB. Finally, we will also discuss our newly discovered criterion for defect-induced amorphization in carbide ceramics.

NUCL 28

Atomistic approach to study a metal surface behavior under high electric fields in particle accelerators

***Flyura Djurabekova**[1], flyura.djurabekova@helsinki.fi, Aarne Pohjonen[1], Stefan Parviainen[1], Avaz Ruzibaev[1], Helga Timko[2], Kai Nordlund[1]. (1) Helsinki Institute of Physics, University of Helsinki, Helsinki, Finland (2) CERN, Switzerland*

Modification of the surface exposed to high electric fields results in frequent breakdowns -- a nuisance limiting the value of applied fields. An atom-level theoretical model of surface behavior under high electric fields, which we are currently developing, suggests

the possibility of surface hardening under applied fields. The dislocation-based mechanism may explain the formation of a surface protrusion, acting on the later stage as a full size field emitter, which may develop at the certain circumstances in a breakdown spot. Hence our model aims to explain the physical limitation of a metal surface due to electrical breakdowns at the fields that are still well below the critical values known to cause field-assisted evaporation of atoms. We model all three main stages of plasma development ignited in ultra-high vacuum, i.e. plasma onset, plasma evolution and surface damage due to the plasma discharge. The main emphasis of the presentation will be on the triggering process of plasma ignition event due to the high electric field, as well as the discussion on the plasma-ion ``shower'' during the vacuum arcing and the resulting surface response. A possible mechanism for formation of a surface protrusion mediated by dislocations nucleated on a near surface void under high electric field will be discussed in detail. A modified molecular dynamics code, which includes the effects of electric fields such as partial charge on surface atoms as well as the Joule heating of surface asperities due to electron currents will also be presented. This information is plugged to the simulation of plasma development, whose output is used to simulate the surface damage. Comparison to the available experiments will be made.

NUCL 29

Structural transformations in actinide and analog materials induced by highly ionizing irradiation

Maik Lang[1], *mlang2@utk.edu, Cameron L. Tracy*[2], *Fuxiang Zhang*[2], *Jiaming Zhang*[2], *Rodney C. Ewing*[2]. *(1) Department of Nuclear Engineering, University of Tennessee, Knoxville, TN 37996, United States (2) Department of Materials Science & Engineering and Earth & Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, United States*

The tolerance of actinide and analogue materials for exreme conditions is an important issue in the design of nuclear materials. Motivated by the influence of their complex electronic configurations on their radiation response, we have performed systematic experiments on *f*-block ionic compounds using high energy ions and high pressure. The induced structural modifications were analyzed by synchrotron x-ray diffraction and x-ray absorption spectroscopy. The radiation response at ambient conditions of fluorite-structured oxides CeO_2 and ThO_2 was investigated by irradiation with 950 MeV Au ions to fluences up to 5×10^{13} ions/cm^2. The analytical approach revealed reduction in the oxidation state of some actinide and analogue elements following exposure to ion irradiation, and showed that radiation tolerance is enhanced in materials for which this reduction is inhibited.ThO_2, which has a single oxidation state, is highly resistant to radiation damage. In contrast, easily reduced CeO_2 is less resistant. Enhanced efficiency of cerium reduction is evident in nanocrystalline CeO_2, and this further decreases radiation tolerance. These results show that ionizing radiation can strongly influence the electronic configuration of actinide materials and charge state changes play a critical role in the resulting radiation tolerance. We have further demonstrated

that the radiation response of actinide and analogue materials is significantly modified when high pressure is combined with the use of ion beams. This was experimentally realized by injecting relativistic heavy ions (energy: ~50 GeV) through a mm-thick diamond anvil of a high-pressure cell into the pressurized samples. The cubic starting phases of CeO_2, UO_2, and ThO_2 could be fully transformed into a remarkably well crystallized orthorhombic high-pressure phase at only ~30% of the critical transformation pressure. A kinetic component of the deceleration process of energetic ions in pressurized materials (*e.g.*, rapid nanoscale heating or pressure waves) is possibly the trigger for the induced structural transformations.

NUCL 30

Ion tracks: New insights using small angle X-ray scattering measurements

***Patrick Kluth**, patrick.kluth@anu.edu.au.Department of Electronic Materials Engineering, Australian National University, Canberra, ACT 0200, Australia*

Ion tracks in solids are narrow trails of permanent damage generated along the ion paths of highly energetic heavy ions facilitated by their inelastic interactions with the target electrons. Ion tracks have applications in a variety of disciplines including materials science and engineering, nuclear physics, geochronology, archaeology, and interplanetary science. Small angle X-ray scattering (SAXS) provides an interesting tool to study the structure of ion tracks, as it is sensitive to small density changes that often exist in the damaged regions. An example of a typical SAXS scattering image of ion tracks in natural apatite is shown in the image.

The strong oscillations of the curved streaks in the scattering image enable determination of the ion track radii with high precision. Short acquisition times associated with the high photon flux at 3rd generation synchrotron devices facilitate *in situ* studies to determine the annealing kinetics of ion tracks as well as the use of diamond anvil cells to investigate track stability under high pressure conditions.

The presentation will give an overview of our recent results including: the observation of a fine structure in ion tracks in amorphous SiO_2[1]; measurement of the morphology and temperature dependent elastic behavior of ion tracks in α-quartz; determination of the track recovery kinetics in minerals[2], and characterization of the morphology and annealing behavior of ion tracks in amorphous metallic alloys[3] and semiconductors[4]. First results on the stability of ion tracks under high-pressure conditions will be discussed. In several of these studies, the SAXS measurements are supplemented by molecular dynamics simulations and calculations using an inelastic thermal spike model.

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NUCL 31

Swift heavy ion irradiation-induced phase transformation in $BaTiO_3$

Ram Devanathan*, ram.devanathan@pnnl.gov, Weilin Jiang.Pacific Northwest National Laboratory, Richland, WA 99352, United States*

Barium titanate ($BaTiO_3$) is a technologically important ceramic because of its ferroelectric, dielectric and optical properties. It is currently being used to fabricate transducers, ceramic capacitors, self-regulating electric heaters, and thermal cameras. $BaTiO_3$ has potential applications in advanced nuclear energy systems and space stations of the future, where the material will be required to maintain phase stability under irradiation. We have used molecular dynamics simulations of swift heavy ion irradiation effects in $BaTiO_3$ in conjunction with experimental ion irradiation using 635 MeV $238U^+$ ions and electron microscopy to understand radiation-induced phase transformations. The simulations show that a cylindrical amorphous track with a radius of 1.2 nm forms along the ion track for energy deposition of 5 keV/nm. The track radius increases to 4.5 nm for energy deposition of 20 keV/nm. These simulations, in light of experimental evidence, reveal the atomic-level details of the competition between damage accumulation and annealing in complex ceramics.

NUCL 32

My chemical bonds with Norman Edelstein

Lester R Morss*, morssl@verizon.net.Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742-4454, United States*

Norman Edelstein has been my scientific mentor and collaborator for almost a half century. Norman and I coauthored five peer-reviewed papers, the first of which, “Preparation of Cubic Chloro Complex Compounds of Trivalent Metals - Cs_2NaMCl_6,” *Inorg. Chem.* 9, 1771 (1970) has been cited 236 times. That paper was my second-most-cited paper! Among Norman's 234 research articles, it was his fourth most-cited. Our most recent and our major collaboration was in co-editing the third and fourth editions of *THE CHEMISTRY OF THE ACTINIDE AND TRANSACTINIDE ELEMENTS* with Jean Fuger. (The first edition, *THE CHEMISTRY OF THE ACTINIDE ELEMENTS,* was authored by actinide science pioneers Joseph Katz and Glenn Seaborg in 1957, with whom I edited the second edition.) Norman and my joint publications encapsulate my entire scientific career, representing Norman's mentorship during my graduate-student years at Berkeley and his mastery of many segments of f-element chemistry. In this talk I'll describe some of the ongoing puzzles of actinide chemistry that we attempted to solve: chemical synthesis, actinide electronic structure, and bonding of f-elements with many other elements in the Periodic Table. I will also mention a few additional scientific themes to illustrate the breadth and depth of Norman's leadership in contemporary inorganic, physical, and environmental chemistry.

NUCL 33

Something old and something new: Evolving ligand constructs for f-element ion recognition

*Daniel Rosario-Amorin[1], Sabrina Ouizem[1], Diane A. Dickie[1], Benjamin P. Hay[2], Julien Podair[2], Laetitia H. Delmau[2], **Robert T. Paine**[1], rtpaine@unm.edu. (1) Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States*

Over the last thirty years, numerous groups worldwide have been engaged in expansive ligand design activities stimulated by a very diverse range of fundamental and applied science objectives. In particular, several groups have sought to discover new ligand constructs that reveal unique features in the coordination chemistry of f-element cations and subsequently provide for improved separations and/or detection methods for these technically important elements. Contributing to these efforts, we have used a combination of computational molecular modeling, organic ligand syntheses, f-element coordination chemistry, spectroscopy, X-ray crystallography and solvent extraction analyses to support development of new f-element selective multidonor-site ligands and to identify electronic and architectural features that impact ligand/f-element ion chelation events operating in solvent extraction processes. In this presentation, the evolution of a new family of ligands based upon pyridine and pyridine N-oxide platforms decorated with phosphine oxide and amide groups will be described, and the coordination chemistry and extraction performance of selected ligands will be discussed and compared against other well studied extractants.

NUCL 34

Accessing new actinide chemistry by fragmentation of gas-phase coordination complexes

***John K Gibson**, jkgibson@lbl.gov.Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

Fragmentation of gas-phase actinide coordination complexes presents opportunities to access new types of transformations and bonding that may be elusive or inaccessible in condensed phase due to interactions with neighboring atoms or molecules. Gas-phase complexes with ligands tailored to exhibit particular types of transformations or fragmentations are produced by electrospray ionization of solutions containing the metal ion and one or more ligands. A particular focus is on actinyl anion complexes, $AnO_2(L)_3^-$, where An = U, Np or Pu, and L is an anion ligand, one example being acetate, L^- =

$CH_3CO_2^-$. Fragmentation of the complex in a quadrupole ion trap is achieved by collision induced dissociation, in which the ion undergoes multiple energetic collisions with helium atoms; products are identified by mass-selective ejection from the trap. For strongly bound ligands with sufficiently facile fragmentation pathways, formation of new complexes via elimination of a neutral molecule, for example CO_2 from acetate, can dominate over straightforward ligand loss. This gas-phase synthetic approach has resulted in the production of novel organoactinyl complexes, and the previously elusive transformation of a uranyl oxo bond to a nitrido bond. Computational studies provide information on the mechanisms of the transformations, and the structures and bonding of the species involved in the observed processes. Insights into gas-phase transformations provided by experiment and theory can contribute to the development of new condensed phase synthetic schemes.

NUCL 35

Coordination chemistry of lanthanide and actinide complexes with mixed O- and N-donor ligand scaffolds

Jessie L. Brown[1]*, jmcdonald@lanl.gov, Andrew J. Gaunt*[1]*, Mathew B. Jones*[1]*, Sean D. Rielly*[1]*, Brian L. Scott*[1]*, Timothy J. Boyle*[2]*, Cora E. MacBeth*[3]*, John C. Gordon*[1]*. (1) Chemistry Division, Inorganic, Isotope and Actinide Chemistry, Los Alamos National Laboratory, Los Alamos, NM 87545, United States (2) Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM 87106, United States (3) Department of Chemistry, Emory University, Atlanta, GA 30322, United States*

The separation of middle to late actinides (U-Cm) from the lanthanide fission products in spent nuclear fuel would greatly facilitate some advanced nuclear fuel cycle options to reduce the volume of waste and minimize the radiotoxic lifetime of waste sent for geological disposal. The most promising ligands suggested for effecting the most difficult An(III)/Ln(III) separations are those containing soft donors (e.g., N, S), an observation that has been rationalized with the hypothesis of increased covalency within An−L bonds versus Ln−L bonds.

Our recent research uncovered some interesting covalency differences in 5f-element complexes with a ligand platform that contained both relatively 'hard' (O) and 'soft' (N) donor atoms. In order to better understand the bonding modes within mixed An-O/N fragments across a wider ligand set, we have been investigating the chelating trianionic *tris*(amidate) scaffold and its coordination to the actinides, with a focus upon the transuranic elements. Several lanthanide (La, Ce and Nd) analogues were also prepared for comparative purposes. Spectroscopic and structural characterization will be discussed along with concomitant advances in non-aqueous transuranic starting materials.

NUCL 36

Chemistry of protactinium fluorides

***Richard E Wilson**, rewilson@anl.gov, Stephanie DeSio.Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States*

Protactinium occupies an important position in the periodic table, located at the electronic intersection between f- and d-element chemistries. Electronic structure calculations suggest that at Pa the energetics of the 5f and 6d orbitals are nearly degenerate. This is unlike Th, where the 5f states are higher in energy than the 6d, and unlike U where the 5f are lower in energy than the 6d. Inspired by the interesting chemical and electronic questions that these calculations pose we are undertaking a study of the coordination chemistry and physical properties of Pa compounds. Because of the complex aqueous chemical behavior of Pa(V) we have initiated our studies using fluoride solutions and precipitates from these solutions. Initial studies have focused on the coordination chemistry of Pa fluorides in the solid state and the speciation of Pa(V) in aqueous media using a series of spectroscopic and structural techniques.

A series of homoleptic fluoride complexes have been synthesized and their single crystal structures determined. These complexes serve as models for our spectroscopic studies of Pa(V) in aqueous solution, providing insight into the speciation of Pa(V) in these systems. They provide a starting point for further studies aimed at investigating the electronic structure using Pa(IV), for which there is a single 5f electron . This work is funded by the U.S. DOE Early Career Research Award program and was performed at Argonne National Laboratory for the U.S. DOE, OBES, Division of Chemical Sciences, Geosciences, and Biosciences, under contract DE-AC02-06CH11357.

NUCL 37

Mixed-valent plutonium(III/IV) coordination complexes and their pure Pu(III) and Pu(IV) end members

***Thomas E Albrecht-Schmitt**, talbrechtschmitt@gmail.com.Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States*

The synthesis, structure, and spectroscopy of a series of mixed-valent Pu(III)/(IV) coordination complexes will be described and compared with their single-valent Pu(III) and Pu(IV) end members.

NUCL 38

Photochemical route to actinide-transition metal bonds: Synthesis, characterization and reactivity of a series of thorium and uranium heterobimetallics

Ashleigh L Ward[1]*, wardal@berkeley.edu, Wayne W Lukens*[2]*, Connie C Lu*[3]*, John Arnold*[1,2]*. (1) Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, United States (2) Chemical Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA 94720, United States (3) Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, United States*

A series of actinide-transition metal heterobimetallics have been prepared featuring thorium, uranium and cobalt. Complexes utilizing a binucleating ligand with hard and soft donors, Th(IV) and U(IV) and an isocarbonyl ligated cobalt unit were irradiated with ultraviolet light to afford actinide-metal interactions. The synthesis of a rare U-Co bond and what we believe to be the first Th-Co bond, as well as their precursors, is presented. The series of compounds was characterized by single-crystal X-ray diffraction, infrared and UV-Vis/NIR spectroscopy, ^{1}H, ^{1}H-^{1}H COSY, variable-temperature and ^{31}P NMR spectroscopy, and variable-temperature magnetic susceptibility. These actinide compounds demonstrate a novel way to achieve actinide-metal bonds and represent an exciting platform for the expansion of the study of actinide metal-metal bonding and reactivity.

NUCL 39

New methods for the synthesis of actinide-chalcogen multiple bonds

***Trevor W. Hayton**, hayton@chem.ucsb.edu, Danil E. Smiles.Department of Chemistry, UC Santa Barbara, Santa Barbara, CA 93106, United States*

Complexes with actinide-ligand multiple bonds are of interest for a variety of reasons, including their ability to engage the 5f orbitals in metal-ligand bonding. Within this class of compounds, those featuring actinide-chalcogen multiple bonds have received considerable attention in recent years. Despite several successes in the synthesis of these compounds, there is still a need for the development of new routes to these materials. In this regard, we have focused our recent efforts on the development of new chalcogen transfer reagents, especially those in which the chalcogen atom is formally in the -1 oxidation state. One reagent that fits this criterion is potassium trityl thiolate, $K[SCPh_3]$, and the reactivity of this reagent with the common uranium(III) precursor, $U[N(SiMe_3)_2]_3$, will be presented in detail. Our search for other novel chalcogen sources will also be discussed.

NUCL 40

Probing the electronic structures of low oxidation-state uranium molecules

***Lai-Sheng Wang**, Lai-Sheng_Wang@brown.edu.Department of Chemistry, Brown University, Providence, RI 02912, United States*

The electronic structures of actinide systems are extremely complicated and pose considerable challenges both experimentally and theoretically because of strong electron correlation and relativistic effects. We report the investigation of the electronic structure and chemical bonding of a series of uranium oxide (UO_2^-) and fluorides (UF_x^-, x = 2-4) using photoelectron spectroscopy and relativistic quantum chemistry. The electron affinities of the corresponding neutral molecules are accurately measured. For UO_2^-, intense photoelectron bands are observed from its low-lying $(7s\sigma g)^2(5f\varphi u)^1$ orbitals and the more deeply-bound O2p-based molecular orbitals with a large energy gap. Surprisingly, numerous weak photodetachment transitions are also observed in the gap region due to extensive two-electron transitions, suggesting strong electron correlations among the $(7s\sigma g)^2(5f\varphi u)^1$ electrons in UO_2^-. The experimental data are interpreted using multi-reference *ab initio* calculations with inclusion of spin-orbit coupling. Vibrationally resolved photoelectron spectra are obtained for the three fluoride anions. Significant multi-electron transitions, similar to those of UO_2^-, are observed in the case of only $U(5f^37s^2)F_2^-$, as a result of strong electron correlation effects of the two 7s electrons. The U−F symmetric stretching vibrational modes are resolved for the ground states of all UF_x (x = 2−4) neutrals. Theoretical calculations are performed to qualitatively understand the photoelectron spectra. The current data provide experimental electronic structure information to test various relativistic quantum chemistry methods aimed at strongly correlated electron systems.

NUCL 41

Global perspective on the underutilized potential of nuclear energy

***Kenneth L Nash**, knash@wsu.edu.Department of Chemistry, Washington State University, Pullman, WA 99164-4630, United States*

The “Modern Problems” of global climate change, increasing planet-wide population, resource limitations, and energy supply are interconnected issues that human civilization must face in the coming decades. These issues have emerged as important focal points as we have passed the end of an unbelievable century of growth that was built on readily available and inexpensive energy. The technological expansion seen in the 20th Century was based primarily on the combustion of fossil carbon and characterized by comparatively recent consideration of the resulting impacts on the ecosystem. Nuclear reactors began contributing CO_2–free energy to this consumption in the 1960s, ultimately rising to the present 19% of U.S. electricity production, 15% globally. To address the expected energy demands of the present century, it is virtually assured that the nuclear footprint in the “green” energy mix will expand (with the developing world possibly leading the way). At present 70 new reactors are under construction around the globe, 30 of those in China, 20 more in India and Russia. This

expansion will occur despite the concerns raised by the accident at Fukushima primarily because nuclear fission is the highest energy density option, it has a small footprint, and it is already integrated into the existing energy distribution system. The underpinning science of fission energy is reasonably well understood and it is a mature industry with a 50-year performance record (including a few accidents that led to safety improvements). Among the challenges and choices to be made in the future development of nuclear energy are the interconnected issues of long-term supplies of fuel and the development of viable strategies for managing the radioactive byproducts of fission. This presentation will focus primarily on the promise and challenges arising from the production of power based on nuclear fission.

NUCL 42

US fuel cycle R&D program: Overview and significant results

***Terry A. Todd**, terry.todd@inl.gov.Fuel Cycle Science and Technology Division, Idaho National Laboratory, Idaho Falls, ID 83415, United States*

The United States Department of Energy's Fuel Cycle Research and Development Separations and Waste Form program is developing advanced technologies to support potential new fuel cycles. The program is evaluating alternative fuel cycle concepts, many of which require the recycle of uranium, plutonium and/or minor actinides (Np, Am, Cm). The focus of the Separations and Waste Form Research and Development program is to identify technologies for the separation of select fuel constituents as well as immobilization of waste streams in durable waste forms. The program is performing research on understanding the fundamental separation mechanisms to enable more robust technologies and effective predictive capabilities, as well as applied development needed for eventual implementation of technologies. The R&D program has a very long term focus, with implementation of future fuel cycle options around mid-century. An overview of the program activities in actinide separation will be provided, along with perspectives on challenges that need to be addressed prior to implementation. A summary of significant R&D progress and accomplishments will also be discussed.

NUCL 43

Development of advanced hydrometallurgical processes for actinide partitioning

***Manuel Miguirditchian**, manuel.miguirditchian@cea.fr, Xavier Hérès, Michel Masson, Christophe Poinssot.Radiochemistry & Processes Department, CEA Marcoule, Nuclear Energy Direction, Bagnols-sur-Ceze, France*

This paper gives an overview of the major results recently obtained in France at CEA Marcoule on new partitioning processes developed for the recycling of minor actinides (MA). Depending on the scenario selected for the MA recycling (homogenous or heterogeneous recycling), different hydrometallurgical processed have been developed and will be presented:

- Innovative SANEX processes (DIAMEX-SANEX, SANEX-TODGA) for the heterogeneous recycling of MA (americium & curium)
- EXAm process for the heterogeneous recycling of the sole americium
- GANEX process for the homogeneous recycling of the grouped actinides.

Important results have been obtained in the past few years demonstrating the scientific feasibility of these different recycling options. Several high active tests were performed in the Marcoule Atalante facility on genuine solutions of nuclear spent fuels demonstrating the feasibility of the different concepts. For the next years, an important part of R&D work will focus on the extrapolation of these processes to industrial conditions, with issues such as management of input and output flows including solvent clean up and assessment of long term behaviour of separation systems towards hydrolysis and radiolysis, scale-up of new extractants, downstream effects, definition of the implementation conditions in continuous contactors, assessment of on-line analysis, etc. Improvements of these processes are also done thanks to fruitful collaborations with several European teams in the framework of the ACSEPT and SACSESS projects. The aim is to develop mature processes for an efficient management of actinides in future GEN IV cycles.

NUCL 44

Degradation in minor actinide separations: Addressing the challenges of radiation chemistry

Leigh R Martin[1]*, Leigh.Martin@inl.gov, Stephen P Mezyk*[2]*, Bruce J Mincher*[1]*. (1) Aqueous Separations and Radiochemistry, Idaho National Laboratory, Idaho Falls, ID 83415, United States (2) Department of Chemistry and Biochemistry, California State University at Long Beach, Long Beach, CA 90840, United States*

To improve the viability of a sustainable closed nuclear fuel cycle, research into new and improved methods for the partial or complete recycling of the minor actinides from used nuclear fuel is of paramount interest. It is envisaged that any large-scale process for the recycling of light water reactor fuel will be an extension of the solvent extraction technologies that are already deployed for the recovery of uranium and plutonium from used fuel. Even after several years of cooling the dissolved fuel is still highly radioactive and therefore the radiation chemistry of the separations reagents, metal ions and their complexes in these systems has to be considered. Here, a general overview of the chemistry of the reactive species found in these liquid-liquid extraction systems will be presented. Specific examples of the effects of radiation chemistry effects related to the separation of the actinide elements and metal ion oxidations states will also be discussed.

NUCL 45

Small modular reactors: Can they be built in a timely, cost effective manner?

***Jeff Terry**, terryj@iit.edu.Department of Physics, Illinois Institute of Technology, Chicago, IL 60616, United States*

Small Modular Reactors (SMR) are touted as a panacea for the nuclear industry. The small size reduces the cost to a potential customer. I will present research detailing the economic drivers of the potential SMR Industry. Specifically, I will focus on the cost drivers of Integrated Reactor Vessel (IRV) manufacturing of an SMR using pressurized water reactor (PWR) technology. The manufacturing of SMRs was studied by developing a model for a dedicated vendor factory. This model was specifically designed to allow for future optimization of the fabrication of SMR components starting with the IRV from a Generic SMR design. A series of Monte Carlo calculations allowed for a comparison of the variances over a spectrum of reactor cost estimates using slightly different parameters such as labor rate and material quantity to be conducted.

NUCL 46

Complete recovery of actinides from simulated used fuel raffinates using a hard and soft donor ligands

***Dean R. Peterman**, dean.peterman@inl.gov, Peter R. Zalupski, Dale D. Ensor, Catherine L. Riddle.Department of Aqueous Separations and Radiochemistry, Idaho National Laboratory, Idaho Falls, ID 83402-6158, United States*

Studies have shown a much enhanced differentiation between trivalent actinides and trivalent lanthanides when substituted alkyl dithiophosphinic acids are utilized as the active phase transfer reagents. We present a study evaluating the use of a synergistic combination of bis(o-trifluoromethylphenyl)dithiophosphinic acid and trioctylphosphine oxide for the complete actinide recovery from UREX-like raffinates. A complete single-step separation of uranium, neptunium, plutonium and americium from aqueous mixtures containing 0.5 M nitric acid and a total fission product content of 5.5 g/L (45 mM) has been demonstrated.

NUCL 47

Extraction chromatographic materials for selective recovery of uranium in a thorium nuclear fuel cycle

***Jessica A Drader**, jdrader@mines.edu, Jenifer C Braley.Chemistry, Colorado School of Mines, Golden, CO 80401, United States*

In the thorium fuel cycle, it is necessary to breed fissile ^{233}U from fertile and naturally available ^{232}Th to produce the energy dense material required for power generation. As ^{233}U fissions, neutron siphoning fission products build-in. Eventually a separation of the ^{233}U fuel from the fission products as well as the remaining thorium is necessary to

reestablish an environment that favors ^{233}U fission. These separations are conventionally examined using solvent extraction technologies due the relatively cost-effective and high throughput nature of the technique. However; sometimes a final cleanup of uranium after bulk solvent extraction purification is appropriate. In these instances, extraction chromatographic separations may prove more advantageous. This presentation will discuss the development and application of extraction chromatographic materials for the separation of uranium from thorium. Results examining the kinetics and distribution of f-elements in batch contacts with the developed material will be discussed.

NUCL 48

Partitioning of used nuclear fuel using mixed extractants: A fundamental approach

Aaron Johnson, *aarontj73@wsu.edu, Kenneth L Nash.Department of Chemistry, Washington State University, Pullman, WA 99163, United States*

The efficient separation of used nuclear fuel into its relative components remains a critical challenge in the operation of a closed nuclear fuel cycle. Many solvent extraction processes have been either successfully applied or proposed to accomplish this separation. However, most of these processes necessitate several different discrete processes to fully partition fuel, which introduces challenges for industrial implementation. To reduce the cost and complexity of the separations, the concept of combining an acidic and solvating extractant into one solvent has become the focus of a large amount of research. Initial studies have shown that these processes hold great promise in their ability to partition used nuclear fuel. However, the fundamental chemistry controlling these processes is not well understood. Adducts are known to form between the extractants in the organic phase and evidence of mixed complexes forming between metals and the extractants has been reported. Investigations into these problems have been complicated by the structures of the multifunctional extractants used. To better understand the underlying chemistry of mixed extractant systems, we have proposed a new combination of extractants, Cyanex-923 and HEH[EHP], each monofunctional organophosphorus extractants. By using simple solvating and cation exchanging extractants the fundamental chemistry that will define the performance of this combination is simpler to elucidate. The combination of these extractants has been investigated by solvent extraction, variable temperature NMR, FT-IR, UV-Vis, and time resolved fluorescence spectroscopy. The work presented here is the results of this study. It is hoped that these findings can be applied to other systems to better understand the nature of mixed extractant systems. This work was conducted atWashingtonStateUniversitywith support from the U.S. Department of Energy Fuel Cycle Research and Development Program, Sigma Team for Minor Actinide Separations.

NUCL 49

Recent progress in molecular uranium nitride chemistry

Steve Liddle[1]*, stephen.liddle@nottingham.ac.uk, David King*[1]*, Benedict Gardner*[1]*, Ashley Wooles*[1]*, Peter Cleaves*[1]*, Jonathan McMaster*[1]*, William Lewis*[1]*, Alexander Blake*[1]*, Eric McInnes*[2]*, Floriana Tuna*[2]*. (1) School of Chemistry, University of Nottingham, Nottingham, United Kingdom (2) Department of Chemistry, University of Manchester, Manchester, United Kingdom*

There is currently great interest in the nature and reactivity of molecular uranium-ligand multiple bonds. This is because the nature and extent of 5f/6d orbital participation in uranium-ligand bonding is still a topic of debate and the unique orbital-hybridisation patterns available to uranium promises novel applications in atom-efficient catalysis and small molecule activation.

Molecular uranium nitrides are of special interest because of their potential as precursors to uranium nitride materials via 'soft' routes, but perhaps more importantly because in contrast to commonly observed U=O, U=NR, and U=CR_2linkages the U≡N triple bond was prominent for its paucity. For example, the only examples of the U≡N triple bond were previously confined to matrix isolation experiments at ~5 K and attempts to prepare molecular species under ambient conditions in exploitable quantities resulted in compounds where the nitride bridges to 2-4 metal atoms or is trapped by a covalently bound borane group. The U≡N triple bond was proposed by calculations to be a transient species formed during photolysis of uranium(IV)-azides, but it could not be trapped and instead reacts with ancillary-ligand C-H bonds to give amide derivatives.

Recently, we reported that a sterically encumbered uranium(III)-triamidoamine complex [U($Tren^{TIPS}$)] [$Tren^{TIPS}$ = $N(CH_2CH_2SiPr^i{}_3)_3$] reacts with sodium azide to afford the bridging uranium(V)-nitride complex [{U($Tren^{TIPS}$)(μ-N)(μ-Na)}$_2$]. Abstraction and sequestration of the sodium ion by 12-crown-4 ether results in the separated ion pair complex [U($Tren^{TIPS}$)(N)][Na(12-crown-4)$_2$] which contains the terminal U≡N triple bond linkage under ambient conditions and in multi-gram quantities.

We will discuss this chemistry and the factors that contributed to the success of this relatively simple strategy and will detail more recent work in this area including the isolation and reactivity of the long-sought terminal uranium(VI)-nitride triple bond, general reactivity studies, and magnetic behaviour.

NUCL 50

F-element chemistry supported by corrole ligands

John Arnold[1,2]*, arnold@berkeley.edu, Ashleigh L Ward*[1]*, Heather L Buckley*[1]*, Wayne W Lukens*[2]*, Mitchell Anstey*[3]*. (1) Chemistry, University of California, Berkeley, Berkeley, California 94720, United States (2) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States (3) Advanced*

Systems Engineering and Deployment 8125, Sandia National Laboratory, California, Livermore, California 94550, United States

This presentation will focus on the preparation and characterization of a new series of corrole complexes with lanthanide and actinide elements. Two synthetic routes have been established: the first involves a metathesis reaction employing a new Li_3corrole species in combination with metal halide salts; the second exploits amine elimination chemistry via the H_3corrole macrocycle and well-known $M[N(SiMe_3)_2]_2$ complexes. In studying these complexes, a range of characterization techniques have been employed including X-ray crystallography, electronic and IR spectroscopy, electrochemistry, and magnetism.

NUCL 51

Absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

***J G Tobin**, JGTobin@LBL.Gov.Lawrence Livermore National Lab, Livermore, CA 94550, United States*

Recently, X-ray absorption spectroscopy (XAS) and related derivative measurements have been used to demonstrate the Pu 5f states are strongly relativistic and have a 5f occupation number near 5. [1] Owing to the success in this regime, it has been argued that the XAS measurements should be a powerful tool to probe 5f occupation variation, both as a function of elemental nature (actinide atomic number) and as a function of physical and chemical perturbation, e.g. oxidation state. It will be shown here that XAS and its related measurements fail in this latter aspect for a wide variety of uranium compounds and materials. Possible causes will be discussed.

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. This work was supported by the DOE Office of Science, Office of Basic Energy Science, Division of Materials Science and Engineering. JGT wishes to thank Professor Guenter Kaindl for his critical reading of the manuscript and use of his XAS data.

1. J.G. Tobin, P. Söderlind, A. Landa, K.T. Moore, A.J. Schwartz, B.W. Chung, M.A. Wall, J.M. Wills, R.G. Haire, and A.L. Kutepov, J. Phys. Cond. Matter **20** , 125204 (2008), and references therein.

NUCL 52

Theoretical studies of orbital mixing in actinide-ligand bonds

Enrique R Batista[1]*, erb@lanl.gov, Richard L. Martin*[1]*, David L. Clark*[2]*, Stosh A. Kozimor*[2]*. (1) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States (2) Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States*

For the past few years we have put a significant amount of effort into quantifying the amount of covalent interactions in actinide-ligand bonds. These studies aided the interpretation of ligand core-level spectroscopy measurements by some members of the team and the two efforts together yielded solid evidence of covalent bonding and 5f participation in that interaction. An implicit misunderstanding has been the connection between this evidence of covalent interaction and the relative strength of these bonds. In this presentation we address that issue with standard quantum mechanical methods to try to clarify and separate the two concepts. These developments are illustrated in a series of molecular complexes where the bonds are clearly defined and described in “simple” language.

NUCL 53

WITHDRAWN

NUCL 54

Tetravalent actinide nanparticles in aqueous solution: Structure and reactivity

L. Soderholm[1]*, LS@anl.gov, S. Skanthakumar*[1]*, Karah Knope*[1]*, Richard Wilson*[1]*, Monica Vasiliu*[2]*, David A. Dixon*[2]*. (1) Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States (2) Department of Chemistry, University of Alabama, Tuscaloosa, Alabama, United States*

Hydrolysis and subsequent condensation reactions play an important role in the aqueous chemistry of tetravalent actinide ions. The resultant oligomers are known to exhibit chemistries very different from that of their monomeric counterparts. First forming in solution, the resulting precipitates have been historically characterized as chemically ill-defined and amorphous. Recent studies have begun to change this perception as the characterization of structural correlations in solutions reveals well-defined metal interactions, suggesting the possibility of harnessing this intractable chemistry. Our investigations have found that tetravalent-actinide hydrolysis products are often well defined nanoparticles that can be crystallized and structurally characterized via standard single-crystal techniques. The presence of these oligomeric species in solution, often as monodisperse nanoclusters, is verified and quantified by high-energy x-ray scattering (HEXS).The results from these structural studies are being used as input for electronic calculations that in turn are providing a wealth of insight into the means by which these clusters form, including the important role played by pH, temperature, and anion. This work was performed for the U.S. DOE, OBES, Division of Chemical Sciences, Geosciences, and Biosciences, under contract DE-AC02-06CH11357.

NUCL 55

From small photons to big photons: Nearly two decades of actinide science in Berkeley with Norman Edelstein

***David K Shuh**, DKShuh@lbl.gov.Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

The Actinide Chemistry Group of Lawrence Berkeley National Laboratory (LBNL) with Norman M. Edelstein as the Group Leader the early 1990's began to utilize synchrotron radiation methodologies to investigate the electronic structure of and to determine the speciation of radionuclides. This primarily consisted of extended x-ray absorption fine structure (EXAFS) experiments, both independent and collaborative, at the then Stanford Synchrotron Radiation Laboratory (SSRL). These first studies included the investigation of actinide solution species and technetium materials that would later develop into more comprehensive efforts from LBNL directed at understanding a range of important topics in the chemistry and physics of f-element materials. At this time, there were successful efforts to establish beamlines that could support efficient studies of radioactive materials, first with a hard x-ray beamline at SSRL and followed shortly thereafter by a soft x-ray counterpart at the Advanced Light Source. Some of the results from these early studies coupled with those of others in the field will be discussed, and how the impact of these early studies have helped shape the contemporary landscape of actinide science to this point in time. The discoveries and developments made possible by the utility of synchrotron radiation in actinide science have in many ways been revolutionized the field and Norman Edelstein has been a large part of this in multiple ways - where would he want us to go now and into the future?

NUCL 56

Neptunium: The key to understanding the behavior of actinide chalcogenides

***Geng Bang Jin**, gjin@anl.gov.Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, United States*

Across the first third of the actinide series 5f electrons exhibit behavior intermediate between the delocalized regime often found in d-block transition-metal series and the almost exclusively localized 4f electrons. This complex electronic behavior of actinides has been well illustrated in the chalcogenides, where early actinides, notably Th/U, tend to act like larger tetravalent transition metals whereas the heavier actinides such as Pu behave like a trivalent lanthanide. A small number of Np chalcogenide compounds have been reported. They are either isostructural with Th/U analogues within which Np is predominantly tetravalent or isostructural with Pu/lanthanide analogues within which Np is trivalent. Based on these limited data, the 5f electrons of Np in chalcogenide environments appear intermediate between the itinerant and localized regimes, which makes Np the key to understanding the behavior of actinide chalcogenides. Evidence for this intermediate role is provided in our recent studies on Np_2Se_5 and $NpSe_2$. Np_2Se_5

displays a deviation from the Th analogues in An–Q and Q–Q interactions despite of their same compositions and structure-types. The newly discovered $NpSe_2$ adopts a structure different from those of $AnSe_2$ (An = Th–U)or $AnSe_2$ (An = Pu–Cf), with distinct An–Q and Q–Q interactions. Structural, spectroscopic and magnetic results are described to illustrate some unusual properties pointing to a Np valence intermediate between +3 and +4. This work is supported by the U.S. DOE, OBES, Chemical Sciences, Geosciences, and Biosciences Division, Heavy Elements Program, under contract DE-AC02-06CH11357.

NUCL 57

Coordination of actinyl ions to nitrogenous heterocyclic ligands: A joint theoretical and experimental study

Ping Yang[1], *ping.yang@pnnl.gov, Zheming Wang*[1]*, Duoqiang Pan*[1]*, Yu Gong*[2]*, John Gibson*[2]*. (1) Pacific Northwest National Laboratory, Richland, WA 99352, United States (2) Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

Nuclear energy represents a critical tool available to meet the demand of increasing energy supply, at the same time reducing green house gas emissions. To reduce the need for long-term nuclear waste storage, it is important to develop efficient strategies for selective separations. A better molecular-level understanding of the coordination modes and affinities of ligands with multiple binding sites to actinyl ions can pave the way to designing new ligands with improved extraction efficiency and selectivity. We will discuss the coordination chemistry of actinyl ions with ligands composed of multiple competitive binding sites, including sulfur, nitrogen and oxygen chelating groups. We will present the interactions between actinide centers and selected nitrogenous heterocyclic ligands using first-principle methods that include relativistic effects and electron correlation. The theoretical results will be further validated by gas phase collision-induced dissociation experiments and solution spectroscopic characterizations.

NUCL 58

Soft X-ray investigations of covalent orbital mixing in lanthanide oxides

Stefan G Minasian[2,3], *sgminasian@lbl.gov, Enrique R Batista*[3]*, Jason M Keith*[4]*, Wayne W Lukens*[2]*, Stosh A Kozimor*[3]*, Richard L Martin*[3]*, Dennis Nordlund*[1]*, David K Shuh*[2]*, Dimosthenis Sokaras*[1]*, Tolek Tyliszczak*[2]*, Tsu-Chein Weng*[1]*. (1) SLAC National Accelerator Laboratory, Menlo Park, CA 94025, United States (2) Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (3) Los Alamos National Laboratory, Los Alamos, NM 87545, United States (4) Colgate University, Hamilton, NY 13346, United States*

Developing insight into how metal oxide electronic structure changes for a range compounds and materials will greatly benefit a variety of existing and emerging energy technologies. Many of the technologically desirable chemical, magnetic, electronic, and

thermal properties of metal oxides are derived from strongly covalent metal–oxygen multiple bonds (metal oxos). Among approaches explored previously, ligand K-edge X-ray absorption spectroscopy (XAS) has emerged as an effective method for quantitatively probing electronic structure and orbital mixing. The presence of covalent mixing is observed as a pre-edge feature in the ligand K-edge XAS, which only has transition intensity if the final state metal orbital contains a component of ligand p orbital character. Recent advances have shown that insights regarding the nature of orbital mixing in metal oxides can be obtained at the K-edge for oxygen through a combination of XAS with a scanning transmission X-ray microscope (STXM), non-resonant inelastic X-ray scattering (NIXS), and hybrid density functional theory calculations (DFT).

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in d- and f-block oxides. Oxygen K-edge XAS measurements and DFT studies began with a series of six tetrahedral oxyanions, MO_4^{2-} and MO_4^{1-} (M = Cr, Mo W and Mn, Tc, Re). Despite the similarities of the isoelectronic d^0 MO_4^{2-} and MO_4^{1-} anions, unexpected differences in metal oxo orbital mixing were observed for adjacent metals in the periodic table. The lanthanide dioxides and sesquioxides, LnO_2 and Ln_2O_3 (Ln = Ce, Pr, Tb), were chosen for subsequent work because their electronic structures are well-established from hard X-ray spectroscopies. Features in the O K-edge XAS follow anticipated trends based on 4f and 5d orbital energies and occupancies. Overall, the research shows that orbital composition is influenced by a complex interplay between periodic changes in both orbital energy and radial extension.

NUCL 59

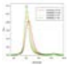
Spectroscopy of Neptunium (V) at variable temperature and ionic strength

***Donald T Reed**, dreed@lanl.gov, Michael K Richmann, Juliet S Swanson, Jean-Francois Lucchini, Danielle Cleveland.Department of Repository Science and Operations, Los Alamos National Laboratory, Carlsbad, NM 88220, United States*

The spectroscopy of neptunium (V) as a function of temperature, ionic strength, and complexation is being used to establish the speciation of Np(V) and model its behaviour in the geosphere. Under oxic to sub-oxic conditions in near-neutral pH, $Np(V)O_2^+$is the predominant species and is relatively mobile in the environment due to its high solubility and low tendency toward hydrolysis and complexation. Its potential migration in a high-level nuclear waste repository and its importance as an analog for Pu(V) in a TRU waste repository make it important to study the effects of temperature and ionic-strength on its speciation.

Herein we report the progress we have made to characterize the absorption spectroscopy of Np(V) as a function of temperature (20-90 ^oC), ionic strength (0 to 6 M Na/Mg-Cl system), and complexation of key environmental complexants (borate, carbonate and hydrolysis). Both ionic-strength and temperature impact and slightly change the spectrum of the Np(V) aquo species. The model fits of these spectra are used to establish the effects of temperature and ionic-strength on the complexation of

Np(V) where new band formation is almost always observed. The effect of borate concentration on the Np(V) spectrum is shown in Figure 1 and shows an isobestic point indicating the formation of a 1:1 complex. Formation constants and associated Pitzer/SIT parameters were determined for chloride, borate and carbonate are reported.



NUCL 60

New nuclear: How might that happen?

***Todd R Allen**, todd.allen@inl.gov.Idaho National Laboratory, Idaho Falls, Idaho 83415, United States*

Electricity demand globally is likely to continue to grow as populations grow and transition to modern standards of health and accommodations. The growth will be met through some combination of intermittent renewable resources such as solar, wind, and biomass, as well as base load sources such as hydro, nuclear, coal, and gas generation. Decisions will be made in a decision framework that includes cost, global warming concerns, and dependability. The current state of nuclear deployment will be discussed and key elements that may improve the likelihood that nuclear will be deployed will be outlined.

NUCL 61

Future nuclear technologies to open exploration of the solar system: Current activities at the Center for Space Nuclear Research

***Steven D Howe**, showe@usra.edu.Center for Space Nuclear Research, Idaho Falls, Idaho 83402, United States*

Nuclear power has been considered for space applications since the 1960s. Radioisotope Thermo-electric Generators (RTGs) have been used on all robotic missions beyond Mars and on human missions since the Apollo program. Between 1955 and 1972 the US built and tested nuclear thermal rocket (NTR) engines to be able to send humans to Mars and beyond. In 2008, the NASA Mars Architecture Team found that the use of a Fission Surface Power (FSP) reactor was ENABLING for human missions to the Mars surface and that the NTR was the PREFERRED propulsion system for the mission. The Center for Space Nuclear Research (CSNR) is pursuing development of tungsten based fuels for use in a NTR, for a surface power reactor, and to encapsulate radioisotopes for advanced, low mass, compact power sources. Fabrication of sub-length, tungsten cermet elements reminiscent of NERVA fuel has been completed using depleted uranium oxide. In addition, the CSNR Summer Fellows program has examined several human mission scenarios that benefit from the use of

the NTR or robotic missions that would use small power sources. Conceptually, Cubesats may soon be able to be launched to the outer planets affordably allowing universities to send probes throughout the solar system. The results of recent investigations into alternatives in design and materials for future systems will be discussed.

NUCL 62

Status of electrochemical processes for used nuclear fuel

***Kenneth Michael Goff**, mike.goff@inl.gov, K C Marsden.Nuclear Nonproliferation Division, Idaho National Laboratory, Idaho Falls, ID 83415, United States*

Electrochemical processes for the treatment of used nuclear fuel to enhance waste management options and/or resource utilization are being examined by a number of countries including theUnited States,Korea,Russia,Japan,France,United Kingdom,China, andIndia. These technologies employ molten salt systems to facilitate the separation of actinides from fission products. The technical maturity of these technologies varies depending on the potential application. Processing to support disposition of fuels from fast neutron reactors is performed at an engineering scale routinely. Some process operations need further development and demonstration, including head-end steps for application to the recycle of commercial light water reactor oxide fuel to recover feed material for a fast reactor. Research is ongoing to support the development and scaling of electrochemical recycling technology to these broader applications. This presentation addresses the status of these efforts.

NUCL 63

Fuel property and characteristic studies on metallic alloy actinide bearing systems for fast reactor applications

***J Rory Kennedy**, rory.kennedy@inl.gov.Idaho National Laboratory, Idaho Falls, ID, United States*

Idaho National Laboratory continues to study metallic alloys of the actinides in the context of fuel development for fast neutron spectra nuclear reactor applications within a closed nuclear fuel cycle. Despite this long standing activity, much of the fundamental thermodynamic data for the actinide elements and actinide bearing systems of relevance to the fuel development program have not been thoroughly investigated and assessed. In addition, the fundamental chemical reactivity and mass transport properties of actinide systems require extensive study in order to better understand the behaviour of the metallic alloys while in reactor where the materials are subject to a very high degree of irradiation damage. Important phenomena such as phase and microstructure development, element migration and redistribution, thermal conductivity, and fuel-cladding chemical interaction will be briefly described for general background information. Following this, an overview of results pertaining to these important

phenomena will be given including a comparison of the thermal diffusivity at 50mm spatial resolution between unirradiated and irradiated metallic alloy fuels, fundamental reaction and diffusion kinetics between actinides and iron based materials representing stainless steel cladding, re-evaluation of the actinide alloy Np-Zr phase diagram, advances in the chemical sequestration of elements to inhibit mass transport under a steep thermal gradient, and recent advances in the application of focused ion beam techniques to highly radioactive materials for determining 3D grain orientation (EBSD), mechanical properties by nano/micro indentation or compression testing, microstructure through transmission electron microscopy, and nano-scale element distribution by atom probe tomography.

NUCL 64

Thermodynamic modeling of fission product release from the Fukushima Daiichi nuclear accident

***David G Abrecht**, David.Abrecht@pnnl.gov, Jon M. Schwantes.Pacific Northwest National Laboratory, Richland, WA 99352, United States*

In March 2011, a loss of coolant accident at the Fukushima Daiichi Nuclear Power Plant following the Tohoku earthquake caused significant release of radioactive material to the environment. Since then, significant efforts have been made to reconstruct the events leading to the release, particularly identification of the primary source of released materials following both intentional venting from Units 1 and 3 and a series of hydrogen explosions within the on-site spent-fuel pool, in attempts to improve safeguards against future releases during accident conditions. From analysis of short-lived radionuclide activities in local soil samples taken within 20 days of the accident, Schwantes et al. (*Envir. Sci. & Tech.* **2012** , *46,* 8621) determined the primary source of released materials to be from the venting of Units 1 and 3, based on a thermodynamically-controlled model of fission product volatilization from the spent fuel rods. In this work, we expand on that model by examining the correlation between the reduction reaction potentials of the fission products at reactor temperatures and fission product molar quantities in the soil samples. We find strong correlations between the released quantities of fission products and reduction potentials, which may provide new insight into conditions within the primary containment vessel at the time of venting.

NUCL 65

Two-phase calorimetric measurements of the enthalpy of extraction of f-elements by trioctylphosphine oxide: The mechanism of solvation

***Travis S Grimes**[1], Travis.Grimes@inl.gov, Leigh R Martin[2]. (1) Aqueous Separations & Radiochemistry Department, Idaho National Laboratory, Idaho Falls, ID 83415, United States (2) Aqueous Separations & Radiochemistry Department, Idaho National Laboratory, Idaho Falls, ID 83415, United States*

Building thermodynamic models to describe metal partitioning in liquid-liquid separations systems is a key component to process development. Traditionally, thermodynamic parameters (ΔH and ΔS) for biphasic reactions have been determined indirectly using the van 't Hoff method. Though this method is sound, direct calorimetric measurements of the enthalpy of metal ion transport across the liquid-liquid boundary can provide accurate results and simultaneously highlight important features of a given extraction system. In this presentation, we will demonstrate a calorimetric approach to determining the heat of extraction for a solvating organic extractant, illustrating the delicate thermodynamic balance between the metal ion extraction and acid partitioning equilibria. A systematic study of the enthalpy of extraction for the f-elements (lanthanide series and minor actinides) with the solvating extractant TOPO will be reported. The results obtained will be compared with van 't Hoff measurements for the same extractant and the merits of applying heats of extraction obtained via calorimetry will be discussed.

NUCL 66

Synthesis and characterization of new nitrogen-containing ligands for actinide/lanthanide separations

Julie M Muller, *julie.muller@wsu.edu, Kenneth L Nash.Chemistry, Washington State University, Pullman, WA 99164, United States*

Nuclear energy has numerous advantages as a source of primary power. However, challenges for proper management of its high-level radioactive waste still remain. Well-known solvent extraction processes can be used to recycle and reuse plutonium and uranium from the used nuclear fuel, but the most important species still present in the waste are long-lived minor actinides and fission product lanthanides. Minor actinides are a major source of radiotoxicity and thus their transmutation into shorter lived nuclides is desirable before final disposal. Complicating this matter, lanthanides are neutron poisons, which means that they compete with the minor actinides for transmutation: separation of those isotopes is required. Unfortunately, due to the similarity in their chemical properties, trivalent lanthanides/actinides group separation is a continuing challenge. One approach is through the development of highly selective organic extractants. Many nitrogen-donor ligands, such as BTBPs (bis-triazinyl bipyridines), have been studied during the past fifteen years for the purpose of conducting An(III)/Ln(III) separations. Despite their good selectivity, many of these reagents have been found to be unstable with respect to acid hydrolysis and radiolysis and to suffer comparatively slow rates of extraction. However, triazole compounds have been shown to be more stable and to have good metal binding kinetics. This work investigates several novel nitrogen-containing tetradentate ligands that combine the functionalities of bipyridine with triazole functional groups, sharing similar structural features with the BTBP analogues. Solvent extraction studies on An(III) and Ln(III) ions have been completed to evaluate the efficiency of these extractants as well as characterization of some features of their coordination chemistry.

Work performed with support from the U.S. Department of Energy, Office of Nuclear Energy, Nuclear Energy University Programs (NEUP) project number 10-881.

NUCL 67

New nitrogen based extractants for the separation of minor actinides from lanthanides

Kayron N Tevepaugh[1,2]*, kntevepaug42@students.tntech.edu, Dale D Ensor*[1]*, Jesse D Carrick*[1]*, Serene Tai*[1]*, Laetitia H Delmau*[2]*. (1) Department of Chemistry, Tennessee Technological University, Cookeville, TN 38501, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

Spent nuclear fuel taken from commercial power reactors contains a small amount of minor actinides (Am^{3+} and Cm^{3+}),as well as fission products which include the chemically similar lanthanide elements. The minor actinides represent less than 1% of the bulk waste, but are responsible for a majority of the spent fuel's heat-load and radiotoxicity. A strategy to deal with the minor actinides is to separate them from the spent nuclear fuel and subsequently transmute them into shorter-lived isotopes using a fast neutron reactor. For this process to be efficient, the minor actinides must first be separated from the chemically similar lanthanide fission products, a particularly difficult separation. This research focuses on optimizing the separation of long-lived minor actinides from lanthanides via solvent extraction systems that utilize extractants containing nitrogen donors. A series of compounds based on a *bis*-triazinyl phenanthroline (BTPhen) scaffold and containing various functional groups have been synthesized. The effectiveness of these BTPhen compounds to extract Am(III) in the presence of macro amounts of light lanthanides has been measured. The influence of the attached functional groups on the separation of Am(III) from light lanthanides will be presented.

NUCL 68

NMR spectra of paramagnetic compounds and unpaired spin-density

Richard A. Andersen*, raandersen@lbl.gov.Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States*

Norman Edelstein's career focused on determining the electronic structure of f-block metal compounds. He learned EPR spectroscopy as a graduate student, applied the technique to determine the electronic structure of d-transition metal dithiolenes as a post-doctoral student, and extended his interests in EPR spectroscopy, and magnetic properties in general, to the f-block metals as a founding member of the Actinide Group at LBNL. This presentation will focus on the application of NMR spectroscopy to paramagnetic metallocene compounds in order to determine the site of unpaired spin-density in the ligands and therefore the role of spin-density in determining the site of reactivity.

NUCL 69

Gas-phase thermochromatographic separations of fission and activation products

John D. Auxier II[3], *jauxier@utk.edu, Daniel E. Hanson*[1], *Jerrad P. Auxier*[1], *Matthew L. Marsh*[2], *Howard L. Hall*[3]. *(1) Department of Nuclear Engineering, University of Tennessee, Knoxville, TN 37760, United States (2) Department of Chemistry, University of Tennessee, Knoxville, TN 37760, United States (3) Institute of Nuclear Security, University of Tennessee, Knoxville, TN 37996, United States*

Solution phase separations are a fundamental process for performing radiochemical analysis. However, traditional solution based separations are generally slow, hence the need for more rapid separation techniques. This work involves the exploitation of gas-phase chemistry for the isolation of fission and activation products in the immediate aftermath of a nuclear explosion. Gas thermochromatographic separations of rare earth elements (REEs), heavy transition metals ($Z > 72$), thorium, and uranium followed by subsequent detection by time-of-flight mass spectrometry (TOF-MS) will be discussed. The REEs can be readily volatilized with 1,1,1,5,5,5-hexafluoroacetyl-acetonate in temperatures between 175 – 250 degrees C. In order to improve the separation efficiency, Monte Carlo simulations have been employed to reduce the separation times, by using the free energy of adsorption and entropy of desorption. In this work, the experimental separations as well as determination of key thermodynamic parameters that control these systems have been explored. This method offers the advantage of rapid, carrier free separations, in addition to providing elemental and isotopic composition information regarding a given sample. Furthermore, this work also supports the growing need for rapid separation and analysis of short lived isotopes currently being used in the radiopharmaceutical and nuclear medicine community and the super heavy element discovery research efforts.

NUCL 70

Synthetic routes toward uranium phosphinidene complexes for probing actinide covalency

Robert K Thomson, *rthomson@ou.edu.Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, United States*

Understanding covalency in actinide-element bonds is crucial to developing new ligand frameworks for separations that are relevant to the nuclear fuel cycle and the isolation of rare earth elements that are critical to the electronics industry. Metal-element multiple bonds are inherently more covalent, and uranium phosphinidene (U=PR) complexes offer the additional advantage of a 31P nucleus that can be probed spectroscopically to evaluate the electronic structure of the actinide center. Here we describe our efforts to generate uranium phosphinidene species and evaluate their electronic structure and reactivity patterns as a means of probing covalency in the U=P bond.

NUCL 71

Uranyl(VI) and plutonyl(VI) coordination and dynamics in a task-specific ionic liquid

Katie A Maerzke, *kmaerzke@nd.edu, William F Schneider, Edward J Maginn.Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, United States*

Ionic liquids (ILs) are a unique class of solvents with potential applications in advanced separation technologies relevant to the nuclear industry. ILs are salts with low melting points and a wide range of tunable physical properties, such as viscosity, hydrophobicity, conductivity, and liquidus range. ILs have negligible vapor pressure, are often non-flammable, and can have high thermal stability and a wide electrochemical window, making them attractive for use in separations processes relevant to the nuclear industry. Metal salts generally have a low solubility in ILs; however, by incorporating new functional groups into the IL cation or anion that promote complexation with the metal, the solubility can be greatly increased. One such task-specific ionic liquid (TSIL) is 1-carboxy-*N,N,N*-trimethylmethanaminium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf2N]) [Nockemann et al., *J. Phys. Chem. B***2006** *, 110*, 20978-20992]. Water, which is detrimental for electrochemical separations, is a common impurity in ILs and can coordinate with actinyl cations, particularly in ILs containing only weakly coordinating components. Understanding the behavior of actinides in TSIL/water mixtures on a molecular level is vital for designing improved separations processes. Classical molecular dynamics simulations of uranyl(VI) and plutonyl(VI) in 1-ethyl,3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][Tf2N]) with de-protonated Hbet (betaine) and water have been performed to understand the coordination and dynamics of the actinyl cations. We find that the betaine is a much stronger ligand than water and prefers to coordinate the metal in a bidentate manner. When very little betaine is present, all of it coordinates the actinide, with the remainder of first solvation shell filled by water. As the amount of betaine coordinated to the actinide increases, the diffusion coefficient of the actinyl cation decreases.

The betaine ligand is able to bridge between two metal centers, resulting in dimeric complexes with actinide-actinide distances of approximately 5 Å. Potential of mean force simulations show that these structures are stable, with relative free energies of up to −40 kJ/mol. The crystal structure for uranyl betaine shows that the betaine bridges between two uranium atoms to form dimeric complexes similar to those found in our simulations [Nockemann et al, *Inorg. Chem.***2010** , *49*, 3351-3360].

NUCL 72

Covalency and strong correlations in actinide materials

Richard L Martin, *rlmartin@lanl.gov.Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87, United States*

I will describe collaborative efforts combining synthesis, characterization and theory in order to assess the predictions of various many-body approaches for the strongly correlated actinide dioxides. A particular focus will be the counterintuitive prediction from hybrid density functional theory (DFT) that while UO_2 is a classic Mott insulator and quite ionic, the PuO_2 analogue, also insulating, shows significant Pu5f/O2p orbital mixing and band dispersion, indicative of covalent interactions. This has spurred efforts to synthesize high quality thin films of UO_2, NpO_2, and PuO_2 using the technique of polymer assisted deposition (PAD), and to characterize them with optical spectroscopy, angle-resolved photoemission, and X-ray absorption spectroscopy. I will discuss the results of the experiments, and compare them with predictions of several many-body theories including screened hybrid DFT, the widely used DFT+U approximations, and dynamic mean-field theory (DMFT). As time permits I will sketch the direction we are taking to address the strongly correlated metals.

NUCL 73

Higher oxidation states of the actinides

Claude Musikas, *musikas.claude@neuf.fr.CEA –Fontenay-aux-Roses, France*

At the end of the nineteen sixties the actinides chemists were surprised to learn that neptunium and plutonium can exist in aqueous solutions at the oxidation state VII. They have been synthesised in alkaline solutions and their stability decreases as follow Np(VII) > Pu(VII) , Np(VII) at elevated pH > Np(VII) in acidic solution. The ionic form of the heptavalent d transition elements in aqueous solutions MO_4- is well known and such knowledge is still missing in acidic media for the 5f heptavalent ions. In aqueous alkaline media it has been established that the Np(VII) Is the octahedral ion $NpO_4(OH)_2^{3-}$ and the hexa coordination of Np(VII) has been observed in several solids. By acidification to pH 10 to 3, Np(VII) gives a rather insoluble compound and at lower pH to a soluble species. Old work done in my laboratory showed that this species was a cation with a charge +1. However $NpO_3^+.xH_2O$ as proposed, at that time is one improbable species and its identification with modern tools , such as EXAFS, might solve the problem.

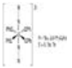
The oxidation of Pu(VI) in alkaline medium gave a strongly colored species which has been considered as Pu(VII) by analogy with Np. However if one looks to the 4d and 5 d transition elements Ru and Os , ions at the VIII valence state could be expected for Pu. So it seems interesting to revisit the oxidation of Pu(VI) in alkaline medium by using rapid electrochemical methods which are able to detect transient species and to check if the redox couple observed was really Pu(VI) - 1e => Pu(VII).

NUCL 74

Synthesis, structure, bonding, and reactivity of U(VI) aryl chacogenate complexes

James M Boncella[1]*, boncella@lanl.gov, Neil C Tomson*[1]*, Brian L Scott*[1]*, Stosh Kozimor*[2]*, Gregory L. Wagner*[2]*, Angela C Olson*[2]*, Matthias W Loeble*[2]*, Juan S. Lezama*[3]*, Enrique R Batista*[4]*. (1) Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States (2) Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States (3) Department of Earth and Earth Systems Science, Stanford University, Palo Alto, CA 94305, United States (4) Theory Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States*

We have synthesised a new class of U(VI) bis(imido) complexes: $[U(=NR)_2(EPh)_4]^{2-}$, R = tBu, Ar (Ph, $(2,6\text{-iPr})_2C_6H_3$); E = S, Se, Te. These complexes have an unusual combination of a hard U(VI) acceptor with soft chacogen donors. The surprising stability of these compounds suggest that there is a significant amount of covalency in the U-E interactions. The bonding in these complexes has been probed experimentally using chalcogen ligand K-edge X-ray Absorption Spectroscopy and theoretically using TDDFT calculations. The nature of the U-E bonding interactions will be discussed as will the reactivity of the novel family of compounds.



NUCL 75

Coordination, sensitization, and separation of trivalent lanthanide and actinide ions using hydroxypyridinonate hard donor ligands

Rebecca J Abergel*, rjabergel@lbl.gov, Manuel Sturzbecher-Hoehne, Solene Hebert.Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

Recent events have called attention to the persistent possibilities of environmental and human contamination with radioisotopes such as lanthanide fission products and actinides. The challenge of limiting exposure to radionuclides and of establishing controlled industrial processes has given rise to unprecedented interest in developing specific lanthanide and actinide binding agents for separation and decontamination purposes. Separation of lanthanides and actinides is a challenging task due to the similarities in their ionic radii and the existence of most of these metal ions in the trivalent oxidation state. Our studies utilize luminescence sensitization and UV-Visible spectroscopic techniques to investigate the specific coordination of *f*-elements by hydroxypyridinonate hard oxygen-donor ligands. The solution thermodynamic properties of Ln(III), Cm(III), and Am(III) complexes formed with these strong chelating agents were investigated and leveraged to separate the different complexes using high performance liquid chromatography. Mass spectrometry and luminescence spectroscopy were then used to detect and identify the isolated species. While mostly soft donor ligands are used in actinide extraction processes, hydroxypyridinonate moieties have proven effective at separating the investigated trivalent ions. Moreover, the separation followed the lanthanide contraction over the *f*-shell, consistent with the measured complex stabilities. A predictive thermodynamic model was then devised to correlate the respective stabilities of other f-element complexes with coordination sphere properties and ligand separation potential.

NUCL 76

Bonding and electronic structure in actinide complexes: Being part of the Norman conquest

Bruce E. Bursten, *bbursten@utk.edu.Department of Chemistry, University of Tennessee, Knoxville, Knoxville, TN 37996, United States*

The use of modern electronic structure methods, particularly relativistic density functional theory, has allowed our understandig of structure and bonding in actinide complexes to grow markedly over the last 25 years. The author will present some of the results from his group that have led to a greater synergy between theory and experiment within actinide science. The author will also thank Dr. Norman Edelstein for his scientific contributions as well as his leadership and vision in recognizing the importance of such work to help advance this multidisciplinary field.

NUCL 77

Stretch of f-element spectroscopy – work with Norman Edelstein

Guokui Liu, *gkliu@anl.gov.Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United States*

The successful applications of crystal-field theory in f-elements (4f lanthanides and 5f actinide) spectroscopy are a significant part of Norman Edelstein's scientific accomplishments. This presentation highlights several recent and current topics in experimental and theoretical studies of actinde systems, including in particular Edelstein's contributions to crystal field modeling. In analyses of electronic energy levels obtained from optical spectroscopic experiments on Ce(III), U(III), Cm(IV) and other f-element ions in crystalline compounds, a quantitative understanding of crystal-field interaction and configuration mixing was achieved. A method of combining crystal-field splitting and vibronic coupling was proven effective for analyzing electronic interaction and quantification of f-d spectra complicated by vibronic transitions. A semi-empirical approach to simulating the 5f-6d transitions of Pa(IV) in compounds and charge transfer vibronic transitions in uranyl complexes will be discussed.

NUCL 78

Covalency in the tris-cyclopentadienyl lanthanides and their cations

Jennifer C Green[1], *jennifer.green@chem.ox.ac.uk, Robert G Denning*[1], *Jeffrey Harmer*[1], *Mark Irwin*[1], *Mark S Denning*[1], *Nicholas Kaltsoyannis*[2], *Andrea Sella*[2], *Naima*

Narband[2], Rosemary Coates[2], Andrew Kerrridge[2], Charlene Hunston[2], Monica de Simone[3], Marcello Coreno[4]. (1) Department of Chemistry, Oxford University, Oxford, United Kingdom (2) Department of Chemistry, University College London, London, United Kingdom (3) CNR-INFM, Laboratorio Nazionale TASC, Trieste, Basovizza 34149, Italy (4) Gas Phase Beamline, CNR-IMIP Roma, Trieste, Italy

Evidence is presented of significant covalency in the ytterbium 4f shell of tris-cyclopentadienyl ytterbium ($YbCp_3$) in its electronic ground state, which can be represented by the superposition of an ionic configuration Yb(III):$4f^{13}(Cp_3)$ and a charge-transfer configuration Yb(II):$4f^{14}(Cp_3)^{-1}$. The relative weights of these configurations were determined from the difference in their 4f photoionization cross sections, the accumulation of spin-density centered on the ^{13}C atoms of the Cp ring, as measured by a pulsed EPR (HYSCORE) experiment, the reduction in the spin-density in the 4f shell, manifest in the ^{171}Yb hyperfine interaction, and the principal values of the **g** -tensor, obtained from the EPR spectrum of a frozen glass solution at 5.4 K. Each of these methods finds that the spin density attributable to the charge transfer configuration is in the range 12**-** 17%. The presence of configuration interaction also accounts for the highly anomalous energies, intensities, and vibronic structure in the **"** f-f**"** region of the optical spectrum, as well as the strict adherence of the magnetic susceptibility to the Curie law in the range 30**-** 300 K.

The gas phase photoelectron spectrum of $Ce(\eta\text{-}C_5H_5)_3$ demonstrates a similar covalent interaction in the $CeCp_3^+$ cation giving a mixed configuration ground state. For other $LnCp_3^+$ cations (Ln = Pr, Nd, Sm, Yb, Lu) the ground states have single configuration ground states Ln(III)$4f^n$:$(Cp_3)^{-1}$.

Significant covalency in lathanide complexes of ligands with high basicity is a consequence of a small energy gap between 4f and ligand frontier orbitals, and may result when the molecular symmetry is such that a ligand frontier orbital cannot be stabilized by interaction with the Ln 5d or 6p orbitals.

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(3) Denning, R. G., et al., *J. Am. Chem. Soc.* **2011** , *133*, 20644-20660.

NUCL 79

Radioisotope micropower source technologies and applications

***David E. Meier**, david.meier@pnnl.gov.Pacific Northwest National Laboratory, Richland, WA 99352, United States*

Radioisotope micropower source (RIMS) technologies have been developed to safely and efficiently convert the energy released from radioactive decay to either electrical or mechanical power. The ability to generate usable, long-lasting power in a compact package is critical for varied hostile environment applications (spaced based). When compared to chemical batteries, nuclear batteries have a much greater specific energy density and can operate in inaccessible and extreme environments. Also, power requirements of modern microelectromechanical (MEMS) systems are low enough to consider the incorporation of RIMS as a viable power source. A review of different types of conversion technologies as well as ideal radionuclides will be evaluated and potential applications will be discussed.

NUCL 80

Development of a betavoltaic device

Viswanath Krishnamoorthy, *wish@qynergy.com.Qynergy Corporation, Albuquerque, NM 87106, United States*

Qynergy engineers have developed an NRC licensed betavoltaic device based on a high energy Kr-85 beta emitting radioisotope. This presentation documents the development of this NRC licensed device. The device is a p-i-n diode fabricated using SiC. The radiation hardness of SiC is necessary for withstanding the high energy beta radiation. The optimal isotopes were determined as Kr-85 and Pm-147 based on a detailed evaluation process that considered several factors including isotope cost, availability, enrichment, energy of the beta particle and energy density. Once the isotope was chosen, the device was designed and fabricated. The layer thickness and doping was varied for the different layers and the devices were tested using Kr-85 and P-33 radioisotope sources. P-33 was used as a testing surrogate for Pm-147. Efficiencies of 11% and 1.5% were obtained when tested under P-33 and Kr-85, respectively. Aging studies were conducted over several weeks to evaluate device degradation. The studies showed no degradation under P-33 and initial degradation that tapered off over time under Kr-85. Packages were designed and fabricated for Kr-85 and Pm-147 devices. The packages were tested for NRC compliance. Based on the test results an NRC compliant package was fabricated. An isotope loading procedure was developed for loading Kr-85. Multiple devices were fabricated and loaded with 650mCi of Kr-85. After some initial degradation, these devices consistently delivered >1uW of power over a year of monitoring.

NUCL 81

Simulations of novel nuclear battery concepts

Mark A Stoyer[1], *mastoyer@llnl.gov, Rebecca J Nikolic*[2], *Victor P Karpenko*[2], *Roger A Henderson*[3], *Lars F Voss*[2], *Adam M Conway*[2], *Qinghui Shao*[2], *Clint D Frye*[2]. *(1) Physics Division, LLNL, Livermore, CA 94550, United States (2) Engineering, LLNL, Livermore, CA 94550, United States (3) Chemistry, LLNL, Livermore, CA 94550, United States*

Beta-voltaic batteries have been studied for 50 years [1] and have included the development of low power nuclear batteries utilizing tritium [2] and radiation resistant nuclear batteries [3]. Less attention has been devoted to alpha-voltaic batteries, although some work has tested alpha emitters [4]. We present simulations of novel nuclear battery geometries, including 3D structures and concentrating on alpha-emitters to maximize electron-hole pair production. SRIM calculations were performed for a variety of potential semiconductor materials. Electron/hole pair calculations for several radionuclides were performed to estimate current production as a function of the lifetime of the battery. Some initial radionuclide coating strategies were tested with ^{233}U as a long-lived surrogate on various Si substrates. Radiation resistant, self-annealing, or annealable materials will be discussed and initial small scale tests will be shown.

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

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NUCL 82

^{35}S based liquid semiconductor nuclear battery

Bradley R Nullmeyer[1]*, brnc65@mail.missouri.edu, Alex Garnov*[3]*, Jae Kwon*[1]*, J David Robertson*[2,3]*. (1) Department of Electrical & Computer Engineering, University of Missouri - Columbia, Columbia, Missouri 65211, United States (2) Department of Chemistry, University of Missouri - Columbia, Columbia, Missouri 65211, United States (3) University of Missouri Research Reactor, University of Missouri - Columbia, Columbia, Missouri 65211, United States*

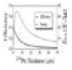
The specific energy density available in radioactive decay is five orders of magnitude greater than the specific energy density available from chemical reactions in traditional batteries and fuel cells. As a result, radioisotope micro-power sources (RIMS) hold great promise for the development of small power sources with dimensions consistent with the miniaturization advances being made in microelectromechanical (MEMS) systems. While a number of conversion schemes can be employed in RIMS, direct voltaic conversion technologies are compatible with the semiconductor manufacturing processes used in MEMS. We are currently investigating the use of liquid semiconductors based betavoltaics as a way to avoid the radiation damage that occurs in solid state semiconductor RIMS devices. The production and use of ^{35}S in liquid semiconductor RIMS will be presented.

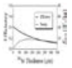
NUCL 83

High efficiency direct energy conversion nuclear battery

Eric Lukosi[1]*, elukosi@utk.edu, Mark Prelas*[2]*. (1) Nuclear Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States (2) Nuclear Science and Engineering Institute, University of Missouri, Columbia, Misouri 65211, United States*

Initial investigations on a novel High Temperature Direct Energy Conversion (HiTDEC) nuclear battery is presented. Initial simulations and radiation damage studies on diamond transducing layers have been conducted to identify the optimal battery design and fabrication methodology. Concentrating on optimizing the battery core mass using ^{239}Pu and $^{90}Sr/^{90}Y$ radioisotopes, we have determined that a theoretical maximum energy density of 70.2 W_e/kg or 18.3 W_e/kg is achievable, respectively, with a conversion efficiency of up to 24% for both radioisotopes. The relationship between radioisotope thickness, energy density (E_{Tot}), and battery efficiency are displayed for ^{239}Pu and $^{90}Sr/^{90}Y$, respectively. Radiation damage studies currently under way will be presented on diamond transducers using 3 MeV alpha particles and $^{90}Sr/^{90}Y$ beta particles at temperatures between 300-800ºK. The effect of temperature on the charge carrier properties of diamond after exposure to ionizing radiation will be quantified via cathodoluminescence (CL), charge collection efficiency (CCE), and the transient current technique (TCT).





NUCL 84

Miniature radioisotope thermoelectric generator shielding design and power generation

Nicholas Baldasaro*, nbaldasaro@rti.org, David Stokes.Electronics and Applied Physics Division, RTI International, Research Triangle Park, North Carolina 27709, United States*

Large-scale Radioisotope Thermoelectric Generators (RTGs) have been successfully developed for long-range satellite, remote unmanned station, and planetary rover applications to provide persistent power for sensors, beacons, telemetry and mobility.

However, the challenges associated with miniaturizing the technology for smaller applications have limited the development of the radioisotope micropower sources.

The purpose of this research was to develop a cubic centimeter-scale RTG to produce >10 mW of electric power. Significantly reducing the size of traditional cubic meter-scale RTGs presents several challenges in areas of the thermal and thermoelectric (TE) design, radiation shielding, and radioisotope fuel selection. For this program, we addressed the specific aspects of selecting an appropriate low-dose and procurable radioisotope, thermal parasitic minimization, adequate radiation shielding, long-term design stability, safety and cost minimization. Details of a working prototype mini-RTG will be presented along with qualitative and quantitative information about design tradeoffs.

This research was supported by the Microsystems Technology Office (MTO) of the Defense Advanced Research Projects Agency (DARPA).

NUCL 85

Lanthanide time resolved luminescence: From basics to business

Kenneth N. Raymond*, raymond@socrates.berkeley.edu.Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720-1460, United StatesLumiphore, Inc., Berkeley, CA 94710-2224, United States*

An overview of the design and development of highly luminescent Ln(III) complexes (with Ln = Tb, Eu) for applications in biotechnology will be presented. In particular, developments utilizing the 2-hydroxyisophthalamide (IAM) chelate for Tb(III).(1-3)

These Tb(III) complexes exhibit highly efficient emission (Φ_{total} > 50%), large extinction coefficients (ε_{max} >20,000 M^{-1} cm^{-1}), and long luminescence lifetimes (τ_{H2O}> 2.45 ms) at dilute concentrations in standard biological buffers.The Tb(III) complexes thus formed display long-term stability, with little if any change in their spectral properties (including lifetime, quantum yield, and emission spectrum) over time or in different chemical environments. Functionalized derivatives with terminal amine, carboxylate, and N-hydroxysuccinimide groups suitable for derivatization and protein bioconjugation have also been developed. These bifunctional ligands have been covalently attached to a number of different proteins, and the terbium complexes' exceptional photophysical properties are retained. These compounds establish a new aqueous stability and quantum yield standard for long-lifetime lanthanide reporters. They are now in commercial agents for use in Homogeneous Time Resolved Fluorescence (HTRF) technology. Such assays have become widespread in pharmacology and biotechnology. By using the long-lived luminescence of a lanthanide energy donor, the sensitivity of this assay format can be vastly improved by using time gated excitation and detection. These compounds are now used in commercial products by three different companies.(4)

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NUCL 86

Covalency in actinide extractants

***Stosh A. Kozimor**[1], stosh@lanl.gov, Angela C. Olson[1], Jason M. Keith[2], Enrique R. Batista[1], Richard L. Martin[1], David L. Clark[1], Andrew J. Gaunt[1], Gordon D. Jarvinen[1], Matthias W. Löble[1]. (1) Chemistry, Los Alamos National Laboratory, Los Alamos, NM 87025, United States (2) Chemistry, Colgate University, Hamilton, NY 13346, United States*

Nuclear energy is the most viable alternative to fossil fuel combustion until large-scale renewable energy technologies can be implemented. However, use of nuclear energy is limited by the difficulties in remediation, management, and disposal of nuclear waste and the significant hazard posed by the minor actinides present in spent fuel. Efficient separation of trivalent minor actinides from lanthanide ions represents a long-standing challenge because of the similar chemical properties shared by 4*f*- and 5*f*-elements. For reasons not well understood, some soft-donor ligands (e.g., dithiophosphinic acids, R_2PS_2H) are known to selectively extract actinides from lanthanides, with Am/Eu separation factors on the order of 100,000 observed (Klaehn, J. R. *et al*. *Inorg. Chim. Acta* **2008** , *361*, 2522). It is likely that this phenomenon results from increased covalency with actinides over lanthanides; however, a clear understanding of *f*-element participation in covalent bonding has not been established. Recent pioneering work of Solomon, Hedman, and Hodgson significantly advanced capabilities in ligand K-edge X-ray absorption spectroscopy (XAS) to directly measure covalency in bonding (Solomon, E. I. *et al. Coord. Chem. Rev.* **2005** , *249*, 97). We will discuss the use of ligand K-edge XAS and time-dependent density functional theory (TDDFT) to evaluate a novel family of dithiophosphinate extractants. We investigate $M–S_2PR_2$ orbital mixing for a carefully selected series of dithiophosphinate complexes by comparing the solid-state and solution-phase sulfur K-edge X-ray absorption spectra, in conjunction with TDDFT. The conclusions derived from solid-state S K-edge measurements are validated through comparison with extractants in solution, providing a foundation for *in situ* studies of liquid-liquid extraction systems. Furthermore, we investigate the relative roles of 3*d*, 4*d*, 5*d*, and 6*d*/5*f*-orbitals in M–S covalent bonding and provide preliminary insight into the structure-to-function relationships that may correlate with the selective extraction of trivalent minor actinides from trivalent lanthanides.

NUCL 87

Free-electron laser and synchrotron radiation studies of excitonic states in rare-earth phosphor materials

***Michael F Reid**[1,2], mike.reid@canterbury.ac.nz, Jon-Paul R Wells[1], Pubudu S Senanayake[1], Rosa B Hughes-Currie[1], Alexander J Salkeld[1], Konstantin V Ivanovskikh[1], Roger J Reeves[1,2], Giel Berden[3], Andries Meijerink[4]. (1) Department of Physics and Astronomy, University of Canterbury, Christchurch, Canterbury 8140, New Zealand (2) MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand (3) FELIX Free-Electron Laser Facilility, The Netherlands (4) University of Utrecht, The Netherlands*

Materials doped with rare-earth (lanthanide) ions are widely used in applications, including lighting phosphors, scintillators, lasers, and optical amplifiers. When a phosphor material is excited by high-energy UV or X-ray radiation, electrons may be ejected from the ions into the conduction band, leaving a hole in the valence band. This can lead to the formation of an exciton, where an electron and hole form a bound state.

Impurity-trapped excitons (ITEs) in rare-earth doped phosphor materials play an important role in both radiative and non-radiative decay processes [1]. We have demonstrated a method to directly measure the energy levels and dynamics of ITEs in various fluoride hosts [2,3]. A UV pulse is used to excite divalent ytterbium ions. The excited electron de-localises, forming the ITE state. IR excitation from the Dutch free electron laser (FELIX) is probes intra-excitonic transitions which can be observed as an enhancement of exciton photoluminescence. We observe sharp transitions arising from changes in the wavefunction of the localised 4f hole and broad bands associated with rearrangement of the delocalized electron.

We have also made measurements using UV and VUV radiation at a synchrotron facility, studying both bulk crystals and nano-scale layered structures. These experiments allow us to monitor energy transfer between conduction-band electrons and ITEs. Measurements at different temperatures give insight into the coupling between bulk and localized states.

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NUCL 88

Spectroscopy properties and hydration of Eu(III) and Cm(III) aqua ions at elevated temperatures

***Guoxin Tian**, gtian@lbl.gov, Linfeng Rao, Norman M. Edelstein.Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

The optical absorption, fluorescence excitation, and emission spectra of the Eu(III) and Cm(III) aqua ions in 0.001 M perchloric acid were studied in pure H_2O, pure D_2O, and mixtures of H_2O-D_2O at temperatures from 10 to 85 °C. The quantum yields of the fluorescence of the Eu(III) and Cm(III) aqua ions in pure H_2O and D_2O were also measured in this temperature range and the radiative decay rate constants were obtained from these data. The results indicate that, from 10 to 85 °C, the effect of temperature on the absorption, excitation, and emission spectra is very small for both Eu(III) and Cm(III) aqua ions. By correcting the observed decay rate constants for the radiative rate constants, a set of correlations between the observed fluorescence decay rate constant and the hydration number of Eu(III)/Cm(III) in H_2O at temperatures from 10 to 85 °C was developed.

NUCL 89

High resolution NMR spectroscopy of radioactive solids

***Herman Cho**, hm.cho@pnnl.gov, Nancy Washton, Karl Mueller, Jesse Sears.Pacific Northwest National Laboratory, Richland, WA 99352, United States*

Nuclear magnetic resonance spectroscopy offers great promise as a probe of electronic structure in heavy element systems, yet until recently NMR studies of solids containing actinide isotopes have been constrained by the inability to perform high resolution experiments on radioactive samples. New approaches for securely containing samples during NMR measurements have been introduced in the past few years, and now several groups have begun to apply modern magic-angle-spinning experiments on hazardous radioactive materials, acquiring data of interest to nuclear waste form development, environmental remediation research, nuclear medicine, and fundamental electronic structure theory. The sealed probe technology developed at the Pacific Northwest National Laboratory will be described, and recent applications of MAS methods to radioactive materials presented.

NUCL 90

Recent developments in pentavalent uranium chemistry

***Marinella Mazzanti**, marinella.mazzanti@cea.fr.Department of Nanoscience and Cryogeny, CEA, Grenoble, France, France*

Pentavalent uranium with is $5f^1$ configuration is a good starting point for the study of the magnetic properties, the electronic structure and bonding in actinides and for the development of functional materials.. Moreover the chemistry of pentavalent uranyl and of its polymetallic complexes are relevant in environmental migration of actinides and in spent nuclear fuel separation. We will present different ligand environments leading to unusual pentavalent uranium complexes and to polymetallic complexes of pentavalent uranyl that behave as single molecule magnets.

NUCL 91

Investigating the σ- and π-interactions between U(V) and halide, alkoxide, amide and ketimide ligands

***Wayne Lukens**[1], wwlukens@lbl.gov, Trevor W Hayton[2], Norman M Edelstein[1], Nicola Magnani[1], Skye W Fortier[2], Lani A Seaman[2]. (1) Chemical Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA 94720, United States (2) Department of Chemistry, University of California, Santa Barbara, California 93106, United States*

The octahedral U(V) complexes recently reported by Hayton and co-workers represent a unique opportunity to directly probe the strengths of pi and sigma interactions between uranium and a variety of ligands. These octahedral complexes, $[UX_6]^-$, consist of pentavalent uranium coordinated by a variety of ligands including alkyl (X = CH_2SiMe_3), alkoxide (X = O^tBu), amide (X = NC_5H_{10}), and ketimide (X = $N{=}C^tBuPh$). This family of complexes is ideal for studying f-orbital bonding it spans a range of commonly used ligands in organouranium chemistry and the spectroscopic data necessary to investigate the bonding is available. The bonding in these compounds may be compared to that in the well-known halide complexes ($[UX_6]^-$, X = F, Cl, Br; $CeCl_6^{3-}$; $PaCl_6^{2-}$; NpF_6), which have been extensively investigated. In this study, the MO model developed by Thornley was modified to include the effects of covalency on spin-orbit coupling itself in addition to the effect of covalency on orbital angular momentum. This model is used to fit the optical and EPR spectra for the octahedral f^1 complexes to determine the splitting of the f-orbitals. This information is then used to estimate the stabilization of ligand orbitals due to f-orbital bonding using the estimated energies of the metal and ligand orbitals. The results show that the oxidation state of the metal center is much more important than the identity of the ligand in determining the degree of covalency and the strength of the covalent bond formed between the ligand and the f-orbital. The results can be explained using a second order model.

NUCL 92

Covalency and bond strength in molecular f element compounds from the quantum theory of atoms-in-molecules

***Nikolas Kaltsoyannis**, n.kaltsoyannis@ucl.ac.uk.Department of Chemistry, University College London, London, United Kingdom*

The extent to which the lanthanides and actinides bond covalently to other elements is of great fundamental interest and also of relevance to, for example, minor actinide partitioning technologies. Quantum chemistry allows the detailed study of the electronic structure of f element compounds, and provides many different methods for assessing covalency, including partial atomic charges, orbital compositions and spin densities. None of these analysis tools is ideal, however, in part because they are typically not rooted in physical observables. By contrast, the quantum theory of atoms-in-molecules (QTAIM) approach of Bader and co-workers [1] is based on topological analysis of the electron density, lending it a rigour not always associated with other approaches. It can also offer significant insight into chemical bonding.

In the last few years, we have employed the QTAIM extensively to analyse a variety of lanthanide and actinide molecular electron densities [*e.g.* 2-6]. In this presentation I will explore some results from these studies, and in particular discuss the application of the QTAIM to the strength of actinide–element bonds [7].

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NUCL 93

Modeling the reactivity and formation of gas-phase actinide species

***Wibe A de Jong**[1], WAdeJong@lbl.gov, Samual Odoh[2], Georg Schreckenbach[3]. (1) Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (2) Department of Chemistry, University of Minnesota, Minneapolis, MN 555455-0431, United States (3) Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

The reactivity and formation of actinide species in the gas-phase plays a key role in obtaining insights into the role that 5f-electrons play in actinide chemistry. Computational actinide chemistry models and tolls such as NWCHem complement extensive experimental work and can make significant contributions to the fundamental understanding of how 5f-electrons contribute to the chemical and physical behavior of actinide species. We will present recent results of gas-phase studies on the formation of plutonium complexes and multimeric uranium species.

NUCL 94

Americium and curium: Are they as simple as we would like?

***Gerard H Lander**, lander@ill.fr.European Commission, JRC, Institute for Transuranium Elements, Karlsruhe, Germany 76125, Germany*

Most physicists treat Am and Cm as “simple lanthanide-like” actinide metals. Part of this attitude is related to the relief encountered after discussing the really complex behavior of the light actinides (U, Np, and Pu), and part is related to ignorance, as we have not performed a great number of sophisticated experiments on Am and Cm. This talk will review the experiments, and some theory, that have been performed on these elements at ITU, and elsewhere, over the last decade. Indeed, the properties of these elements do appear simpler than Pu, in particular, but recent experiments under pressure and using the technique of x-ray magnetic circular dichroism, show that we need to be careful in simply attributing the well-known properties of lanthanide elements to Am and Cm. They appear to have their own richness and uniqueness.

NUCL 95

Tritium power source matched for long-lived sensors

*M Litz[1], **D Katsis**[2], dkatsis@vt.edu, J Russo[1], D Burns[1], J J Carroll[1]. (1) RDRL-SED-E, Army Research Laboratory, Adelphi, MD 20783, United States (2) Athena Energy Corp., Bowie, MD 20720, United States*

A tritium-based photovoltaic power source is introduced as a long-lived power source for sensor networks (15 yrs. operational lifetime). We chose tritium as a benign and low-cost isotope. We present our tritium emitter in an indirect-converter design that mates a phosphor (beta to optical converter) to a commercial PV cell (photon to electrical converter). We use this system to provide a direct current of at least 30uA to a sensor payload. The tritium, phosphor and PV are sealed in a NRC-approved military battery (BA5590) with connector and container. This DC energy feeds the 100uW sensor electronics payload. We designed the sensor to detect radiation levels in the energy range of 400 keV to 2 MeV. The electronics in the sensor employ a low-power scintillator-photodiode sensor and a low self-leakage ultra-capacitor coupled to a nano-power microprocessor. By incorporating best practices in energy-efficient circuit design, the sensor can operate over the lifetime of the isotope source. This sensors detects small changes in background radiation; a 20 µCi source of ^{137}Cs can be detected out to a distance of ~three meters (9 ft.). The microprocessor controlled APD, discriminator and counting circuits all together operate within the 100uW average power window of

the isotope power source. We believe that this low-cost approach is the ideal trajectory for the development of low-cost long-lived compact electronics and sensor applications for battlefield and environmental detection.

NUCL 96

Voyages of endurance: The science of space nuclear power

***Christofer E Whiting**[1], chris.whiting@udri.udayton.edu, Dirk Cairns-Gallimore[2], Chadwick D Barklay[1], Daniel P Kramer[1]. (1) Research Institute, University of Dayton, Dayton, OH 45459, United States (2) Space and Defense Power Systems, Department of Energy, Germantown, MD 20874, United States*

From Apollo to Voyager to Curiosity, the Department of Energy's Radioisotope Power Systems (RPS) have been the beating heart powering a majority of NASA's planetary and deep space exploration. Quietly producing electricity using solid-state thermoelectric conversion of heat generated by the radioactive decay of ^{238}Pu, this remarkable technology rarely grabs the spotlight, but without it, headlines about Voyager exploring beyond the heliosheath 35 years after launch, and Curiosity searching for life on Mars simply wouldn't exist. With a perfect track record, the U.S. RPS program continues to impress by safely providing dependable power for space exploration well beyond almost all expectations.

Safely harnessing the energy of a high specific activity isotope like ^{238}Pu has required a lot of innovative science and engineering over the past 60 years including: new methods for the production of the ^{238}Pu fuel; evolution of the fuel-form from metal, to PuO_2–Mo cermet, to the current PuO_2; efficient and safe processing of the PuO_2 material into its final ceramic form; improvements in thermoelectric materials for greater conversion efficiency; rigorous system design to endure the hardships of launch, landing, and interplanetary travel; and most importantly, preventing release and exposure in an accident scenario. Here we will survey the history of the RPS program and discuss some of the scientific and engineering accomplishments that have successfully guided the program throughout the solar system and beyond.

NUCL 97

Warfighter power needs and lightening the load

***Howard Choe**, choe@raytheon.com.Raytheon Company, McKinney, TX 75023, United States*

We enjoy mobile electronics, e.g., smart phones, tablets, etc. We also often are frustrated as the battery bar becomes short and the device's screen eventually goes to black, especially when we have no charger in hand or when there is not an electrical outlet nearby. But such frustration is typically short-lived for most of us as we can recharge the mobile electronics at home, office, restaurants, airport, and so on.

However, this is not the case for our warfighters on foot in battlefield. Exhausted battery in warfighter's portable electronics, e.g., radios, GPS, weapon sights, flashlight, etc., directly impacts his/her warfighting capabilities, and subsequently his/her life. Of the 100 pounds in the load, approximately 25 percent is from batteries in order to avoid the situations of running out of battery power and to power all electronic devices a warfighter carries. If the battery load can be decreased, while still allowing the devices to be powered, the warfighter could carry more ammunition, water and other warfighting gear. Or it will simply help the soldier feel less fatigued when on the battlefield. At Raytheon, understanding our warfighters' needs for lightening the load while extending portable power life, Raytheon and its collaborators have been working to find the solutions for our warfighters ranging from long duration high density ultra capacitors, photovoltaic power system, fuel cell, intelligent power and energy management and others. In this presentation, we will review the historical soldier's load weight, modern warfighter's power needs and requirements, research areas in soldier power, and one of Raytheon's projects associated with the solider power needs.

NUCL 98

Betavoltaic power sources for ultra low power electronics

Christopher Thomas[1], *cthomas@widetronix.com, Samuel Portnoff*[1], *Michael Spencer*[2]. *(1) Widetronix, Inc., Ithaca, NY 14850, United States (2) Department of Electrical and Computer Engineering, Cornell University, Ithaca, NY 14850, United States*

Betavoltaics use the electron voltaic effect in semiconductor junctions to harvest the energy of beta particles, producing a direct current output. The promise of betavoltaic technology lies in its ability to create an extremely high energy density power source. Other key advantages of the technology are long operational lifetimes, ability to operate in harsh environments, and scalability down to board and chip level integration. Widetronix is developing betavoltaics from silicon carbide (SiC), which, due to its wide bandgap and low leakage currents, enables the design of betavoltaic devices with high conversion efficiencies (> 20%) and a high open circuit voltage (2.0 V). The current line of planar SiC devices, when connected in series and parallel like traditional batteries, can generate up to 0.38 $\mu W/cm^3$ continuously for over a decade, this can be increased to over 1.0 $\mu W/cm^3$ with wafer thinning. Widetronix has also begun to fabricate textured betavoltaics that will increase the power density of a 1 cm^3 betavoltaic stack by a factor of 100. This enables Widetronix to achieve energy densities over 100 times greater than Li-ion battery technologies for battery sizes below 1 cc. Widetronix has built betavoltaic enabled electronics to perform sensor measurements (temperature, light, etc) on a given duty cycle between active and sleep modes. Charge from the betavoltaic is accumulated in either capacitors or thin film rechargeable batteries while directly powering the circuit sleep mode power draw and this accumulated power is then used to power the active cycle of the circuit and store the data. The next generation of Widetronix electronics is designed to not only take and store sensor measurements, but also to transmit the data via Bluetooth 4.0.

NUCL 99

Isotopic oxygen exchange kinetics and mechanisms with $^{238}PuO_2$

Christofer E Whiting[1], *chris.whiting@udri.udayton.edu, L Kevin Felker*[2], *Robert M Wham*[2], *Chadwick D Barklay*[1], *Daniel P Kramer*[1]. *(1) Research Institute, University of Dayton, Dayton, OH 45469, United States (2) Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

$^{238}PuO_2$, the fuel used in Radioisotope Power Systems for space exploration, undergoes a secondary (α,n) reaction with the naturally occurring ^{17}O and ^{18}O found in the oxide. This (α,n) is the primary source of worker dose rates and can have a detrimental impact on spacecraft components. Currently, isotopic exchange with ^{16}O is used to minimize the (α,n) reaction, but the kinetics and mechanism of this reaction are not well understood. Previous work on CeO_2 suggests that the rate limiting step in the oxygen isotopic exchange rate for CeO_2 and PuO_2 is small polaron hopping (i.e. the movement of Ce^{3+} through the material), which is very interesting because this suggests that the exchange rate would be independent of the atmospheric composition and the physical characteristics of the PuO_2 powder.

New experiments to study the oxygen isotopic exchange kinetics and mechanism on $^{238}PuO_2$ are in the planning stage. Results from these experiments will be presented and compared to previous PuO_2 and CeO_2 exchange data in an attempt to determine the full rate law, mechanism, and thermodynamic properties of this reaction.

NUCL 100

Connecting the molecular and solid-state chemistry of technetium

Alfred P. Sattelberger, *asattelberger@anl.gov.Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Argonne, IL 60439, United StatesDepartment of Chemistry, University of Nevada Las Vegas, Las Vegas, NV 89154, United StatesDepartment of Chemistry, Northwestern University, Evanston, IL 60208, United States*

Almost every element in the periodic table has well-defined halide chemistry. Technetium, the first radioelement, is a notable exception. Prior to 2008, only 3 binary halides of technetium had been reported, *viz.*, TcF_6, TcF_5 and $TcCl_4$. These compounds were prepared almost 60 years ago from the reactions of the metal with F_2 or Cl_2. Since 2008, a team of scientists at Argonne, UNLV and Northwestern has synthesized and characterized an additional 6 binary halides, including two polymorphs of $TcCl_3$, $TcCl_2$, $TcBr_4$, $TcBr_3$ and TcI_3, and several related cluster compounds. These new halides can be binned into one of three categories: (1) those that have molybdenum and/or ruthenium analogues, (2) those that have rhenium analogues, and (3) those for which

no analogues with neighboring elements currently exist. The synthetic routes to the new halides and their relationship to molecular technetium systems will be described. Solid-state structures, thermal stabilities, and selected aqueous and non-aqueous chemistry will be discussed. The synthesis of these new halide compounds opens up exciting new opportunities for exploring the synthetic and mechanistic chemistry of low-valent technetium, as well as the possibility of new applications for the nuclear fuel cycle.

NUCL 101

Synthesis and reactivity of thorium and uranium complexes with soft donor ligands

*Andrew C Behrle, **Justin R Walensky**, walenskyj@missouri.edu.Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States*

Soft donor ligands have received more attention in recent years due to their selectivity in separation of actinides from lanthanides. We have synthesized a number of homoleptic complexes with soft donor ligands (especially dithio- and diselenophosphonate) and examined their structure, spectroscopy, and reactivity. ^{77}Se and ^{31}P NMR spectroscopy and Se K-edge measurements are used to correlate the electronic and molecular structures. We have also used the 2,2'-selenobis(4,6-di-*tert*-butylphenolate), (OSeO)$^{2-}$, ligand to stabilize Ce(IV), U(IV), U(V), and U(VI) complexes.

NUCL 102

Synchrotron-based investigations of selected actinide-containing systems

***Melissa A Denecke**, melissa.denecke@manchester.ac.uk.Dalton Nuclear Institute, The University of Manchester, Manchester, United Kingdom*

Understanding the chemistry and behavior of the actinide elements and other long lived nuclides under various conditions remains a frontier for discovery. By application of synchrotron-based spectroscopy techniques and combining or extending insights into the coordination chemistry [1,2,3], redox behavior [4] and spectroscopic features [5] gained from past investigations, more recent studies have increased our level of understanding, thus enabling us to, e.g., evaluate performance of partitioning ligands [6], to more reliably predict radionuclide behavior in environmental systems [7], such as those related to the long-term safety of nuclear waste repositories, and to characterize electronic structure [8] as a tool for fundamental understanding of actinide behavior.

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NUCL 103

Functionalization and characterization of uranium bis- and tris(Imido) complexes supported by pyridine(diimine) ligands

***Suzanne C Bart**, sbart@purdue.edu, Nickolas H Anderson, John J Kiernicki, Phillip E Fanwick.Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States*

Our laboratory has synthesized uranium bis- and tris(imido) complexes bearing pyridine(diimine) ligands. These species have been characterized using a variety of spectroscopic and computational methods, which has have uncovered unusual electronic structures in some cases. The reactivity of these species towards small molecules including isocyanates, carbon dioxide, and iodotrimethylsilane will be discussed as well as their characterization by spectroscopic methods and X-ray crystallography.

NUCL 104

Oxo ligand exchange of actinyl ions

***David L Clark**, dlclark@lanl.gov.National Security Education Center, Los Alamos National Laboratory, Los Alamos, NM 87545, United States*

The light actinide elements in their higher oxidation states form a unique series of trans dioxo cations, AnO_2^{2+} (U, Np, Pu, Am). These cations are remarkably stable and characterized by a covalent An-O triple bond that is chemically inert under a broad range of neutral to acidic aqueous conditions. Under strongly alkaline solutions, we found that the oxo ligands exchange readily with water solvent. The stoichiometry, chemical composition, electronic structure, and highly unusual oxo ligand exchange of the actinyl(VI) ion in strongly alkaline solutions will be discussed.

NUCL 105

Adducts to Cp^x_2Yb as analogs to metals displaying the Kondo effect under quantum confinement

Corwin H. Booth[1], *chbooth@lbl.gov, Wayne W. Lukens*[1], *Richard A. Andersen*[1,2]. *(1) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (2) Department of Chemistry, University of California, Berkeley, CA 94720, United States*

Beginning with Peter Fulde's suggestion in the late 1980s that a molecular analogue to the Kondo effect may exist in certain Ce- and Yb-based organometallic molecules, an incredibly rich array of adducts to Cp^*_2Yb have been synthesized that demonstrate intermediate valence in Yb in conjunction with magnetic singlet formation, two coupled hallmarks of the Kondo effect. Although a metallic band does not exist in these molecules, and therefore the comparison to the Kondo effect remains only a strong analogy, these molecules are essentially quantum-confined metals where the conduction band is eliminated by size effects, and therefore should be thought of as quantum confined Kondo materials. These molecules and our progress in sythesizing and studying them will be reviewed (including Norman's role), with an emphasis on the temperature dependence of the x-ray spectroscopy and the magnetism. Progress toward understanding these molecules in terms of multiconfigurational ground states and the role of covalence will also be described.

NUCL 106

Comparison of experimental and calculated (on the basis of density functional theory) frequencies of normal vibrations of $LaCp_3(NCCH_3)_2$, $La(C_5Me_4H)_3$ and $La(C_5Me_5)_3$

Hanns-Dieter Amberger, *fc3a501@uni-hamburg.de, Hauke Reddmann.Chemie, Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Hamburg, Germany*

Little is known about the vibrational structures of homoleptic pseudo(y)-trigonal-planar complexes of f elements with unsubstituted, partly and totally methyl substituted cyclopentadienyl ligands.

In the frame of our search for direct f-f transitions in the far (FIR) and mid (MIR) infrared ranges (pellets, polyoil suspensions) and polarized electronic Raman transitions

(oriented single crystals) of y-trigonal-bipyramidal $LaCp_3(NCCH_3)_2$:Ln^{3+} [1] as well as (y)-trigonal-planar $Ln(C_5Me_4H)_3$ [2] and $La(C_5Me_5)_3$ [3] (Ln = Ce, Pr, Nd, Sm) we also obtained the vibrational spectra of these complexes and the corresponding La compounds.

In case of the two latter classes of complexes, the principle axes of the two molecules per unit cell are aligned and thus the simple selection rules of C_{3h} symmetry may be applied in order to determine the irreps of the observed normal vibrations. The four $LaCp_3(NCCH_3)_2$ (**1**) molecules are pairwise perpendicular to each other. For this reason, the selection rules for analyzing the FIR/MIR and polarized Raman spectra are rendered somewhat more complicated.

The thus experimentally derived irreps (and frequencies) of normal vibrations of **1** , $Ln(C_5Me_4H)_3$ (**2**) and $La(C_5Me_5)_3$ (**3**) were compared to the results of model calculations on the basis of density functional theory assuming molecular C_{3h} symmetry [4-6]. Omitting the nCH normal modes, the calculated frequencies were 5-25 cm^{-1} lower than the experimental ones. This holds for both the skeletal and the intra-ligand normal vibrations. In case of compound **2** , for example, an r.m.s. deviation of 22.1 cm^{-1} (71 assignments) could be achieved [5].

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NUCL 107

Fifty years of actinide science at the Lawrence Berkeley National Laboratory

***Norman M Edelstein**, NMEdelstein@lbl.gov.Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

In November, 1964, I joined the Actinide Chemistry Group, which was led by Professor Burris B. Cunningham, after spending two years of postdoctoral research at Harvard University with Professor August H. Maki working on 3d transition metal complexes. At the time I knew where the actinides were in the periodic table and not much else about them. It turns out that the High Flux Reactor (HIFR) at ORNL had just started producing the transcurium isotopes in relatively high abundance and the Cunningham group was carrying out investigations of these elements to understand their basic chemical properties. My job was to investigate the magnetic properties of these elements using electron paramagnetic resonance (EPR). In this talk I will describe some of the highlights of my work in actinide chemistry during my career at LBNL.