Department of Energy
Office of Science
Chemical Sciences, Geosciences and Biosciences Division

Heavy Element Chemistry Contractors' Meeting

Advanced Photon Source Office Building
Argonne National Laboratory

November 19 - 21, 2000

Program and Abstracts

Heavy Element Chemistry Contractors' Meeting

November 19 - 21, 2000

Program

Sunday, November 19, 2000; 1630 - 2100 Put up posters in APS Office Building Gallery

Monday Morning, November 20, 2000

700 - 900 Breakfast at the hotel; Poster set up in APS Office Building Gallery

900 Start of meeting - APS Office Building - E1100 and E1200

900 - 905	Edelstein, Norman	Welcome and Introductions	Department of Energy, Office of Science, Chemical Sciences, Geosciences and Biosciences Division
905 - 930	Smith, Paul	The View of Heavy Element Chemistry from DOE, Washington	Department of Energy, Office of Science, Chemical Sciences, Geosciences and Biosciences Division

930 Short presentations - Oral session I - APS Office Building - E1100 and E1200

Gas Phase

930	Gibson, John	P1-1	GAS-PHASE ACTINIDE ION CHEMISTRY	Oak Ridge National Laboratory
940	Nitsche, H.	P1-2	SUPERHEAVY ELEMENT CHEMISTRY STUDIES AT THE BERKELEY GAS-FILLED SEPARATOR	Chemistry Department, University of California, Berkeley, Nuclear Science Division, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory

Solid State

950	Dorhout, Peter K.	P1-3	STRUCTURAL RELATIONSHIPS AND UNIQUE ASPECTS OF ACTINIDE CHALCOPHOSPHATE MATERIALS: Th, U, Pu.	Department of Chemistry, Colorado State University
1000	Assefa, Z.	P1-4	SPECTROSCOPIC INVESTIGATIONS OF ACTINIDES IN THE SOLID STATE	Oak Ridge National Laboratory
1010	Beitz, J. V.	P1-5	SYNTHESIS AND PHOTOPHYSICS OF HEAVY ELEMENT-CONTAINING NANOPHASES	Chemistry Division, Argonne National Laboratory
1020	Dewey, H. J.	P1-6	ACTINIDE CHEMISTRY UNDER NEAR-NEUTRAL CONDITIONS: 3. EMISSION FROM NEPTUNYL IONS IN THE NEAR IR	Los Alamos National Laboratory
1030	Meek,Thomas	P1-7	THERMOELECTRIC PROPERTIES OF UO2	University of Tennessee, Knoxville

1040 - 1140 Coffee break and Poster Session I - APS Office Building Gallery

1140 Short presentations - Oral session II - APS Office Building - E1100 and E1200

1140	Booth, Corwin H.	P2-1	LOCAL COORDINATION EFFECTS, f-ELECTRON LIGATION AND MAGNETIC BEHAVIOR IN ACTINIDE INTERMETALLICS	Chemical Sciences Division, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory
1150	Conradson, Steven D.	P2-2	HETEROGENEITY AND PHASE SEPARATION IN CRYSTALLINE SOLIDS – MOSTLY CONTAINING PLUTONIUM	Materials Science and Technology Division, Los Alamos National Laboratory
1150	Conradson, Steven D.	P2-3	LOCAL AND NANOSCALE STRUCTURE IN COMPLEX SYSTEMS: A CONFERENCE SCHEDULED FOR SEPTEMBER, 2001, IN SANTA FE	Materials Science and Technology Division, Los Alamos National Laboratory
No oral presentation	Haire, R. G.	P2-4	EXPLORING HEAVY-ELEMENT SCIENCE USING PRESSURE	Oak Ridge National Laboratory
1200	Liu, G. K.	P2-5	ADVANCES IN HEAVY ELEMENTS PHOTOPHYSICS AND LASER SPECTROSCOPY	Chemistry Division, Argonne National Laboratory
1210	Neu, Mary P.	P2-6	STRUCTURES OF PLUTONIUM COORDINATION COMPOUNDS: RECENT SINGLE CRYSTAL X-RAY DIFFRACTION RESULTS	Chemistry Division, Los Alamos National Laboratory

Solutions

1220	Bryan, Jeffrey C.	P2-7	FUNDAMENTAL STUDIES AND APPLICATIONS OF CALIX[4]ARENE-CROWN-6 COMPOUNDS	Oak Ridge National Laboratory
1230	Paine, Robert T.	P2-8	PREORGANIZED and IMMOBILIZED LIGANDS FOR METAL ION SEPARATIONS	Department of Chemistry, University of New Mexico

1240 Lunch served in the APS Office Building Gallery

1330 - 1430 Poster Session II - APS Office Building Gallery

1430 Short presentations - Oral session III - APS Office Building - E1100 and E1200

1430	Rao, Linfeng	P3-1	CHEMICAL THERMODYNAMICS OF ACTINIDES IN SOLUTION UNDER NON-CONVENTIONAL CONDITIONS	Glenn T. Seaborg Center, Chemical Sciences Division, Lawrence Berkeley National Laboratory
1440	Jensen, Mark P.	P3-2	INFLUENCE OF COVALENCY, COMPLEX STRUCTURE, AND SOLVATION ENERGETICS ON ACTINIDE COMPLEXATION	Chemistry Division, Argonne National Laboratory
1450	Andersen, Richard	P3-3	[1,2,4-(CMe3)3C5H2]2 U(bipy): A METALLOCENE OF URANIUM (II)?	Chemistry Department and The Chemical Science Division of Lawrence Berkeley National Laboratory, University of California
1450	Andersen, Richard	P3-4	[1,2,4-(C Me3)3 C5H2]2 Ce(bipy): A METALLOCENE OF Ce (II)?	Chemistry Department and The Chemical Science Division of Lawrence Berkeley National Laboratory, University of California

1500	Antonio, Mark R.	P3-5	HEAVY-ELEMENT POLYOXOANION CHEMISTRY	Chemistry Division, Argonne National Laboratory
1510	Keogh, D. Webster	P3-6	ACTINIDE CHEMISTRY UNDER NEAR-NEUTRAL CONDITIONS: 1. INTERACTION OF MACROCYCLES WITH ACTINIDE IONS	Los Alamos National Laboratory and the Glenn T. Seaborg Institute for Transactinium Science
1510	Clark, David L. and Keogh, D. Webster	P3-7	ACTINIDE CHEMISTRY UNDER NEAR-NEUTRAL CONDITIONS: 2. LIMITING SPECIES IN THE AN(IV) AND LN(III) CARBONATE SYSTEMS AS A TEACHING TOOL FOR NUCLEAR SCIENCE EDUCATION	Los Alamos National Laboratory and the Glenn T. Seaborg Institute for Transactinium Science
1520	Williams, C.W.	P3-8	THE REDOX SPECIATION OF NEPTUNIUM IN ACIDIC AND ALKALINE SOLUTIONS	Chemistry Division, Argonne National Laboratory
1530	Clark, David L.	P3-9	ACTINIDE CHEMISTRY UNDER ALKALINE CONDITIONS: 1. COORDINATION CHEMISTRY OF HEPTAVALENT NEPTUNIUM	Los Alamos National Laboratory and the Glenn T. Seaborg Institute for Transactinium Science

1540 - 1630 Coffee break and Poster Session III - APS Office Building Gallery

1630 Short presentations - Oral session IV - APS Office Building - E1100 and E1200

1630	Neu, Mary P.	P4-1	ACTINIDE CHEMISTRY UNDER ALKALINE CONDITIONS: 2. HYDROLYSIS OF PLUTONIUM(VI)	Chemistry Division, Los Alamos National Laboratory
1640	Sudowe, R.	P4-2	MODEL SYSTEMS FOR THE STUDY OF THE CHEMICAL BEHAVIOUR OF ELEMENT 104 BY SOLVENT EXTRACTION AND EXTRACTION CHROMATOGRAPHY	Nuclear Science Division, Lawrence Berkeley National Laboratory
No oral presentation	Laue, Carola A. and Allen, P. G.	P4-3	TRANS-ACTINIDES—EXPLORING CHEMICAL PROPERTIES OF ELEMENT 114*	Seaborg Institute, Analytical & Nuclear Chemistry Division, Lawrence Livermore National Laboratory
1650 - 1710 REDC presentations	Alexander, C. W.	P4-4	PLUTONIUM-238 PRODUCTION TESTS	Oak Ridge National Laboratory
1650 - 1710 REDC presentations	Benker, D. E.	P4-5	RESEARCH, DEVELOPMENT, AND DEMONSTRATION CAPABILITIES AT THE RADIOCHEMICAL ENGINEERING DEVELOPMENT CENTER	Oak Ridge National Laboratory
1650 - 1710 REDC presentations	Collins, E. D.	P4-6	MEASUREMENT OF ACHIEVABLE PLUTONIUM DECONTAMINATION FROM GALLIUM BY MEANS OF PUREX SOLVENT EXTRACTION	Oak Ridge National Laboratory
1650 - 1710 REDC presentations	Felker, L. K.	P4-7	PRODUCTION, RECOVERY, AND PURIFICATION OF “SPECIAL” ACTINIDES	Oak Ridge National Laboratory

1650 - 1710 REDC presentations	Martin, R. C.	P4-8	DEVELOPMENT OF MINIATURE HIGH-DOSE-RATE 252Cf SOURCES FOR BORON-ENHANCED AND FAST NEUTRON BRACHYTHERAPY	Oak Ridge National Laboratory
1650 - 1710 REDC presentations	Knauer, J. B.	P4-9	RESEARCH AT THE CALIFORNIUM USER FACILITY FOR NEUTRON SCIENCE	Oak Ridge National Laboratory
1720	Burns, Carol J.	P4-10	URANYL ALKOXIDE CHEMISTRY	Chemistry Division, Los Alamos National Laboratory
1720	Burns, Carol J.	P4-11	ACTINIDE-OXO CHEMISTRY IN THE PRESENCE OF STRONG DONOR LIGANDS	Chemistry Division, Los Alamos National Laboratory

1730 - 1830 Poster Session IV - APS Office Building Gallery

1830 Buffet dinner in APS Office Building Gallery

2000 Short presentations - Oral session V - APS Office Building - E1100 and E1200

Interfaces

2000	Chiarizia, R.	P5-1	ORGANIZATION OF SOLUTE SPECIES IN ORGANIC MEDIA	Chemistry Division, Argonne National Laboratory
2010	Gregorich, K.E.	P5-2	EXTENDING THE PERIODIC TABLE: CHEMICAL PROPERTIES OF TRANSACTINIDE AND SUPERHEAVY ELEMENTS	Nuclear Science Division, Lawrence Berkeley National Laboratory, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory

2020	Wilk, Philip	P5-3	FIRST SUCCESSFUL CHEMICAL STUDY OF BOHRIUM (BH, ELEMENT 107)	Nuclear Science Division, Lawrence Berkeley National Laboratory, Chemistry Department, University of California
2030	Nash, Kenneth L.	P5-4	KINETICS OF ACTINIDE COMPLEXATION AND ITS IMPACT ON UNDERSTANDING CHEMICAL PROCESSES IN AQUEOUS AND ORGANIC SOLUTIONS	Chemistry Division, Argonne National Laboratory
2040	Van Horn, J. David	P5-5	ACTINIDE COORDINATION CHEMISTRY FOR THE DESIGN OF DECORPORATION AGENTS, SENSORS, EXTRACTANTS, AND NOVEL STRUCTURES	Lawrence Berkeley National Laboratory and Department of Chemistry, University of California, Berkeley
2050	Dietz, Mark L.	P5-6	METAL ION RECOGNITION IN CHEMICAL SEPARATIONS: STEREOCHEMICAL, SYNERGISTIC, AND SOLVENT EFFECTS IN METAL ION SEPARATIONS USING CROWN ETHERS	Chemistry Division, Argonne National Laboratory

2100 - 2200 Poster Session V - APS Office Building Gallery

Tuesday, November 21

700 - 830 Breakfast at the hotel

830 Short presentations - Oral session VI - APS Office Building - E1100 and E1200

830	Bursten, Bruce E. and Li, Jun	P6-1	RELATIVISTIC DENSITY FUNCTIONAL STUDIES OF THE STRUCTURE AND BONDING OF EXPERIMENTALLY-RELEVANT ACTINIDE SYSTEMS	Department of Chemistry, The Ohio State University
840	Shuh, David K.	P6-2	SOFT X-RAY SYNCHROTRON RADIATION INVESTIGATIONS OF ACTINIDES	Chemical Sciences Division, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory

850	Bucher, J.J.	P6-3	MULTI-PIXEL MONOLITHIC GE FLUORESCENCE DETECTOR, PULSE SIGNAL PROCESSING ELECTRONICS, AND A REAL TIME DIGITAL DATA ACQUISTION SYSTEM FOR XAFS STUDIES	Chemical Sciences Division and G.T. Seaborg Center, LBNL
900	Skanthakumar, S.	P6-4	THE USE OF HIGH-ENERGY X-RAY SCATTERING TO PROBE THE SOLUTION STRUCTURE OF PU “POLYMER”	Chemistry Division, Argonne National Laboratory
910	Nitsche, H.	P6-5	LASER SPECTROSCOPIC INTERFACIAL STUDIES OF ACTINIDES ON BACTERIA AND MINERAL SURFACES	Chemistry Department, University of California, Berkeley, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory
920	Allen, P. G.	P6-6	SURFACE INTERACTIONS OF ACTINIDE IONS WITH GEOLOGIC MATERIALS	Seaborg Institute, Analytical & Nuclear Chemistry Division, Lawrence Livermore National Laboratory
930	Soderholm, L.	P6-7	THE ACTINIDE FACILITY	Chemistry Division, Argonne National Laboratory

940 - 1030 Poster Session VI and Coffee Break - APS Office Building Gallery

Discussion sessions - APS Office Building - E1100 and E1200

1030 - 1120	All	Group Discussion - Gas Phase and Interface Chemistry	John Gibson, Heino Nitsche, and Lynne Soderholm
1120 - 1210	All	Group Discussion - Solution Chemistry	Carol Burns, Mark Jensen, Mark Dietz

1220 - 1300 Lunch - APS Office Building Gallery

Discussion sessions - APS Office Building - E1100 and E1200

1300 - 1350	All	Group Discussion - Solid State	David Shuh, Peter Dorhout
1350 - 1440	All	Group Discussion - Other topics	David Clark, Ken Gregorich, Bruce Bursten
1440 - 1530	All	Group Discussion - Conclusion of meeting	

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Poster Abstracts

GAS-PHASE ACTINIDE ION CHEMISTRY [*]

John Gibson
Richard Haire and Zerihun Assefa
Oak Ridge National Laboratory

A powerful approach to elucidating fundamental aspects of transition metal chemistry is the study of reactions of bare and ligated metal ions. In contrast to condensed phase chemistry, gas-phase ion - molecule reactions are simple two-body encounters that occur in the absence of secondary influences, such as competing reactions, solvation, and crystal fields. Accordingly, gas-phase reaction pathways and efficiencies can directly reveal intrinsic ion - molecule interactions. Techniques are available to probe reaction mechanisms, and the bonding and structures of product complexes. Also, elementary product complexes are amenable to theoretical modeling. For actinides, other advantages of this investigative approach are that only sub-milligram amounts of material are needed and self-radiation is not detrimental.

We employ a laser ablation time-of-flight mass spectrometry technique to study gas-phase chemistry of actinide ions, An^+. To date, we have examined reactions of ten actinide ions, Th^+ through Es^+, and the emphasis has been on reactions with hydrocarbons, where a primary reaction channel is dehydrogenation via C-H activation. The results indicate that dehydrogenation efficiencies are inversely related to the energies required to promote an actinide ion 5f electron to a 6d orbital. Evidently, two non-5f valence electrons are required at the metal center to form a $C\text{-}An^+\text{-}H$ activated intermediate, as the quasi-valence 5f electrons are ineffective at sigma-type organometallic bonding. The 5f-to-6d promotion energies range from zero for Np^+ ($5f^4 6d^1 7s^1$ ground state) to 400 kJ mol^{-1} for Es^+, and reaction cross sections vary by several orders of magnitude across the series. Tremendous fluctuations in gas-phase ion chemistry emerge within the actinide series that are not apparent in the condensed phase. The gas-phase chemistry of oxo-ligated actinide ions was also investigated, and anomalous results for UO^+ suggest that the 5f electrons of uranium may be chemically active. Other types of reactant molecules have been employed, and demonstrated novel actinide reactions and complexes.

Our second major thrust in this area is the synthesis and characterization of gas-phase actinide oxide clusters. As clusters contain multiple metal atoms, they represent a nanoscale form of matter intermediate between the molecular and solid states and can be studied to probe the nature of solids and gas-solid interactions. We have synthesized a variety of binary and mixed oxide clusters where the initial emphasis was on exploring variations in oxidation state stabilities among the actinides. One example is mixed $UPuO_x^+$ cluster ions. Both $UPuO_2^+$ and $Pu_2O_2^+$ (average actinide valence = +2.5) formed (without $U_2O_2^+$). Simultaneously, $UPuO_4^+$ and $U_2O_4^+$ (average valence = +4.5) formed (without $Pu_2O_4^+$). Results such as these demonstrate clearly the lower propensity for the heavier actinides to exist in high oxidation states. We are pursuing a novel approach to synthesize larger actinide oxide clusters with the intent of studying their structures and chemistries to illuminate the behavior of solid materials. We have synthesized plutonium oxide clusters as large as $Pu_{18}O_{23}^+$, have proposed potential nanocrystalline structures, and demonstrated that chemical reactions of actinide oxide clusters can be studied. These preliminary cluster studies open the possibility for preparing nanoscale actinide materials with new properties, and elucidating important processes (e.g., the water-catalyzed oxidation of plutonium).

We are now extending our gas-phase actinide ion - molecule reaction and cluster studies into new directions. Development of a quadrupole ion trap mass spectrometer for transuranics will allow further characterization of actinide atomic, molecular and cluster ion chemistry, as well as the structures and bonding of complexes. Experiments may also be performed in a Fourier transform ion cyclotron resonance mass spectrometer. Ultimately it would be desirable to explore transeinsteinium ion chemistry, to pursue whether relativistic effects modify electronic structures and energetics. These encompassing experimental results will ultimately enable accurate modeling and predictions of actinide and transactinide electronic structures and bonding.

[*] Sponsored by the Office of Science, U.S. Department of Energy

SUPERHEAVY ELEMENT CHEMISTRY STUDIES AT THE BERKELEY GAS-FILLED SEPARATOR

U.W. Kirbach[1, 3], H. Nitsche[1, 2, 3], K.E. Gregorich[1, 3], D.C. Hoffman[1, 2, 3], V. Ninov[1]

[1] Nuclear Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA
[2] Chemistry Department, University of California, Berkeley, CA
[3] The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, CA

Superheavy element chemistry research is used to determine the position of new elements in the periodic table of elements. Currently the last chemically studied superheavy element is bohrium, element 107. Elements in this mass region are radioactive with half-lives of few seconds and can only be produced in nuclear reactions with very low cross sections.

A new concept for heavy element research is the use of an ion separator prior to the chemistry. The ion separator very quickly separates the compound nucleus from unwanted transfer and by-products. Depending on the kinematics, the Berkeley Gas-filled Separator (BGS) is a highly efficient separator, that can be used to study the chemical properties of the heaviest elements, produced at the Lawrence Berkeley National Laboratory 88-Inch Cyclotron.

First, we designed and built the Recoil product Transfer Chamber (RTC), a new transfer device between the BGS and a chemical separation system. We tested the RTC in different experiments to determine the transfer efficiency. The reactions ^{164}Dy(^{40}Ar, xn)$^{204-n}$Po and ^{197}Au(^{22}Ne, xn)$^{219-n}$Ac were used to measure the efficiencies at different kinetic energies of the evaporation residues (EVR) of 43 MeV and 11 MeV, respectively. The overall efficiencies of the transport ranged between 30% and 15%, compared to the activity measured in the focal plane detector of the BGS. These experiments encouraged us that the RTC can be used to connect the BGS with a chemical separation system like the new Cryo-Thermochromatographic Separator (CTS) or the automated liquid-liquid extraction system SISAK 3.

The CTS was designed as a separation and α-decay detection system for the highly volatile tetroxides of osmium and hassium, element 108. The CTS consists of two rows of 32 α detectors arranged along a negative temperature gradient. The tetroxides adsorb on the surface of the silicone photodiode at a certain deposition temperature, and the nuclide is then identified by the α decay. The nuclear reactions used were ^{118}Sn(^{56}Fe, xn)$^{174-n}$Os and ^{120}Sn(^{56}Fe, xn)$^{176-n}$Os. After pre-separation in the BGS a mixture of 90% helium and 10% oxygen was used to transport the osmium to a quartz tube heated to 950 °C, where OsO_4 was formed. The temperature gradient in the CTS ranged from -25 °C to -90 °C. Most of the osmium activity was adsorbed at a temperature of about -70 °C. From the measured α-activity distribution, the adsorption enthalpy of OsO_4 on the detector surface was calculated using Monte Carlo simulations.

STRUCTURAL RELATIONSHIPS AND UNIQUE ASPECTS OF ACTINIDE CHALCOPHOSPHATE MATERIALS: Th, U, Pu.

Paula M. Briggs Piccoli,[a, b] Ryan F. Hess,[a, b] Kent D. Abney,[b] Peter K. Dorhout,[a] [a]Department of Chemistry, Colorado State University, Fort Collins, CO 80523 and [b]Chemistry Division, Los Alamos National Laboratory , Los Alamos, NM 87545.

A series of chalcophosphate actinide materials has been prepared in selenophsphate and thiophaosphate fluxes at moderate to high temperatures. Thiophosphates of Th, U, and Pu have been prepared and their structures and properties will be compared to their 4f-element congeners. Compounds such as $K_{10}An_3(P_2S_7)_4(PS_4)_2$, $A_5An(PS_4)_3$,[1] $AAnP_2S_7$ and $A_3AnP_2S_8$,[2] where An = Pu^{III}, U^{IV}, Th^{IV}, where appropriate; A = alkali metal, demonstrate variations in structural dimensionality from isolated clusters to two-dimensional layered compounds. Thiophosphates have also been prepared that comprise unique "chelating" ligands such as the new $[P_3S_{10}]^{5-}$ cluster seen only in our U(IV) chemistry in the three-dimensional solid: $Cs_8U_5(P_3S_{10})_2(PS_4)_6$.[1] Selenophosphate chemistry has also generated a number of new compounds including $A_2ThP_3Se_9$, $Cs_4Th_2P_5Se_{17}$,[3] and $Cs_4Th_4P_4Se_{26}$,[4] the latter containing a unique selenophosphate ligand that can act as a redox electron shuttle that can be reduced through a two-step, 4-electron reduction to form several important building blocks based on the following model:

$$[P_2Se_9]^{4-} \overset{+\,2e^-}{\leftrightarrow} [P_2Se_9]^{6-} \overset{+\,2e^-}{\leftrightarrow} [PSe_4^{\,3-} + Se^{2-} + PSe_4^{\,3-}]$$

This model allows for the isolation of various selenophosphte configurations based on the relative oxidizing or reducing power of the selenophosphate flux and the relative stability of different oxidation states of the actinide metals, where both Th and U have been incorporated into the structure. For most compounds, Raman vibrational analyses have been performed on single crystal samples and diffuse reflectance spectroscopy and magnetic analyses have been performed on bulk materials. Important structural differences between key oxide materials and these new chalcogenide-based materials, in particular oxo phosphates, will be highlighted and unique synthetic challenges associated with inert atmosphere, high temperature reactions with highly reactive metals will be discussed.

(1) Hess, R. F.; Abney, K. D.; Burris, J. L.; Hochheimer, H. D.; Dorhout, P. K. *Inorg. Chem.* **2000**, submitted.
(2) Hess, R. F.; Abney, K. D.; Dorhout, P. K. *J. Am. Chem. Soc.* **2000**, in preparation. These results were presented at the Plutonium Futures Conference in Santa Fe, NM, July, 2000.
(3) Briggs Piccoli, P. M.; Abney, K. D.; Schoonover, J. R.; Dorhout, P. K. *Inorg. Chem.* **2000**, *39*, 2970-2976.
(4) Briggs-Piccoli, P. M.; Abney, K. D.; Schoonover, J. D.; Dorhout, P. K. *Inorg. Chem.* **2000**, submitted.

SPECTROSCOPIC INVESTIGATIONS OF ACTINIDES IN THE SOLID STATE

Z. Assefa, R. G. Haire, and John K. Gibson
Oak Ridge National Laboratory

We have continued spectroscopic investigations of f-species in selected solid matrices. In one focus area we are performing systematic investigations of excited-state interactions between An/Ln and/or An/An species in host matrices. Numerous reports exist in lanthanide/lanthanide systems, but interactions leading to energy-transfer in either actinide/lanthanide or actinide/actinide donor/acceptor pairs are not well known. We have focused on actinide/lanthanide pairs chosen primarily for spectral overlap within donor/acceptor electronic transitions.

In the Am/Tb pair, for example, a proper energy match-up exist between the $^5D_{2'}$ and $^5L_{6'}$ levels of americium and the $^5D_4$ level of terbium. Exclusive excitation of Am(III) provides a sensitized emission from Tb(III), indicating that energy-transfer occurs between the two species. The direction of the energy transfer process was established with an excitation profile analysis and found to proceed from the donor americium to the acceptor terbium. We are continuing our effort on other actinide/lanthanide pairs which have the proper energy match-up and are expected to display efficient energy-transfer processes.

Information regarding the effects of radiation on the spectroscopy and oxidation state of the progeny species have also been pursued with Es^{3+} and Bk^{3+} containing glasses. A blue self-luminescence band at 455 nm is believed to originate from oxygen defect centers within the Si-O-Si network that are produced by radiation. Other luminescence bands originating from non-bonding oxygen hole centers (NBOHC), and Si-micro cluster sites have also been observed. We are planning for additional collaborative XANES studies (with LBNL) on such systems to complement our spectroscopic investigations.

Another area that we are actively pursuing involves the investigation of energy up-conversion processes in actinide systems. While numerous studies have been conducted on anti-Stokes luminescence of rare-earth doped materials, similar data for the transuranium elements are very limited. Among the transuranium elements, so far only halides of Cm^{3+} and Cf^{3+} in the solid phase have been reported to display this phenomenon. In addition, we have recently discovered anti-Stokes luminescence in Am^{3+}. Our future effort in this area will be two fold. First, due to the limited information currently available on anti-Stokes luminescence from actinides, we will continue with the search for other systems that might display the behavior. For example, it is not known whether halide samples of Am^{3+}, like their Cm^{3+} and Cf^{3+} counterparts, would display this phenomenon. The possibility of energy up-conversion in Bk and/or Es materials will also be explored. Second, we are planning to examine the effects of pressure on up-conversion and energy transfer processes in multi-doped systems. One of the effects of pressure involves a shift in the energy of certain orbitals with respect to others. The consequences of these changes on the efficiency of energy transfer processes will be monitored spectroscopically. An added advantage of this procedure is that we will also be able to collect vibrational Raman data under high pressure and complement the group's effort in high pressure diffraction work. For example, our plan to investigate the correlation between Raman peak width and degree of disorder in actinide pyrochlores, and the initiation of pressure-induced phase transition studies are aimed at complementing the group's high pressure expertise.

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SYNTHESIS AND PHOTOPHYSICS OF HEAVY ELEMENT-CONTAINING NANOPHASES

J. V. Beitz , G. K. Liu, and C. W. Williams, Chemistry Division, Argonne National Laboratory

We are creating actinide (and other heavy element) nanophases in vitreous silica and investigating the optical properties of these unusual materials. Our work is based on a chemically functionalized, porous silica that is termed Diphosil. Diphosil is an ion exchange material. It was developed by R. Chiarizia and coworkers in an OBES-funded collaboration between Argonne National Laboratory and the University of Tennessee to selectively most actinide ions from nitric acid solutions [1]. Diphosphonic acid groups, attached via organic spacer groups to the silica surface, provide the chelating power of Diphosil. Diphosil is ~90% silica by weight.

As shown by our FT-IR studies, heating metal ion-loaded Diphosil in air converts its organic content primarily to water vapor and carbon dioxide. Further heating collapses the pores of the silica (a process termed thermal densification in the sol gel literature) and thereby traps the sorbed metal ions in vitreous silica. Preliminary small angle X-ray scattering studies at the APS and small angle neutron scattering work at IPNS have provided evidence as to the nanophase character of thermally densified, metal ion-loaded Diphosil. Diphosil nearly irreversibly sorbs highly charged metal ions, such as actinides, and, as shown by our work, can encapsulate and chemically fix sorbed metal ions in phosphate-rich nanophases in vitreous silica, one of the most radiation-resistant glasses. For these reasons, Diphosil has potential to both lower the hazard category of nuclear waste solutions and serve as the basis for creating a nuclear waste form suitable for geologic disposal. We are pursuing development of this novel approach to reducing nuclear waste volume in work funded by the Nuclear Energy Research Initiative [2].

Much of our work on characterizing Diphosil prior to and following thermally densified has exploited the f-state spectroscopic and photophysical properties of heavy metal ions that were sorbed into Diphosil from aqueous solution. For example, the photodynamics of sorbed trivalent europium ions prior to and following thermal densification have provided evidence as to the number of its inner sphere coordinated water molecules and the proximity of such sorbed metal ions to each other. We have prepared and presently are investigating the photophysics of thermally densified, metal ion-loaded Diphosil that has been doped with ions of one or more of the following elements: Fe, Cr, La, Pr, Nd, Eu, Ho, Er, and U. All of our photophysical studies on these materials are consistent with the presence of metal ion-rich nanophases. We have demonstrated control of ion-ion energy transfer rates over a broad range in these materials and have observed luminescence decay rates that approach purely radiative values. In other cases, such as Diphosil co-doped with Ho^{3+} and Er^{3+} ions, where nonradiative decay dominates, spectral evidence of facile ion-ion energy transfer has been obtained. Following appropriate treatment, we have found that Diphosil itself can exhibit strong luminescence with decay times longer than one second having been observed. In our future studies on thermally densified, metal ion-loaded Diphosil, we will investigate the oxidation state stability of heavier actinide elements (such as Pu), more fully characterize the local environment surrounding heavy element ions, and assess the potential of these phases as nonlinear optical materials.

1. R. Chiarizia, E. P. Horwitz, K. A. D'Arcy, S. D. Alexandratos, and A. W. Trochimczuk, Solvent Extraction and Ion Exchange, **14**, 1077-1100 (1996).
2. "A Single Material Approach to Reducing Nuclear Waste Volume", J. V. Beitz, principal investigator, Nuclear Energy Research Initiative Project 990219, Office of Nuclear Energy, Science and Technology, U. S.DOE.

ACTINIDE CHEMISTRY UNDER NEAR-NEUTRAL CONDITIONS:
3. EMISSION FROM NEPTUNYL IONS IN THE NEAR IR

H. J. Dewey and T. A. Hopkins
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Although luminescence spectroscopy has proved a powerful diagnostic technique for the f^0 uranium(VI), it has found limited utility for compounds of neptunium, plutonium, or compounds involving the lower oxidation states of uranium. This apparent lack of luminescence from the early actinides containing one or more 5*f* electrons can be explained by the presence of *f-f* transitions at low energies and the absence of large energy gaps between neighboring electronic states. Thus, any luminescence arising from *f-f* transitions is likely to lie in the near infrared region of the spectrum. With recent improvements in near infrared detectors, we have initiated investigations into actinide luminescence in this spectral region and have begun by searching for emission from f^1 neptunyl(VI). Our hope is that, once developed, *f-f* luminescence might serve as a tool for studying actinide speciation and ultimately find utility as an analytical chemistry tool.

We have chosen to begin our studies with the $NpO_2Cl_4^{2-}$ ion because its electronic and vibrational structure has been well characterized by Denning et al.[1] Crystalline cesium hexachlorozirconate was chosen as the matrix material because it lacks any high frequency vibrational modes that could be expected to serve as acceptor modes for radiationless deactivation and also because the hexachlorozirconate sites are about the right size to accommodate the neptunyltetrachloride ions. Indeed, highly resolved emission has been reported for $UO_2Cl_4^{2-}$ doped into cesium hexchlorozirconate.[2,3]

Crystals of Cs_2ZrCl_6 doped with $NpO_2Cl_4^{2-}$ were sealed in quartz capillaries and immersed in liquid nitrogen for the spectroscopic measurements. Both cw and pulsed laer excitation sources have been used. Near IR emission was collected and dispersed through a quarter meter spectrograph and detected on a 512 element InGaAs photodiode array. The origin of the emission is observed at approximately 1440 nm. Its position is in good agreement with the second excited state of $NpO_2Cl_4^{2-}$ doped into $Cs_2UO_2Cl_4$ reported by Denning et al. Vibronic features to lower energy are in reasonable agreement with ground state vibrational frequencies in crystalline $Cs_2NpO_2Cl_4$.

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THERMOELECTRIC PROPERTIES OF UO_2

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The Seebeck coefficient for UO_2 at room temperature is approximately three times greater than the currently most promising thermoelectric materials, e.g., Tl_2SnTe_5. This suggests that UO_2 can be used as a material for thermoelectric devices. Thermoelectric devices have a wide variety of applications in many fields. For example, solid state refrigerators are used to cool high power integrated circuits, superconducting devices, and infrared detectors, while thermoelectric power converters are utilized in waste heat energy applications and deep space probes. Substantial data—thermal conductivity, electrical resistivity, and even the Seebeck coefficient—have been gathered for UO_2 for nuclear reactor safety purposes. However, no data exists for dopants of uranium. Thus, it is concluded that UO_2 has never been seriously considered for uranium-based semiconductor applications such as thermoelectric devices. The performance of a thermoelectric material is quantified using the dimensionless figure-of-merit $ZT = S^2\sigma T/k$, where S is Seebeck coefficient, σ is electrical conductivity, and k is thermal conductivity. It has been shown that for a ZT of ~2–3, thermoelectric refrigerators could be competitive with today's vapor compression devices. Calculations give a ZT ~10^{-4} for UO_2 at 500 K, and, ZT ~0.1 at 2,273 K. The figure-of-merit increases with increasing temperature for UO_2.

LOCAL COORDINATION EFFECTS, *f*-ELECTRON LIGATION AND MAGNETIC BEHAVIOR IN ACTINIDE INTERMETALLICS

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The metal coordination environment around an actinide in an actinide intermetallic compound is an important factor for determining the ground state magnetic and electronic properties of that compound. In particular, the usual assumption that the *f* shell is not extended enough to participate in bonding is not valid generally, even in rare-earth intermetallics. In fact, together with the crystal structure, the *f*-electron interaction with the metallic bond determines the magnetic and electronic properties of the compound. A significant wrinkle to this simple picture can occur when one has a material where the local coordination environment around the actinide species is *disordered*. The consequences of disorder depend on its exact type (site interchange, random bond lengths, etc.) and its extent (both the magnitude and the frequency). We will discuss these effects in the $UCu_{5-x}Pd_x$ system (which can be thought of as having disorder increase with x) and in the antiferromagnet URh_2Ge_2. Moreover, results will be examined in light of recent theories of so called “non-Fermi liquids” and high temperature superconductivity. The future of this type of work is promising: Although a large theoretical, materials and transport community exists within condensed matter physics, very little research has approached this problem as that of the science of disordered materials chemistry on the nano-scale. Modern techniques, such as x-ray absorption fine-structure (XAFS) spectroscopy, magnetic circular dichroism (MCD), pair-distribution function analysis (PDF) of powder diffraction data, diffraction anomalous fine structure (DAFS), surface scattering techniques, and magnetic microscopies should all add vital pieces of information to understanding this puzzle of *f*-electron interactions and, more generally, to strongly correlated electron systems. Pulling together results from all of these techniques will enhance the understanding of *f*-electron chemical bonding in a wide range of systems in addition to disordered actinide materials, including lattice compounds, impurity systems and potentially even molecular systems.

HETEROGENEITY AND PHASE SEPARATION IN CRYSTALLINE SOLIDS – MOSTLY CONTAINING PLUTONIUM

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Within the last ten years, the once contentious idea of local structural distortions as an intrinsic aspect of the arrangement of the atoms in crystalline solids has become a standard tenet of complex materials. This has been fostered experimentally by acknowledgement of the complementarity of conventional diffraction methods and local structure techniques such as XAFS and Pair Distribution Function (PDF) analysis, which have consequently become obligatory tools in structure determination. However, we must now ask whether these advances complete the conceptual basis of crystal structure or whether even more radical ideas are necessary if we are to accurately depict precisely how a crystal is assembled from its constituent atoms? The evidence is overwhelming that in many cases these distortions are not isolated but in fact signify collective behavior by groups of atoms to form nanometer-scale domains with a local composition, charge distribution, and structure that differ from the bulk parameters and that can involve up to one quarter of the material. Such nanoscale heterogeneity is a fundamental aspect of glasses. However, given the constraints on the atom positions imposed by the lattice, its application to crystals has been limited to, e.g., stripes in correlated electron materials, where the distortions are quite modest and regular. In contrast, in many systems we have studied, including magnetic alloys but especially δ plutonium alloys, plutonium oxides, and plutonium substituted into complicated oxides, the deviations from the average structure are quite large. Nanoscale heterogeneity also appears directly coupled to the interesting correlated and transformational properties of complex materials, further stimulating interest in its study. One origin of this heterogeneity or phase separation will be composition fluctuations in non-stoichiometric materials, in which the chemical formula of the compound is not identical with the integral stoichiometry of the unit cell. If a dopant or trace element is randomly distributed the local fluctuations in its con-centration will naturally tend towards the nanometer scale, as shown by percolation theory. Because this size is just at or below the conventional diffraction limit, a lack of registry between the domains will result in the localized structure being invisible in diffraction. A rearrangement of the atoms in these domains of different composition into a different structure will result in the observed effects.

Several examples of collective behavior and nanoscale heterogeneity will be presented. The local structure and strain-relief mechanism of the yttrium is specifically affected by the substitution of U for Ce in quaternary, Y-Er-Ce/U, cubic stabilized zirconias, implying a specific yttrium-uranium inter-action. In the plutonium-substituted zirconolite, $Ca_{0.8}Pu_{0.2}HfTi_{1.8}Al_{0.2}O_7$, anomalous PDF measurements (corroborated by XAFS) show a 5.5 Å Pu-Pu distance that can only occur if plutonium rich domains reorganize into a modified type of structure. Hydrated/protonated plutonium (IV) oxides display many discrete Pu-O distances that indicate the presence of highly specific bonding modes determined by the local composition. PuO_{2+x} is now also shown to contain doubly bound oxo-type moieties within an undistorted PuO_2 host lattice, which also must result in substantial local strain that would be relieved by the formation of separate domains or networks. Finally, δ plutonium alloys with compositions that place them in the metastable range exhibit a second structure which, although also Fm3m on average, is apparently both modulated to conserve the original bond characteristics and contains interstitials that conserve the density and relate it to the α phase. This σ structure most likely occurs in nanoscale regions with locally low concentrations of δ stabilizing elements resulting from a random distribution of such elements in the plutonium host lattice. Whereas the measured sizes of trace elements show that elastic strain and compensation mechanisms are insufficient by themselves for promoting stabilization in the δ phase, density of states calculations in local clusters demonstrate that the plutonium electronic structure is modified differently by different nearest neighbor elements.

LOCAL AND NANOSCALE STRUCTURE IN COMPLEX SYSTEMS: A CONFERENCE SCHEDULED FOR SEPTEMBER, 2001, IN SANTA FE

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Collective interactions among localized phenomena on the Angstrom scale resulting in the formation of structures on the nanometer scale have been observed in many correlated and transformational materials. That examples range from crystalline solids to multiphase catalysts to proteins poses the question of whether the commonality of this behavior is merely coincidental or if it constitutes a fundamental organizational principle for complex systems. The interdisciplinary nature of this issue will be promoted by directly addressing functional issues rather than a division into conventional substantive areas. Thus, although the areas to be addressed will include; correlated electron systems/mixed valence transition metal oxides/photoexcited compounds; actinide and other f electron compounds/metals and alloys; heterogeneous catalysis; and biomolecules and other "soft" materials, the actual topics for the session will be, e.g.: energetics of nanoscale domain formation, including the roles of entropy, solvation energy, etc.; dynamics and transformations; experimental and theoretical approaches; and properties and implications of nanoscale structures. In addition, it is considered timely to explore the technological ramifications of these phenomena as well as methods for controlling the fabrication of spontaneous and contrived nanoscale heterostructures.

EXPLORING HEAVY-ELEMENT SCIENCE USING PRESSURE*

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Zerihun Assefa and John Gibson
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Scientific studies often employ variable experimental parameters to elucidate fundamental and technological aspects of materials. In this regard, pressure provides a very useful and powerful variable. Under laboratory conditions, pressure can alter interatomic distances solids far more than can temperature, and we are employing it to pursue the science of the heavy elements.

There have been significant advancements in the science of f-elements under pressure due in part to new designs of the diamond anvil cell (DAC), the use of synchrotron radiation and laser spectroscopy. These advancements permit one to study the actinides through californium under pressure in the megabar region. With such pressures, materials are compressed to fractions of their initial volumes. The significant reductions in interatomic distances that result can induce important changes in electronic interactions, energy levels and often alter the bonding.

One point of interest with actinides is whether pressure can bring about delocalization of f electrons and permit them to participate in bonding. The spatial extension of the 5f-electrons permits delocalization and/or hybridization processes to occur more readily with the transplutonium elements, as compared to their 4f-homologs. In the case of compounds, the behavior under pressure may be more complex, as electrons and orbitals from two or more different atoms must now be considered. Another facet of interest here is the effect of pressure on electronic transitions in f-electron materials, which may be altered significantly as the relative energies of the states are changed by pressure.

We have multiple interests for using pressure as an experimental variable for probing the heavy elements, and this includes altering temperature and pressure simultaneously. One emphasis has been to determine the effect of pressure by monitoring structures using X-ray diffraction techniques, where the effect of pressure on the electronic nature and the bonding is determined using established structure-bonding relationships. We have also employed spectroscopic techniques to monitor changes in materials brought about by applying pressure.

One recent thrust was to study americium metal up to one megabar using synchrotron radiation. It was found that the americium exhibited four different structures, where two transformations also involved “volume collapses”. The latter are believed to reflect the pressure-induced involvement of americium’s 5f-electrons in the metallic bonding. It was determined that pressure forces americium to adopt known structural forms of plutonium and uranium.

In the future, we plan to pursue systematic, comparative investigations that employ pressure as at least one of the experimental variables. These collaborative [1] efforts will employ synchrotron radiation at the ESRF, and hopefully also at the upcoming APS high-pressure beamline. An immediate goal is to investigate americium-curium alloys, curium and californium (the highest actinide currently feasible to study) under pressure to examine their electronic/structural behavior. We also expect to pursue the effects of pressure on compounds (e.g., actinide pnictides and chalcogenides) to determine the effects of pressure on materials with multiple atoms that may also have a potential for displaying a change in valence. Also planned are studies to examine, via spectroscopy, pressure induced changes in the energies of electronic states, the effect on energy up-conversion processes and energy transfers, and the effect on Raman vibrational spectra. Targeted materials will be single and multiple f elements in hosts (e.g., inorganic ceramic materials), as well as several pure materials.

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[1] Institute for Transuranian Elements (Germany) and ESRF (France).

ADVANCES IN HEAVY ELEMENTS PHOTOPHYSICS AND LASER SPECTROSCOPY

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Using laser spectroscopic techniques in combination with computational modeling and simulation, we study electronic and nuclear interactions of heavy elements, particularly actinide ions, in crystals and glasses. The nature of our research is to reveal fundamental aspects of physical interactions and bonding properties through interpretation of optical spectra and dynamics of excited states. The results from our investigation also provide insight into such nationally important problems as prediction and modeling of the long-term behavior of high level nuclear wastes.

Our work has achieved success in gaining fundamental understanding of electronic and structural properties of actinides, most of them are alpha emitting isotopes, in ceramic and glassy phases such as borosilicate glass. Based on experimental measurements and theoretical modeling of crystal-field and hyperfine energy level structures of f-electron states of actinides and lanthanides in solids, we are achieving a predictive understanding of the relationship between electronic energy level structure and local crystalline structure.[1] Using high-resolution laser excitation, time-resolved and site-selective fluorescence was monitored to probe local structure and radiation-induced structure damage. X-ray spectroscopic (EXAFS) methods were used for gaining supplementary information. Detailed experimental results and theoretical analyses have been reported for uranium and curium isotopes in boron oxide and borosilicate glasses.[2]

As part of our effort in advancing actinide photophysics and spectroscopy, we also address the challenging issues of nuclear spin and nuclear electric quadruple interactions of actinides in solid phases. Using nonlinear laser spectroscopy methods, such as optically-detected nuclear magnetic resonance (ODNMR) and spectral hole burning, we have measured the nuclear electric quadruple energy levels of ^{243}Am in $LaCl_3$ and $CaWO_4$ and analyzed the observed splittings in detail.[3] Due to large crystal-field anti-shielding factors, these splittings differ significantly from those of free actinide atoms and are extremely difficult to measure with conventional NMR and EPR techniques. We are improving our experimental apparatus for Raman heterodyne ODNMR to extend our measurement capability from the MHz range into the GHz region. This improvement is essential for studying the hyperfine energy level structure of most actinide ions in solid phases.

In our present work, theoretical analysis and computer modeling provide a fundamental framework that is essential for productive interpretation of experimental results. Our Windows-based computer program for interactive analysis of f-element crystal field spectra has been released for public distribution at the web site http://chemistry.anl.gov/. We are using a molecular dynamics (MD) simulation method to study structure and structure disordering in solids. Lattice structure, phonon density of states, and infrared spectrum for $ZrSiO_4$ have been calculated and compared with experimental results. Our MD simulation efforts currently are centered on investigation of the local structure and dynamics of uranyl ions in boron oxide glass as a limiting case related to considerably more complex nuclear waste glasses.

This work was performed under the auspices of the DOE Office of Basic Energy Sciences, Division of Chemical Sciences under contract number W-31-109-ENG-38. EXAFS results were obtained from the Actinide Facility.

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Structures of Plutonium Coordination Compounds: Recent Single Crystal X-Ray Diffraction Results

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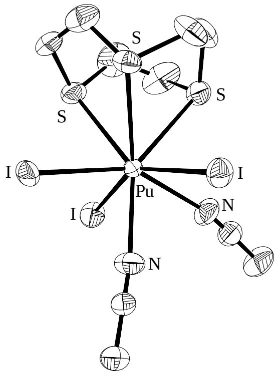
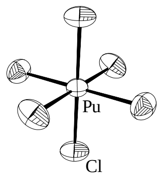
Structural studies of plutonium coordination complexes are rare. There are only three plutonium coordination compounds that have been characterized using single crystal XRD: the Pu(IV) complexes of nitrate, sulfate, and carbonate.[1-3] This paucity of detailed structural data limits the ability to predict plutonium chemistry in general, and particularly hinders the subfields of basic science, separations, environmental behavior, theory and modeling. We and others are revitalizing this research area by using single crystal XRD and advanced spectroscopies to characterize new plutonium complexes.

The compounds we have isolated and characterized include plutonium(III) and plutonium(IV) bound by ligands with a range of donor types and denticity (halide, hydroxamate, phosphine oxide, amine, sulfide) in a variety of coordination geometries. For example, we have obtained the first X-ray structure of Pu(III) complexed by a soft donor ligand. Using a 'one pot' synthesis beginning with Pu metal strips and iodine in acetonitrile and adding trithiacyclononane we isolated the complex, $PuI_3(9S_3)(MeCN)_2$ (below). On the other end of the coordination chemistry spectrum, we have obtained the first single crystal structure of the Pu(IV) hexachloro anion (below). Although this species has been used in plutonium purification via anion exchange chromatography for decades, the bond distances and exact structure were not known. We have also characterized the first plutonium-biomolecule complex, Pu(IV) bound by the siderophore desferrioxamine E.[4] In this presentation we will describe the preparation, structures, and importance of several new complexes and emphasize that the coordination chemistry of plutonium is rich and varied—well worth additional exploration.

$PuI_3(9S3)(MeCN)_2$



$[Et_4N]_2[PuCl_6]$



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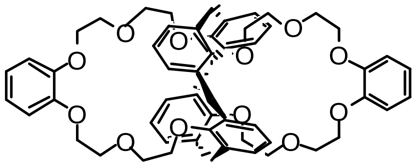
Fundamental Studies and Applications of Calix[4]arene-crown-6 Compounds.

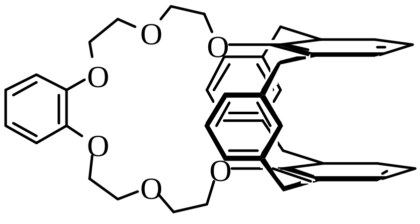
Tamara J. Haverlock, Saed Mirzadeh, Peter V. Bonnesen, Richard A. Sachleben, Haifeng Ji, Reza Dabestani, Gilbert M. Brown, Benjamin P. Hay, Jeffrey C. Bryan, and Bruce A. Moyer

The family of calix[4]arene-crown-6 compounds has attracted intense interest because of their unprecedented selectivity toward Cs$^+$ ion, with obvious impact on development of processes for removal of ^{137}Cs from nuclear waste. Typical selectivity for Cs$^+$ vs. Na$^+$ ion by bis- (**1**) and mono- (**2**) crown members of this family exceed 10,000, expressed as the relative distribution ratios in competitive liquid-liquid extraction experiments. A number of fundamental questions concerning this unprecedented selectivity, and how it could be further enhanced, have been explored at ORNL. This presentation will be an overview of our work examining size preferences of the calix-crown cavity and how it could be refined, and how the extraction solvent containing this ligand can be modified to enhance extraction.



1

Size preference will be presented using two different studies. The first considers the flexibility of the tetrakismethoxycalix[4]arene frame using *ab initio* and molecular mechanics computational techniques. The results suggest that the calix[4]arene frame may be able to accommodate univalent ions larger than Cs$^+$. Experiments comparing Cs$^+$ and ^{221}Fr$^+$ ($t_{1/2}$ = 4.8 min) extraction into 1,2-dichloroethane by **1** show that ^{221}Fr$^+$ is more strongly extracted. Results from this work are of interest for possible radiopharmaceutical applications. The second also begins with computational studies that suggested how Cs$^+$/K$^+$ selectivity could be enhanced. These studies have resulted in the development of a new series of calix[4]arene crown ethers that exhibit significantly enhanced selectivity for cesium over sodium, potassium, and rubidium. This advance in cesium recognition has been used to develop a fluorescence chemosensor with enhanced cesium response and selectivity.



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The strength of cesium extraction afforded by calix[4]arene crown–6 ethers depends upon the solvation environment, and can be modulated by adding solvating components called "modifiers." The cesium extraction strength is far too low to be useful in low polarity solvents, which are generally preferred for extraction processes. However, addition of a particular class of alcohol modifiers developed at ORNL can increase the cesium extraction strength substantially. The magnitude of the increase is dependent not only on the concentration of the alcohol modifier, but also on the hydrogen-bond donor ability of the hydroxyl group. Donor ability, and thereby cesium extraction strength, can be tuned by varying the electronic properties of key substituents in proximity to the alcohol functionality. A solvent extraction process employing a calix[4]arene-crown-6 ether in an alcohol-modified solvent is currently being evaluated for treating High Level Tank Waste at DOE's Savannah River Site.

PREORGANIZED and IMMOBILIZED LIGANDS FOR METAL ION SEPARATIONS

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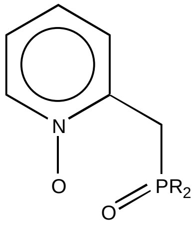
The chemistry of f-element ions impacts a diverse set of DOE nuclear material technical areas, and these elements also enable development of a number of exciting applications in emerging technologies. In order to safely and efficiently utilize these unique elements it is important that a more thorough understanding of f-element coordination chemistry be derived. In particular, it is important that a thorough characterization of molecular level features that control metal-ligand interactions be gained. For some years our program has focused on the development of new chelating ligands for selective f-element binding, and that work has contributed to a better understanding of electronic and architectural factors that influence f-element chelate formation. Recently, we have focused on the design, synthesis and characterization of complexes containing new families of chelates with N–O and P=O donor groups, such as illustrated by **1** and **2**. These studies have revealed a number of unexpected structure/function features as well as powerful, selective chelation of Ln(III) and An(III) ions in strongly acidic media. Indeed, the behavior of trifunctional $[R_2P(O)CH_2]_2C_5H_3NO$ derivatives is superior to the popularly used CMPO extractants. Phosphonic acid derivatives of **1** and **2** also have been studied as chelators for Ln and An ion species formed in basic solutions. The recent findings have inspired new collaborations with colleagues at two DOE laboratories, and current and future BES-funded research will be performed in synergy with these groups. In particular, we are exploring the molecular structures of plutonium complexes formed by NOPO-class, NPO-class and NP-class ligands by using spectroscopic single crystal X-ray diffraction analyses. This work is being done with M. Neu and coworkers at LANL. We are also studying the fundamental chelation chemistry of these and several new classes of ligands with Ln and An ions using solvent extraction and solution calorimetry techniques. This work is being done in collaboration with K. Nash and coworkers at ANL. The UNM/ANL group also is exploring several new ligand classes for f-element binding in neutral and basic solutions.



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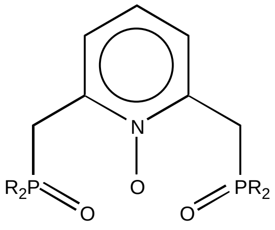

2

CHEMICAL THERMODYNAMICS OF ACTINIDES IN SOLUTION UNDER NON-CONVENTIONAL CONDITIONS

Linfeng Rao

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Lawrence Berkeley National Laboratory

Goal and Focus: The goal is to improve the fundamental understanding of chemical thermodynamics governing the coordination chemistry of actinides in non-conventional solution systems. Currently the focus is on two aspects: 1) the effect of temperature on actinide coordination with organic ligands; 2) the structure/function relationship for the complexation of *f*-elements in non-aqueous and aqueous solvents.

Approach: An integrated approach of thermodynamic measurements and spectroscopic characterization is taken, including variable-temperature potentiometry and calorimetry, and a variety of spectroscopic techniques.

Recent Progress:

- The complexation of *f*-elements with alkyl-substituted diamides is studied by non-aqueous single-phase titration calorimetry and optical spectroscopy. Results suggest that steric effects(1,2) and ligand basicity(2) may play important roles in the complexation.
- An isoperibol titration calorimeter was commissioned in 1999 and has been in continued use for studies of *f*-element coordination at variable temperatures. Studies of the complexation of Nd(III)(3) and U(VI)(4) with acetate at 25°C to 70°C were completed. Results obtained by spectroscopy are consistent with the trends in chemical thermodynamics. Experiments on the complexation of U(VI) with more organic ligands at variable temperatures are in progress.
- Installation of an isothermal titration micro-calorimeter is in progress. It is to be adapted for studies of transuranic elements (Np and Pu, in particular).

Future Directions and Collaborations:

- Extend the thermodynamic studies at variable temperatures to Np and Pu.
- Extend the structure/function relationship for *f*-element coordination to more ligands.
- Continue the collaboration with the research group in Padova, Italy, including Prof. Di Bernardo and Dr. Zanonato (Università di Padova), and Dr. Bismondo (the Istituto di Chimica e Tecnologie dei Materiali Avanzati del C.N.R. of Padova).

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INFLUENCE OF COVALENCY, COMPLEX STRUCTURE, AND SOLVATION ENERGETICS ON ACTINIDE COMPLEXATION

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The fundamental facets of solution phase actinide chemistry have been demonstrated time and again over the last 60 years. The primacy of hard-hard interactions, the variety of accessible oxidation states and the importance of the “-yl” ions, the flexibility of coordination numbers, the importance of cation dehydration in aqueous reactions, and the near equivalence of the trivalent lanthanide and actinide cations are all well documented themes. However these overarching themes cannot always explain the properties of one or more actinide complexes, leaving scientists with good chemical intuition to hypothesize very plausible mechanisms that have qualitative appeal but little quantitative foundation. Often invoked explanations include solvent interactions, enhanced covalency of certain species, and minor but undemonstrated structural differences between the solution phase complexes. This work is concerned with providing quantitative measures of these effects in selected systems to expand our understanding of actinide chemistry at the outer limits of actinide solution chemistry, and to underpin ongoing work in heavy element separations chemistry.

Working with the Chemical Separations Science group, the Actinide Synchrotron Facility, and BESSRC, the actinide (Am, Cm) and lanthanide (Nd, Sm) complexes with dioxo-, oxo(thio)- and dithiophosphinic acid extractants were studied using EXAFS, optical spectroscopy, and solvent extraction. The dithiophosphinic acid has been reported to extract Am^{3+} 6000 times more strongly than Eu^{3+}, presumably because of greater covalence in the Am complex. However, it was not known if the hypothesized covalency is manifested in measurable differences in the solution structures of the complexes. Even though the Cm-dithiophosphinate complex is extracted much more strongly than the Sm-dithiophosphinate complex, the metal-sulfur bond distances are indistinguishable for the Sm and Cm complexes in dodecane. For each ligand the coordination number of the metal and the metal-oxygen (2.30-2.33 Å) or metal-sulfur (2.80-2.81 Å) bond distances are independent of the metal cation, when the slightly different crystal radii (ca. 0.02 Å) of the cations is considered. Also, only sulfur donors are detected in the inner-sphere of the dithiophosphinate complexes despite the affinity of trivalent f-element cations for the water and nitrate present in the system.

To better understand the impact of solvation on the energetics of actinide complexation, we have been attempting to answer the question: how much of the reaction energy arises from intrinsic interactions between metal cations and ligands, and how much arises from the rearrangement of solvent molecules when the complex is formed. Isotopic substitution of the solvent has been employed to quantitatively fractionate the enthalpies, entropies, and free energies of complexation into solvent based and complex based contributions for the 2,6-pyridinedicarboxylate complexes of a several metal ions. In the case of a transition metal cation like Cu(II) that is prone to form bonds with more covalent character, the contribution of solvation to the enthalpy of complex formation is negligibly small. The energy of metal-ligand bond formation dominates. By contrast, a significant fraction of the complexation enthalpy of 2,6-pyridinedicarboxylic acid comes from solvent rearrangement when complexes with harder cations like Ca(II) or Nd(III) are formed.

$[1,2,4\text{-}(CMe_3)_3C_5H_2]_2$ U(bipy): A METALLOCENE OF URANIUM (II)?

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The uranium metallocene, $Cp_2^{'}U$(bipy), where $Cp^{'}$ is the 1,2,4- tri-t-butyl cyclopentadienyl ligand, has been prepared by the reaction of the uranium metallocene halides, either $Cp_2^{'}UCl_2$ or $Cp_2^{'}UCl$, sodium naphthalene, and $2,2^{'}$-bipyridyl. At first glance the adduct appears to be an example of bivalent uranium. However interpretation of all of the physical studies that includes visible, infrared, X-ray crystallography, and XANES points to a ground state electronic structure based upon trivalent uranium and bipyridyl radical anion, $Cp_2^{'}U$ (III)
(bipy $^{-}$). Chemical studies, such as the very slow ligand exchange, are also consistent with this deduction. Even though the metallocene is not a low valent U(II) species, it is an excellent synthon for the oxo and Imido Compounds, $Cp_2^{'}U(O)(py)$ and $Cp_2^{'}$ UNPh. The reactions of these monomeric compounds will provide much information about the nature of the U=E multiple bonds in these simple but important functional groups.

$[1,2,4\text{-}(C\,Me_3)_3\,C_5H_2]_2\,Ce(bipy)$: A METALLOCENE OF Ce (II)?

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The cerium metallocene, $Cp_2^{'}$ Ce(bipy) where $Cp^{'}$ is the 1,2,4-tri-t-butylcyclopentadienyl ligand, has been prepared from the reaction of $Cp_2^{'}$ Ce I, sodium naphthalene, and 2,2$^{'}$-bipyridyl. As in the uranium example, this metallocene might be regarded as an example of Ce(II). However, physical studies, such as visible, infrared, X-ray crystallography, and XANES have been interpreted as showing that the electronic ground state is based upon Ce (III) and a bipyridyl radical anion. In contrast to the uranium metallocene, magnetic studies of the cerium analogue are easier to understand since Ce(III) has a f^{1} electronic structure and the bipyridyl is a spin doublet. Variable temperature magnetic susceptibility studies show that the two spins are uncorrelated at temperatures greater than 10K. Below 10K, the spins couple anti-ferromagnetically. Replacing the bipyridyl ligand with other heterocyclic nitrogenous bases results in dramatically different magnetic behavior. Thus, using 4 4$^{'}$- dimethylbipyridyl gives a metallocene in which the spins are uncorrelated to 4K. In dramatic contrast, using 1, 10-phenanthroline results in coupling of each 1,10 – Phenanthrolyl groups at the 4, 4$^{'}$- positions. Thus, the use of the cerium metallocene to provide an electron drives the stereospecific radical coupling reaction.

HEAVY-ELEMENT POLYOXOANION CHEMISTRY

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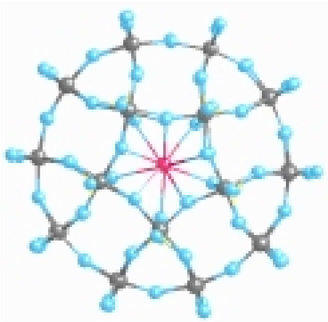
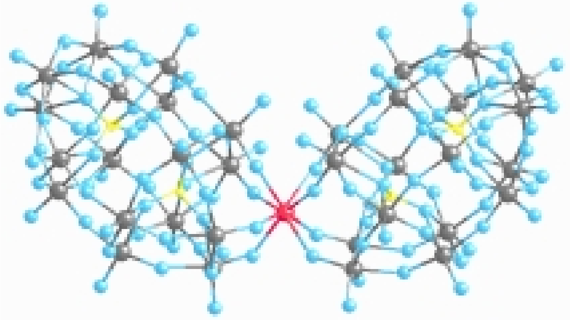
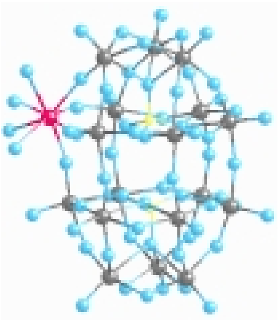
Polyoxoanions of general composition $[X_aM_bO_c]^{d-}$ ($X \equiv P$, Si; $M \equiv W$, Mo) have applications in various disciplines including catalysis and separations science. In prospective applications relating to high-level waste processing, they generally function as chelators to sequester and stabilize *f*-ions, R. Remarkably, there is a dearth of basic information about the redox behavior and coordination of 4*f* and 5*f* ions in polyoxoanion clusters with different X-M-O framework structures. Our fascination with polyoxoanions concerns their interactions with multivalent *f* elements. Two systems—the Preyssler, $[P_5W_{30}O_{110}]^{15-}$, and Wells-Dawson, $[P_2W_{17}O_{61}]^{10-}$, polyoxoanions—have attracted our interest because of their remarkable electrochemistry. Both are oxidants. Multi-electron reduction of the P-W-O frameworks is reversible and nondestructive. We will present insights, obtained from a combination of syntheses, spectroscopic and electrochemical analyses, that are leading to a predictive understanding of the mechanisms by which polyoxoanions and *f*-ions are each affected by their mutual complexation. The general result is that the bulk redox properties of complexes like $[RP_5W_{30}O_{110}]^{12-}$ and $[R(P_2W_{17}O_{61})_2]^{17-}$ are different from the sum of the individual responses of the *f*-ion and polyoxoanion. We will show that the Preyssler and Wells-Dawson polyoxoanions exert direct and opposite influences on the redox chemistry of R for Ce, Eu, U, Np, Pu, and Am. Moreover, the electronic participation of the P-W-O framework in the voltammetric response of $[RP_5W_{30}O_{110}]^{12-}$ and $[R(P_2W_{17}O_{61})_2]^{17-}$ is modified by the R ion. The contrasting redox behavior is understood in terms of R-O bonding. We believe that electrostatic interactions exert minor effects on the stabilities and properties of polyoxoanion complexes with R ions. A detailed understanding of all factors influencing polyoxoanion-*f*-element interactions would be significant from a fundamental science perspective as well as for practical accounts. For this reason, it is our goal to disentangle the intricate and complicated issues regarding electrostatics, bonding, and electron transfer between *f* ions and polyoxoanions in complexes like **I**, **II**, and **III**. This work is funded by the U.S. DOE, Basic Energy Sciences—Chemical Sciences, under contract No. W-31-109-ENG-38.



I
$[R^{3+}P_5W_{30}O_{110}]^{12-}$



II
$[R^{3+}(P_2W_{17}O_{61})_2]^{17-}$



III
$[R^{3+}(P_2W_{17}O_{61})]^{7-}$

ACTINIDE CHEMISTRY UNDER NEAR-NEUTRAL CONDITIONS:
1. INTERACTION OF MACROCYCLES WITH ACTINIDE IONS.

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Macrocycles, e.g. crown ethers and calixarenes have been studied as possible extractants for a number of years. These types of macrocycles can have two distinct interactions with the actinide ions, inner- and outer-sphere. The current ability to predict which of these interactions will dominate in a particular system has significantly reduced the applicability of these ligands as selective actinide extractants. We have previously shown that neptunium exhibits significantly different behavior compared with uranium. For example Np(V) complexation with 18-crown-6 occurs readily in aqueous solutions producing the insoluble, $[NpO_2(18\text{-crown-}6)]ClO_4$,[1] whereas U(VI) inner-sphere complexation can only be obtained under forcing non-aqueous conditions. We have continued these initial studies and have been able to observe both inner- and outer-sphere complexes, sometimes within the same isolated compound, e.g. $[NpO_2(\text{dicyclohexyl-18-crown-6})]_2[NpO_2Cl_4]$. We will report on the progress of Pu(IV), Pu(V), Np(V), and Np(VI) interactions with crown ether ligands in both aqueous and non-aqueous environments. With these results, the conditions, i.e. cavity size, solvent system, and anionic ligand choice, governing the formation of inner-sphere crown complexes are becoming understood; and may in the future lead towards the long-sought development of actinyl separation methods using crown ethers.

We have also ventured into other macrocyclic systems, e.g. expanded porphyrins. The recent finding that 3,7,18,22-tetraethyl-2,8,12,13,17,23-hexamethyl-27-oxasapphyrin (**1**) supports stable complexes with uranyl cations has led us to consider that expanded porphyrin systems could be used to coordinate other actinide cations. Previous work has served to demonstrate that uranyl complexes may be formed with a variety of expanded porphyrin-type macrocycles, including amethyrin (**2**), alaskaphyrin (**3**), and pentaphyrin (**4**). This chemistry will be reviewed and spectroscopic evidence will be presented that neptunium and plutonium complexes can be formed using these same ligands as well as with the recently prepared, dioxaamethryin (**5**).

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ACTINIDE CHEMISTRY UNDER NEAR-NEUTRAL CONDITIONS: 2. LIMITING SPECIES IN THE AN(IV) AND LN(III) CARBONATE SYSTEMS AS A TEACHING TOOL FOR NUCLEAR SCIENCE EDUCATION.

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A knowledge of actinide science continues to be essential to the US and central to the mission of the DOE, including national defense, energy, environmental restoration, and radioactive waste management. With nuclear weapons technology continuing to play a key role in defense policy for the foreseeable future, knowledge and expertise in the production, processing, purification, characterization, analysis, and disposal of actinide elements is essential to US national security. Of grave concern is that a large fraction of Laboratory staff will retire within the next decade. Moreover, the academic component of this field is small and decreasing. Because of concern that the field is becoming subcritical, the Seaborg Institute organized undergraduate/graduate-level courses on current topics in nuclear science. The program is accredited (3 hrs) by three New Mexico universities (UNM, NMSU, NMIMT), and features both lecture courses and selective research fellowships. To help in the DP-sponsored education effort, we expanded our near-neutral chemistry program to include the structural chemistry of trivalent lanthanides as a teaching tool for graduate students as part of our Seaborg Institute-sponsored course on “Modern f-Element Chemistry”. Our summer students were mentored as part of our OBES chemistry program, and the results of student research in lanthanide carbonate chemistry are reported here.

The carbonate anion is a common ligand in nearly all natural water environments and carbonate complexation in aqueous solution is known to affect the solubilities of actinide ions through formation of anionic complexes. This is especially true for Pu(IV) which forms strong complexes with hard O donor ligands. Over the last decade, there have been many studies focused on determination of the identities of the chemical species present in the Pu(IV) carbonate system, and there has been some disagreement in the literature regarding the identity of the solution complexes. We initiated experiments to determine the nature of both the limiting Pu(IV) carbonate species under high carbonate concentrations, and the solution species present under near-neutral pH conditions. Single crystals of $[Na_6Pu(CO_3)_5]_2 \cdot Na_2CO_3 \cdot 33H_2O$ were obtained from a 0.15M solution of Pu(IV) in 2.6M Na_2CO_3. The asymmetric unit contains a complex network consisting of $[Pu(CO_3)_5]^{6-}$ anions and Na^+ cations linked through interactions with CO_3^{2-} and H_2O ligands. EXAFS data for Pu(IV) in 2.5M Na_2CO_3 solution collected at the Pu L_{III} edge are also consistent with the presence of $[Pu(CO_3)_5]^{6-}$ anions, giving nearly identical structural parameters to those found in the solid state. The UV-Vis diffuse reflectance spectrum of a single crystal is nearly identical to the solution absorption spectrum of the limiting Pu(IV) carbonato complex in 2.5 M Na_2CO_3 solution. The peak by peak correspondence by position and relative absorption strengths, along with solution EXAFS data, suggest that the Pu(IV) chromophore is the same in both cases. The plutonium work has been published.[1] Our summer students produced additional peer-reviewed publications on trivalent lanthanide chemistry which will be presented.[2,3]

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THE REDOX SPECIATION OF NEPTUNIUM IN ACIDIC AND ALKALINE SOLUTIONS

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Although there exists a significant body of literature on the occurrence, stability and speciation of high-valent actinide ions in aqueous solution, there remain several unresolved questions. In selected cases, notably the occurrence of Pu(VII), there is even a question about the valence of the actinide ion. An understanding of the chemistry of high-valent actinide ions is of importance both from fundamental and applied perspectives. Knowledge of the coordination geometry in solution is particularly important because configurational stabilities and preferential bonding manifest themselves in the structure about the central ion. From a more applied perspective, an overall understanding of fundamental actinide chemistry in the laboratory will aid in unraveling the chemistry that may occur in more complex situations such as in natural aquatic systems or Hanford tank wastes.

We have begun to address outstanding issues in the chemistry of high-valent actinide ions by focusing on Np speciation in acidic and alkaline solutions. *In situ* capabilities, recently developed in conjunction with the Actinide Facility, have been used to obtain X-ray absorption spectroscopy (XAS) data from Np in these solutions. L-edge XAS data have been obtained from Np in an acidic solution in which Np was electrochemically stabilized in the (III), (IV), (V), (VI) states. Proof-of-concept experiments, designed to demonstrate the use of X-ray absorption near-edge structural (XANES) data for the determination of thermodynamic formal potentials, were collected and analysed. Selected EXAFS data from these experiments have been used to verify the coordination environment of Np ions as a function of oxidation state under acidic conditions [2]. Density Functional Theory (DFT), simple geometric modeling and results from the EXAFS data analyses have been used to augment the EXAFS data for Np(III).

In a related set of experiments, L-edge XAS data of Np(VI) and Np(VII) were obtained from a basic solution [3]. The environments of both Np(VI) and Np(VII) include 6 coordinating ligands, as determined from EXAFS data analyses. Np(VI) has a dioxo coodination with 4 more distant oxygens, whereas Np(VII) has a tetraoxo coordination with 2 more distant oxygens. Again, DFT calculations support and augment the XAS results. The calculations for Np(VII) are particularly noteworthy because they provide insight into the driving force for the unusual coordination environment of this ion in basic solution.

The authors acknowledge the infrastructure support of the Actinide Facility. This work is supported by the U.S. DOE – Basic Energy Sciences, Chemical Sciences, under contract W-31-109-ENG-38. JPB acknowledges support from the Ohio Supercomputer Center.

[1] L. Soderholm, M.R. Antonio, C.W. Williams, S.R. Wasserman, Anal. Chem. 71 (1999) 4622-4628.
[2] M.R. Antonio, L. Soderholm, C.W. Williams, J.-P. Blaudeau and B.E. Bursten, Radiochim. Acta (in the press).
[3] C.W. Williams, J-P. Blaudeau, J.C. Sullivan, M.R. Antonio, B.E. Bursten, and L. Soderholm, (submitted).

ACTINIDE CHEMISTRY UNDER ALKALINE CONDITIONS:
1. COORDINATION CHEMISTRY OF HEPTAVALENT NEPTUNIUM.

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The heptavalent oxidation state of actinide ions has been known for nearly three decades.[1] The majority of heptavalent chemistry has been developed for neptunium, as it displays the greatest stability for the heptavalent state among actinide elements. In the solid state, three structural entities have been observed, the majority of which display an unusual tetra-oxo ion. Based on the molecular structure in the solid state, it has long been proposed that Np(VII) contained the unusual tetra-oxo $NpO_4(OH)_2^{3-}$ ion in alkaline solution. To test this hypothesis, we have employed a combination of cyclic voltammetry, UV-VIS-NIR, X-ray Absorption Fine Structure (XAFS), ^{17}O NMR, and polarized red-Raman spectroscopy to examine the characteristics of the coordination chemistry of Np(VII) under alkaline conditions.

Concentrated solutions of Np(VII) were prepared in 2.5M LiOH or NaOH by bubbling with ozone. The resulting solutions were analyzed by UV-VIS, XAFS, NMR and Raman spectroscopies. ^{17}O-NMR spectroscopy on Np(VII) ions in 2.5 - 3.5 M OH^- revealed chemical exchange between Np=O and H_2O, which was confirmed by Raman spectroscopy on ^{18}O-enriched samples. Direct integration of the ^{17}O-NMR signal for the Np(VII) oxo ligands with the internal H_2O standard suggested a tetra-oxo moiety consistent with previous work,[2] while integration with an internal MoO_4^{2-} standard was indicative of a mixture of species. In order to probe this further, Raman spectroscopy was used along with group theoretical predictions for the number or Raman-active modes, one for the dioxo (A_{1g}) and two for the tetraoxo (A_{1g} and B_{1g}). The Raman spectra were recorded at varying hydroxide concentrations and showed a single invariant peak. Depolarization ratio studies confirmed the assignment of A_{1g} symmetry, suggesting the presence of a trans-dioxo unit. XAFS on NaOH solutions of Np(VII) also suggested the presence of a trans-dioxo , and a communication of this result has appeared.[3]

Single crystals of solid $[Co(NH_3)_6][NpO_4(OH)_2]\cdot H_2O$ were prepared, and a single crystal x-ray diffraction structure determination revealed a tetra-oxo ion similar to that reported previously. Raman spectroscopy on the single crystal revealed a single A_{1g} vibrational mode identical to that observed in the solution. Bulk precipitation of Np(VII) with $[Co(NH_3)_6]Cl_3$ gave the same results as the single crystals. The absence of the B_{1g} vibrational mode prompted a reinvestigation of the XAS data. XAS studies were performed on a series of 6 samples. Single crystals of $NpO_4(OH)_2^{3-}$, a precipitate with $Co(NH_3)_6^{3+}$, Np(VII) in 2.5M LiOH and NaOH solutions, and two precipitates from NaOH solution. The four new data sets on the crystalline $[Co(NH_3)_6][NpO_4(OH)_2]\cdot H_2O$ solid and precipitate and both LiOH and NaOH solutions revealed significant differences in both the XANES and XAFS compared to the original solution data. XAFS data analysis is consistent with a tetra-oxo unit of formula $NpO_4(OH)_2^{3-}$, with bonding parameters nearly identical to the crystal structure determination. The XAFS data on the precipitate from NaOH solution is identical to the published data,[3] and consistent with a trans-dioxo unit similar to the structure of $CsNpO_4$. These studies reveal the inherent difficulties in preparing and shipping TRU samples offsite for synchrotron for study, and the value of multiple methods for a more thorough understanding of the solution chemistry.

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ACTINIDE CHEMISTRY UNDER ALKALINE CONDITIONS:
2. HYDROLYSIS OF PLUTONIUM(VI).

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As part of our program to study the chemistry of actinides under alkaline solution conditions, we have begun to investigate and characterize plutonium(VI) hydrolysis species. Unlike uranium(VI) hydrolysis, which has be studied thoroughly,[1] there are only a handful of publications on plutonium(VI) hydrolysis. We are collecting potentiometric and spectrophotometric data to determine formation constants as a function of plutonium concentration and solution ionic strength (see Figure 1). We are also isolating plutonium(VI) hydroxide solids for characterization and comparison to solution species.

Our studies on solutions of 10^{-2} to 10^{-3} M Pu(VI) confirm the formation of dimeric species, as previously reported. The species that best fit the data are $[PuO_2OH]_2^{2+}$ and $[PuO_2(OH)_2]_2$, with corresponding hydrolysis constants:

log $^*K_1 = -7.8(2)$ and log $^*K_2 = -19.3(5)$, where $^*K_{x=1,2} = [PuO_2(OH)_x]_2^{4-2x}[H^+]^{2x}/[PuO_2^{2+}]^2$
Uranyl hydrolysis species also inlude a dimer with a comparitive log $^*K_1 = -5.6$, indicating that Pu(VI) hydrolyzes much less readily than U(VI).

We have extended our investigation to lower plutonium concentrations (10^{-4} M). At these lower concentrations we see evidence for fewer hydrolysis species and different optical absorbance maxima suggesting a change in speciation. For uranyl, the change in speciation from polymeric to monomeric occurs at approximately 10^{-6} M.

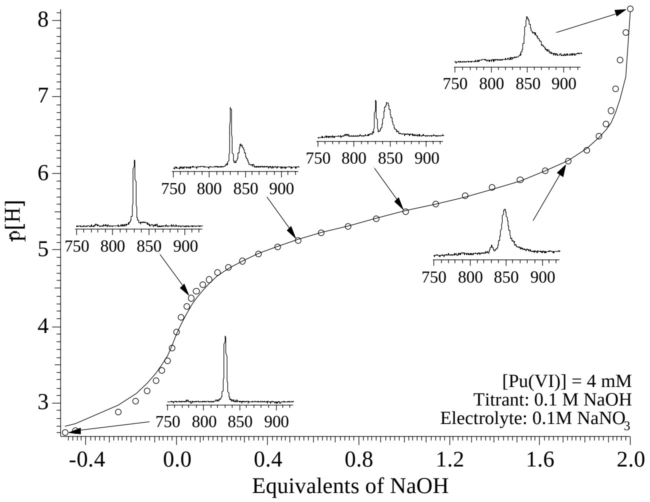

Figure 1. Plutonium(VI) hydrolysis potentiometric titration, with experimental data points (o) and pH calculated using the formation constants for the first two hydrolysis species (—) . Insets show solution optical spectra as hydrolysis progresses.

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MODEL SYSTEMS FOR THE STUDY OF THE CHEMICAL BEHAVIOUR OF ELEMENT 104 BY SOLVENT EXTRACTION AND EXTRACTION CHROMATOGRAPHY

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Due to the short half-lives of the transactinide elements, fast and efficient separations are necessary in order to study their chemical properties and the influence of relativistic effects on those properties. New developments in radiochemical separation techniques based on extraction chromatography and solid phase extraction show promise for achieving the required short separation times, high yields and high separation factors. These techniques are ideal for use in automated or semi-automated systems.

The extraction behavior of the lighter homologues and pseudo-homologues of element 104, rutherfordium, from hydrochloric acid into undiluted and diluted organic extractants has been studied. Tributyl phosphate (TBP) has been used as an extractant for neutral complexes and Aliquat 336 was chosen to study negatively charged complexes. The distribution coefficients for the investigated systems have been determined in liquid-liquid extraction experiments using either the undiluted extractant or toluene/extractant mixtures of different concentrations. The results from these experiments were compared to those obtained with chromatographic resins consisting of either TBP or Aliquat 336 bound to an inert polymer substrate. Batch experiments and experiments using chromatographic columns were performed to study the efficiency and the speed of the resin method. The results show that the chromatographic separation of the lighter homologues of rutherfordium is possible on a reasonable time scale.

Based on the results from the model experiments, procedures for the experiments to study the behavior of rutherfordium under similar conditions have been devised. These procedures include the use of chromatographic columns in manual or semi-automatic experiments. A thorough study of the liquid-liquid extraction systems is being used to devise suitable systems for the automatic separation apparatus SISAK. This automated system is based on the separation of reaction products by liquid-liquid extraction utilizing high-speed centrifuges and has been used to selectively separate and detect fission products, actinide and transactinde elements with half-lives as short as a few seconds. Experiments to study the chemical behavior of element 104 using the SISAK apparatus and different liquid-liquid extraction systems will be carried out at the 88-Inch Cyclotron of the Lawrence Berkeley National Laboratory. To acquire a more complete insight into the properties of the chosen extraction systems, the results obtained in these automated experiments will be complemented by additional experiments using chromatographic columns.

TRANS-ACTINIDES—EXPLORING CHEMICAL PROPERTIES OF ELEMENT 114*

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We will report on our initial studies exploring trends in chemical properties of the group 14 elements of the periodic table. The main emphasis of our research is the behavior of element 114 in aqueous solution. This emphasis is generated by the sudden change in relative occurrence of the major oxidation states (IV and II for group 14 elements), as observed between tin and lead in aqueous solution. Tin is still partly tetravalent, but lead is exclusively divalent [1]. The question we would like to answer is: What is the most common oxidation state for element 114 in aqueous solution? The answer to this question also gives considerable insight into the expected increasing impact of relativistic effects on the electronic structure of the group 14 elements.

A recent literature search did not provide any systematic data on the chemical behavior of group 14 elements in aqueous solution. Tin is the most challenging element in group14, because tin is in a transition position between tetra- and divalency. As a result, we choose tin as starting point for our systematic studies. Our first experiments, presented here, focused on the tin behavior in nitric and hydrochloric acid solutions. We work with ultra-trace quantities (two orders of magnitude below the ppt-level) of in order to simulate one-atom-at-a-time conditions. The isotope ^{113}Sn was selected due to the ease of detecting its γ-decay. First, we observed the tin ion exchange behavior on a resin specifically designed to take up negatively charged complexes of high-valent metal ions. Second, we investigated tin uptake by a chelating agent, in the form of a solid phase extraction chromatography resin. This resin contains a crown-ether, which chelates only divalent metal ions and is widely used to determine lead. Our first experimental results are a step towards being able to extrapolate the expected element 114 behavior in these systems. In addition, we will compare these initial results to the theoretically predicted behavior for element 114 [2, 3].

We will also address the challenges of one-atom-at-a-time chemistry we are facing and provide information on how we would like to proceed to overcome these challenges in the future.

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PLUTONIUM-238 PRODUCTION TESTS

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DOE has developed and supplied radioisotope power systems (radioisotope thermoelectric generators and radioisotope heater units) to NASA for space exploration for more than 30 years. These radioisotope power systems have repeatedly demonstrated their performance, safety, and reliability in various NASA space missions. Without these power systems, these types of space exploration missions could not be performed by NASA. The radioisotope used in these power systems is ^{238}Pu. DOE provides these radioisotope power systems, and the ^{238}Pu that fuels them, for space missions that require or would be enhanced by their use.

Historically, the reactors and chemical processing facilities at DOE's Savannah River Site (SRS) were used to produce ^{238}Pu; however, downsizing of the DOE nuclear weapons complex resulted in the shutdown of the last remaining SRS reactors. DOE has developed assessments of the current nuclear infrastructure and is considering whether or not to enhance the nuclear infrastructure. A draft Programmatic Environmental Impact Statement has been prepared to evaluate the potential environmental impacts associated with the proposed enhancements. DOE is currently conducting studies of capabilities within the DOE nuclear infrastructure to assess the capabilities of producing ^{238}Pu in support of the overall assessment process.

Production of ^{238}Pu requires the irradiation of ^{237}Np targets and subsequent chemical processing to extract and purify the ^{238}Pu. Small-scale irradiation tests, in advance of full-scale production of neptunium targets, are required to provide adequate data analysis prior to the DOE Record of Decision. Results from the tests indicate the amount of ^{236}Pu in the ^{238}Pu product and confirm ^{238}Pu production rates. The objectives for these tests are as follows, in order of decreasing priority.

- Determine the isotopic content of the plutonium generated, with particular emphasis on the ^{236}Pu content in the ^{238}Pu product. This will allow better prediction of the ^{236}Pu content expected in the various production target designs and in the selection of an optimal target design.
- Provide data for use in determining optimal irradiation positions in the Advanced Test Reactor (ATR) and the High Flux Isotope Reactor (HFIR) once the effect of target design parameters on the ^{236}Pu content has been determined.
- Verify calculations on the production rate of ^{238}Pu in the ATR and HFIR once the optimal target design is chosen.

Currently, the experimental phase of the work is being undertaken by ORNL, working in conjunction with INEEL. Technologies used heavily in the Transuranium Element Production Program are being used to build targets and conduct support studies. Results of this experimental program will be summarized.

Array Target Milestones

Conceptual design	12-1-00	Target delivery to ATR	4-8-01
Target final design	1-31-00	Insertion	5-27-01
ATR Target basket final design	2-15-01	Irradiation complete	12-01
Target fabrication complete	4-1-01	Shipping	1-02
ESAP preparation complete	4-8-01	PIE complete	4-02
ESAP approval	5-20-01	PIE report	5-02

RESEARCH, DEVELOPMENT, AND DEMONSTRATION CAPABILITIES AT THE RADIOCHEMICAL ENGINEERING DEVELOPMENT CENTER

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The Radiochemical Engineering Development Center (REDC) includes two remotely operated hot cell facilities, Building 7920 (formerly designated the Transuranium Processing Plant) and Building 7930 (formerly designated the Thorium-Uranium Recycle Facility (TURF), which are under the same management. Building 7920 is perhaps unique among the radiochemical processing hot cell facilities possessed by the U. S. Department of Energy. The REDC 7920 hot cells are built to contain and provide shielding for all types of high-level radioactive materials, including alpha, beta-gamma, and neutron emitters. The equipment in the hot cells can be operated and maintained entirely by remote handling methods—and, the equipment is modular and can be relatively easily replaced, upgraded, or reconfigured. In addition to the hot cell area, Building 7920 contains two shielded caves, several glove-box-contained separations laboratories, and special in-house analytical chemistry hot cells and laboratories. The adjacent Building 7930 hot cells contain the Californium-252 (^{252}Cf) purification and neutron source fabrication facilities and the ^{252}Cf Neutron Science User Facility (CUF). Building 7930 also contains two empty hot cells that are currently a candidate for a new ^{238}Pu Production Facility.

The REDC provides valuable capabilities for many research, development and demonstration projects sponsored by a variety of DOE departments. Examples of those projects previously carried out include:

· Development of ion exchange process used to decontaminate high-activity-level water following the accident at TMI-2	NE	1979-1981
· Production of Actinium-227 for ORNL Isotope Program	ORNL	1982
· Installation of Solvent Extraction Test Facility and performance of development studies for breeder reactor fuel reprocessing	NE	1979-1985
· Development of a chemical recovery and purification process for Nickel-63	NE	1993
· Advances in Radioactive Fission Product WasteTreatment		
- High-activity demonstration of TRUEX Process for ANL	EM	1995
- High-activity demonstration of cesium-137 sorption on resorcinol-formaldehyde resin for SRS	EM	1996
- TRU hydroxide sludge removal via cross-flow filtration	EM	1997
· Measurement of Gallium Decontamination from Weapons-Grade Plutonium prior to Mixed Oxide Fuel Fabrication	NN-60	1999

Other key factors which make the REDC uniquely valuable are that (1) it is located adjacent to the High Flux Isotope Reactor, such that nearby irradiation services are available, (2) it is located remotely away from the main populated portion of the ORNL site, (3) it is currently operating with all Environmental Safety and Health provisions and documentation in place, and (4) it includes a highly trainied technical staff to operate the hot cells and analytical facilities 24 hours per day and 7 days per week, as necessary for many projejcts.

MEASUREMENT OF ACHIEVABLE PLUTONIUM DECONTAMINATION FROM GALLIUM BY MEANS OF PUREX SOLVENT EXTRACTION

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The objective was to measure, experimentally, the achievable decontamination of plutonium from gallium by means of the PUREX solvent extraction process. Gallium may be present in surplus weapons-grade plutonium (WG-Pu) at a concentration of approximately 1 wt %. Plans are to dispose of surplus WG-Pu .by converting it to UO_2–PuO_2 mixed oxide (MOX) fuel and burning it in commercial power reactors. However, the presence of high concentrations of gallium in plutonium is a potential corrosion problem during the process of MOX fuel irradiation.[1] The batch experiments performed in this study were designed to measure the capability of the PUREX solvent extraction process to separate gallium from plutonium under idealized conditions. Radioactive tracing of the gallium with ^{72}Ga enabled the accurate measurement of low concentrations of extractable gallium.

ORNL facilities were ideally suited for the project. The High Flux Isotope Reactor (HFIR) is located adjacent to the Radiochemical Engineering Development Center (REDC) where the tests were conducted. In addition, the REDC contains hot cells, alpha laboratories, and radioanalytical facilities in adjacent rooms and these facilities are operated continuously, 24 hours per day. Thus, the short-lived (14-hour half-life) radioisotope ^{72}Ga could be prepared in the reactor, followed quickly by conducting the solvent extraction tests in the REDC alpha lab, and again, quickly obtaining radioanalytical counting measurements.

Very few data are available for the extractability of gallium in the PUREX system. In a review article, Orth, Wallace, and Karraker state that gallium has a low distribution coefficient but that chloride complexing makes gallium highly extractable in high-TBP and high-chloride concentrations.[2] This latter condition is not applicable to our intended use; therefore, extractability is expected to be low. Screening tests of nearly all the elements in the periodic table (at tracer level), using a range of concentrations of HNO_3 versus 100% TBP, indicate distribution coefficients (K_d values) in the vicinity of 10^{-4} for gallium.[3] Because of the law of mass action, K_d values for gallium in the 30% TBP system would be expected to be much smaller, by more than an order of magnitude.

Results of the tests showed a DF of 3.6×10^6 for the first-stage organic extract. The K_d for gallium in this chemical system was approximately 3×10^{-7}. Both the scrubbed organic and the stripped aqueous plutonium product were below the limit of detection, yielding DFs of $>5 \times 10^6$. The increase in DF, as measured in the scrub and strip stages, implies that even larger DFs are possible, as far as fundamental chemical considerations are concerned. Therefore, the limiting factor in practice will depend on engineering design and operational aspects of the facility.

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PRODUCTION, RECOVERY, AND PURIFICATION OF “SPECIAL” ACTINIDES

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The Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory processes irradiated targets to recover the transplutonium actinides for research and industrial uses. In a typical processing campaign, the recovered products are Bk-249, Cf-252, Es-253/254, Fm-257, and an americium/curium product for recycle into targets for irradiation. In addition to these standard products, a number of other actinide isotopes are made accessible to the research community as the product fractions become available or are requested by the researchers. Recent actinide product fractions recovered for distribution include the milking of Fm-255 from the decay of Es-255 in the REDC campaign 71 (C71) processing. In C71, three milkings of the einsteinium product solution were performed, with each of the Fm-255 recoveries in the 2- to 4-ng range. These three Fm-255 fractions were made available to researchers in the Physics Division at Argonne National Laboratory (ANL). High-isotopic-purity Cm-245 (99.94 at %) as a second-decay daughter of Bk-249 has also been recovered at the REDC. This product proved to be attractive for the optically detected nuclear magnetic resonance studies at ANL because it is an odd-numbered isotope with a negative spin. Interest in the use of Cf-251 for a variety of research projects has increased recently; such initiatives include studies of the fission product distribution from thermal-neutron-induced fission of Cf-252 and investigations of optically detected nuclear magnetic resonance. The best sources for Cf-251 are the initial Cf-252 products produced in the late 1960s and early 1970s. Californium-252 sources produced from these early Cf-252 products have been retrieved from storage for processing and recovery of the Cf-251 as a product fraction. Continuing interest in Cm-248, the first-decay daughter of Cf-252, and Cf-249, the first-decay daughter of Bk-249 is evidenced by recent requests for milligram quantities of both of these actinide products. All the above-named products were recovered, separated, and purified using standard actinide-processing techniques such as separation of the trivalent actinide products from other decay and corrosion products via cation exchange and separation of the individual actinides via cation exchange using ammonium alpha-hydroxyisobutyrate eluent. A separation utilizing TEVA® resin is often included when an actinide product free from fission products is desired.

Another area of special product preparations is the electrodeposition of actinides, especially Cf-252, on various matrices for either neutron sources or studies of fission fragments. In addition to the standard fission chamber source on platinum or stainless steel, we have electrodeposited Cf-252 on gold, gadolinium, iron, and copper foils and a copper cylinder. All these source fabrications require high-purity feed solutions, free of extraneous mass, for successful deposition of the actinide. In addition to the Cf-252 depositions, Cm-244 has been successfully electrodeposited on platinum disks.

The REDC continues to provide the facilities/capabilities necessary to produce, recover, separate and purify the wide variety of heavy actinide isotopes required to meet the needs of the research community. Many of these products are produced by the irradiation of target materials in the High Flux Isotope Reactor, including special irradiations of various actinides. However, as evidenced above, others are recovered as decay products having unique isotopic compositions that are more favorable for certain research applications. The return of actinide materials from other U.S. Department of Energy sites for recovery and/or repurification has increased over the last few years as the number of facilities capable of handling these materials and the quantities of these materials allowed have decreased. Our current capabilities have allowed us to accept these materials for processing and redistribution in the quantities needed for specific research activities. The intrinsic value of these products has been recognized, and our ability to recycle the materials for use by the scientific community is proving to be a valuable asset to various research programs.

DEVELOPMENT OF MINIATURE HIGH-DOSE-RATE ^{252}Cf SOURCES FOR BORON-ENHANCED AND FAST NEUTRON BRACHYTHERAPY

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Californium-252 neutron source capsules are being used for brachytherapy applications where the source is inserted through a catheter and positioned in or near the tumor to kill cancerous cells. Tumors can be surgically debulked prior to brachytherapy; alternatively, tumor mass will rapidly shrink as a result of fast neutron brachytherapy. Conventional brachytherapy employs photon sources, such as iridium-192, that require less shielding and are simpler to fabricate than ^{252}Cf, but are less effective than neutrons in treating radioresistant tumors (e.g., bulky and hypoxic tumors such as glioblastoma of the brain). Clinical treatments of several thousand patients have clearly demonstrated the radiobiological advantages of ^{252}Cf neutron brachytherapy in treating radioresistant tumors.

Brachytherapy sources can either be manually afterloaded into patients (e.g., by medical personnel with tweezers working behind biological shielding) or remotely afterloaded with the source attached to a cable and precision computer-controlled positioning within the catheter. In the United States, several manually afterloaded low-dose-rate (LDR) source designs, containing up to a few tens of micrograms of ^{252}Cf, have been produced. Internationally, only four high-dose-rate (HDR) remote afterloader systems (RASs) are known to have been demonstrated (Japan, Russia, the Czech Republic, and China). These Russian-made HDR sources contain up to 2 mg of ^{252}Cf in ~3-mm-diameter capsules, too large to treat certain geometrically constrained or neurologically sensitive tumors. For maximum radiobiological advantage and minimum treatment times, ^{252}Cf HDR sources are required, but potential for significant dose to clinical personnel precludes manual afterloading.

The Californium Program at Oak Ridge National Laboratory (ORNL), in collaboration with Isotron, Inc., is developing a family of miniature ^{252}Cf HDR source designs to be coupled to an RAS for treatment of a variety of tumors. Providing a significantly smaller HDR brachytherapy source than currently available will enable unprecedented treatments of radioresistant cancers. Such cancers exist in melanomas; sarcomas; gliomas; tumors of the salivary glands; adenocarcinomas of the prostate; locally advanced breast cancer; cervical cancer; and cancers of the head, neck, and oral cavity. The sources can either be used for stand-alone fast neutron brachytherapy or coupled with boronated pharmaceuticals for boron-enhanced neutron brachytherapy. Isotron has developed a computer model to study the dose enhancement factor based on the presence of boron compounds. Boron-enhanced ^{252}Cf brachytherapy promises improved tumor control by providing a capability for tailoring the dose distribution around the region of the tumor and enhancing dose delivery to neighboring metastases.

ORNL fabricates a cermet wire source form (Cf_2O_3 embedded in a palladium matrix). Until recently, the thinnest cermet wires fabricated at ORNL exceeded 1 mm in diagonal dimension with typical linear loadings of ~200 □g/mm. A customized rolling mill was recently developed and tested; the first submillimeter ^{252}Cf core wire was produced earlier this year, containing the highest volumetric ^{252}Cf loading ever reported—in the range of several hundred micrograms per cubic millimeter of wire. Source capsules were designed to encapsulate this wire into the first miniature HDR ^{252}Cf sources. Using a figure of merit of ^{252}Cf mass per total capsule volume, the prototype sources will approach a twofold increase in volumetric loading over that of currently available sources, but in a significantly reduced capsule geometry. Prototype sources will be fabricated at ORNL for distribution and clinical testing. The sources are designed to couple with an RAS designed by Isotron, Inc., for practical clinical handling. Fabrication development for further source miniaturization is ongoing to broaden the potential range of therapeutic applications.

RESEARCH AT THE CALIFORNIUM USER FACILITY FOR NEUTRON SCIENCE

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The Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL) is the ^{252}Cf production and distribution center for the U.S. Department of Energy (DOE) ^{252}Cf Neutron Source. Portable sources of ^{252}Cf, emitting up to ~10^{11} neutron s^{-1}, are fabricated for loan to agencies and subcontractors of the U.S. government for a variety of research and industrial applications and to universities for educational, research, and medical applications. The DOE also sells ^{252}Cf to commercial encapsulators, both domestically and internationally for a variety of industrial applications. These applications include neutron radiography, neutron activation analysis, on-line monitoring of coal and cement blending, fissile materials analyses, nuclear waste assays, reactor start-up sources, calibration standards, contraband detection, and cancer therapy/research.

The Californium User Facility (CUF) for Neutron Science has been established to promote research and other applications of ^{252}Cf by making available to users for their particular experimental purposes the large inventory of neutron sources, existing facility infrastructure, and technical support staff located at the REDC. As such, the CUF is a unique resource for fast and thermal neutron radiation effects testing and is ideal for experiments requiring moderate neutron fluxes. It provides users a cost-effective option for ^{252}Cf-based studies without the capital outlay or regulatory issues typically involved.

The CUF encompasses two large, uncontaminated, walk-in hot cells, a water-filled storage pool, an inventory of more than 200 neutron sources, pneumatic transfer capabilities, and associated infrastructure and technical support. Sources containing submicrogram quantities to tens of milligrams of ^{252}Cf are routinely handled. A maximum of 60 mg of ^{252}Cf (>10^8 cm^2 s^{-1} thermal and fast fluxes) can be handled in the uncontaminated hot cells while total fluxes of >10^9 cm^2 s^{-1} are available for irradiations within the water-filled storage pool. Operations within the CUF are facilitated by hands-on experimental set-up, remote handling, and real-time data acquisition capabilities.

To date the CUF has been utilized effectively by a number researchers in a wide variety of applications. Most recently experiments were conducted in the CUF by researchers from the Advanced Photon Source (APS) of Argonne National Laboratory to determine the onset of neutron-induced demagnetization in high-magnetic field Nd-Fe-B permanent magnets. The APS uses these magnets inside their insertion devices to produce x-rays for scientific research and any magnet degradation during the operational lifetime of the APS could impact its precision alignments. Using neutrons from sources ranging from 41 μg to 48 mg in ^{252}Cf content, systematic irradiations of the sample magnets were conducted and it was determined that the onset of demagnetization occurred at a fast neutron fluence of ~10^{13} cm^{-2} s^{-1}.

In other experiments a university consortium has used ~59 mg of ^{252}Cf in a series of irradiations to test the neutron hardness of avalanche photodiode detectors for use in Compact Muon Solenoid detector at the CERN accelerator. Real-time data acquisition and computer control were provided by cables connecting the experiment (in-cell) to the electronic hardware (out-of-cell). These experiments simulated the expected in-service fast neutron flux of 2×10^5 cm^2 s^{-1}, and accelerated irradiations provided the predicted lifetime fast fluence of 1.2×10^{13} cm^{-2} s^{-1} in 335 hours of irradiation thus permitting the full characterization of the radiation degradation of the detectors.

Additional CUF applications to be highlighted include experiments for the Canadian Department of National Defense to optimize a land mine detection system based on thermal neutron activation, boron neutron capture therapy experiments on the relative effectiveness of prototype boron-containing compounds for cancer treatment, and irradiations of rice and other seeds to induce genetic mutations.

URANYL ALKOXIDE CHEMISTRY

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Electronic structure and bonding in actinyl complexes (AnO_2^{n+} where An = U - Am) continue to attract the attention of experimentalists and theorists alike.[1-3] Studies of the non-aqueous alkoxide chemistry of UO_2^{2+} provide the means to examine the reactivity and electronic structure of these species in the absence of complicating side reactions such as hydrolysis. Metathesis and protonation reactions permit isolation of a broad range of discrete molecular uranyl entities both as solids and in aprotic solvents in which it is possible to vary the ligand basicity and steric encumbrance. Uranyl complexes have been isolated as monomers, dimers, and higher order oligomers. These complexes afford an opportunity to examine in some detail the relative importance of ligand basicity and steric demand in directing structural preferences (monomer vs. dimer, *cis* vs. *trans* isomers) and in determining electronic structural properties and relative bond strengths in the "yl" and equatorial bonds.

In the presence of more basic alkoxide ligands, simple monomeric uranyl alkoxide complexes are unstable, and react further to generate a variety of products which depend on the basicity and solubility of the ligand. These compounds can undergo intermolecular ligand exchange, or can generate aggregates that exhibit coordinative behavior previously not seen for actinyl species obtained from aqueous solutions. The AnO_2^{n+} chromophore imparts electronic and vibrational spectroscopic characteristics that are quite sensitive to changes in symmetries and bond strengths in the equatorial plane of the "yl" moiety as well as any dative interactions involving the "yl" oxygen atoms.

Optical spectroscopy is a useful tool for determining the relative degree of aggregation in the solid state or solution. Comparison of the emission spectra of these compounds shows that there is a red shift in the $E_{0\text{-}0}$ transition as the degree of oligomerization is increased. Therefore, solvent induced deaggregation may be determined. Furthermore, the reactivity of these uranyl alkoxide compounds is directly related to the degree of oligomerization in solution. Aggregates that remain intact are unreactive, while those that are either monomeric or fragmented allow for the preparation of new chemical species.

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ACTINIDE-OXO CHEMISTRY IN THE PRESENCE OF STRONG DONOR LIGANDS

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The coordination chemistry of the uranyl ion in aqueous media is traditionally described to be dominated by strong covalent bonding along the axial O=U=O unit, which contrasts dramatically with the weaker electrostatic interactions observed to the ligands (typically 4-6) that coordinate in the equatorial plane.[1] More recent results, however, indicate that the presence of strong donor ligands in the "belly band" of the actinyl ion perturb this bonding picture.[2] We are currently examining new coordination environments for the uranyl ion in *non-aqueous* media, particularly employing strong-donor amide and alkoxide ligands in the equatorial plane. These ligands effectively compete with the axial dioxo unit for bonding to the high-valent uranium center, generating a subtle electronic balance that labilizes the normally inert U=O bonds and introduces interesting new reactivity. This reactivity has been explored as a function of the donor strength and steric bulk of the equatorial ligands, with particular emphasis on the use of chelating tripodal ligand sets to direct the linear uranyl moiety to a *cis* geometry. Results from these studies have included isolation of a series of mixed-valent uranium complexes supported by tripodal amide ligands.

Another possible synthetic route to uranium *cis*-dioxo complexes would entail the sequential introduction of oxo groups to an organometallic precursor in which a *cis* geometry is already enforced by the ancillary ligands. This strategy is an extension of the previously demonstrated ability to synthesize the analogous bis(imido) uranium bent-metallocene complexes $(C_5Me_5)_2U(=NR)_2$. In contrast to the general stability observed for the uranium(VI) bis(imido) species, however, the analogous dioxo derivatives are unstable with respect to reduction of the uranium center. For example, utilizing the sterically encumbered cyclopentadienyl ligand $(C_5Bu^t{}_3H_2)^-$, the major product obtained is an unprecedented hexanuclear cluster consisting of uranium(V) centers arrayed in a structure that bears a striking resemblance to the known polyoxometalates of Mo and W. Issues of metal valence and electron localization/delocalization are being probed in all polymetallic complexes by a combination of methods including vibrational and electronic spectroscopy, NMR, EPR, and magnetic susceptibility measurements.

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ORGANIZATION OF SOLUTE SPECIES IN ORGANIC MEDIA

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Metal solvent extraction data obtained with P,P′-di(2-ethylhexyl) methane-, ethane-, and butanediphosphonic acids (H_2DEH[MDP], H_2DEH[EDP] and H_2DEH[BuDP], respectively) exhibit features that are difficult to explain without knowledge of the aggregation state of the extractants and their metal complexes. Extractant structure and diluent type determine these aggregation phenomena which, in turn, have a pronounced effect on metal extraction chemistry.

Information on the aggregation of the dialkylsubstituted diphosphonic acids in aromatic diluents has been obtained using the complementary techniques of vapor pressure osmometry (VPO), infrared spectroscopy, molecular mechanics and small angle neutron scattering (SANS). In toluene, H_2DEH[MDP], H_2DEH[EDP] and H_2DEH[BuDP] molecules form dimeric, hexameric, and trimeric aggregates, respectively.

SANS data indicate that the H_2DEH[EDP] hexameric aggregate assumes a spherical shape. In this structure, reminiscent of a reverse meicelle, the alkyl groups are probably oriented outwards (toward the solvent) and a large hydrophilic internal cavity is available to accommodate metal cations and/or water molecules.

SANS investigations confirm that large aggregates form when solutions of H_2DEH[MDP] and H_2DEH[BuDP] are used to extract certain cations under high metal loading conditions. The largest aggregates were observed in the extraction of Fe(III) and Th(IV) by H_2DEH[MDP]. The Fe(III)-H_2DEH[MDP] aggregates are rods of constant radius whose length increases with the metal concentration in the organic phase. The Th(IV)-H_2DEH[MDP] and Fe(III)-H_2DEH[BuDP] aggregates are cylindrical but growth also occurs laterally as more metal is transferred into the organic phase.

With H_2DEH[EDP], the average aggregation number remained essentially unchanged after extraction of metal ions at high concentration. This result reaffirms the unique solvent extraction behavior of H_2DEH[EDP]. The highly aggregated state of H_2DEH[EDP], which is not disrupted by metal extraction, and the strong water absorption bands observed in the infrared for H_2DEH[EDP], confirm that this extractant in aromatic diluents behaves in a way similar to reverse micelles. The first-power extractant dependency observed in the extraction of various metal cations by H_2DEH[EDP] fully agrees with the results of the aggregation studies.

EXTENDING THE PERIODIC TABLE: CHEMICAL PROPERTIES OF TRANSACTINIDE AND SUPERHEAVY ELEMENTS

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Determination of the chemical properties of the elements is the most fundamental goal in all of chemistry. Measurement of the chemical properties of the transactinide elements ($Z>103$) is especially difficult because the longest-lived isotopes have sub-minute half-lives, and production rates vary from only atoms-per-minute for rutherfordium (Rf, $Z=104$) to atoms-per week for superheavy elements $114<Z<118$.

Fifteen years ago, the only chemical information for transactinide elements was from two rudimentary experiments showing that Rf behaves like Hf, its periodic table homolog. Since that time, the Lawrence Berkeley National Laboratory's Heavy Element Nuclear and Radiochemistry Group has performed extensive studies on the chemical properties of Rf and dubnium (Db, $Z=105$), in both the aqueous and gas phase. Some of these experiments were performed in collaboration with European groups from GSI/U. Mainz (Germany), and PSI/U. Bern (Switzerland). Rf and Db have chemical properties that clearly place them in their expected periodic table positions at the bottom of groups 4 and 5, respectively. However, unexpected trends in chemical properties within these groups show that increased relativistic effects on even the valence electrons are important in understanding the chemical properties. Recent improvements in experimental techniques and sensitivity have resulted in the first measurements of chemical properties for seaborgium (Sg, $Z=106$) and bohrium (Bh, $Z=107$). These latest experiments were performed on isotopes with half-lives on the order of 20 seconds, and detection rates of only about one atom per week.

During the last two years, new elements have been discovered up to element 118, confirming theories of strongly enhanced nuclear stability for the superheavy elements. It is now clear that isotopes of elements up to at least $Z=114$ have half-lives which are long enough to allow chemical separations. Opportunities and techniques for extending our knowledge of chemical properties throughout the seventh row of he periodic table during the next ten years will be presented.

FIRST SUCCESSFUL CHEMICAL STUDY OF BOHRIUM (BH, ELEMENT 107)

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The arrangement of the chemical elements in the periodic table indicates similarities of chemical properties, which reflect the elements' electronic structure. For the heaviest elements, however, deviations in the periodicity of chemical properties are expected due to relativistic effects. The discovery of ^{267}Bh with a half-life of ~17 s makes it an ideal candidate for gas phase chromatographic separation studies with the OLGA system, since the typical separation time with this device is about 5 s. The nuclides ^{267}Bh and ^{266}Bh were discovered at LBNL a few months previously via the ^{249}Bk(^{22}Ne,4*n*) and ^{249}Bk(^{22}Ne,5*n*) reactions [1]. For this experiment our rotating wheel system used a parent-daughter stepping mode to provide detection of α-α correlations with a greatly reduced background. Six atoms of bohrium were detected during this experiment by correlating their decay unambiguously with the decay of their daughters.

Between August 20 and October 26, 1999, an experiment to study Bh chemistry was performed at PSI, Switzerland. A 670 μg/cm^2 ^{249}Bk target was irradiated with ^{22}Ne^{6+} at 118 MeV for a total beam dose of $3.0\text{x}10^{18}$ particles. The behavior of Bh was investigated at 180, 150, and also at 75°C. The target material was provided by Office of Science, Office of Basic Energy Research, Division of Chemical Sciences, of the U.S. Department of Energy, through the transplutonium element production program at the Oak Ridge National Laboratory.

The unambiguous identification of Bh after chemical separation allows us to conclude that like its lighter homologues, Bh forms a volatile oxychloride compound, presumably BhO_3Cl, and behaves like a typical group seven element, taking its place on the periodic table [2]. Further experimentation is being performed at PSI right now, through the end of December to investigate its chemistry in more detail relative to its lighter homologues.

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Abstract for Heavy Elements Contractors Meeting November 20-21, 2000

Kinetics of Actinide Complexation and its Impact on Understanding Chemical Processes in Aqueous and Organic Solutions

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The effective design of new chelating agents that address current and future needs for energy production, site decontamination, and environment restoration demands the input of several different types of information. Investigations of organic and inorganic synthesis methods, of the structures of chelating agents and their metal complexes, and of the kinetics and thermodynamics of metal-ligand interactions in solution phases all contribute to greater understanding of the chemical processes. Increased understanding of the interplay of these factors leads to the development of successful applications of the fundamental science. All components of this formula (synthesis, structure, physical chemistry) must be applied in tandem to achieve a complete understanding of the chemical principles that govern the interactions between metal ions and organic chelating agents. The particular focus of this portion of our research program is on the contributions of studies of the kinetics of metal complexation reactions in aqueous and organic media to a more complete understanding of actinide ligation. In general, actinide complexation reactions tend to be rapid, particularly in acidic solutions relevant to process chemistry. The fast reaction kinetics usually demand the application of rapid detection techniques like stopped-flow spectrophotometry and NMR spectroscopy. This presentation will briefly present correlations of earlier data on the relative rates of complexation reactions of actinide ions, mainly in the upper oxidations states. The results of more recent studies of the rate of formation of an unusual ternary complex between actinyl ions, dipicolinic acid, and a colorimetric indicator ligand, and our first studies of ligand exchange rates in organic media also will be presented. The latter studies presage planned investigations of the kinetics of ligand exchange in highly ordered media like micelles or “third phases” that can form under some conditions in solvent extraction. From our investigations to date, the role of the solvation of metal complexes in governing the rates of metal complexation reactions has emerged as an important focus for this research. Differences between the relatively well-known behavior of water as a solvent as compared with organic solvents are of particular interest.

ACTINIDE COORDINATION CHEMISTRY FOR THE DESIGN OF DECORPORATION AGENTS, SENSORS, EXTRACTANTS, AND NOVEL STRUCTURES

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The development of actinide sequestering agents in our laboratory has relied on data from several areas of coordination chemistry. Direct study of the coordination chemistry of the actinides allows for comparison of structural, thermodynamic and solution chemistry of metal complexes. Also, understanding coordination chemistry of the lanthanides allows for these metal ions to be used as models for actinides. Siderophores, the naturally occurring iron(III) sequestering agents, have inspired a biomimetic approach for the design of preorganized sequestering agents for actinides. Animal studies comparing efficacy and toxicity provide important feedback for optimizing the design of new effective actinide decorporation agents.

As part of our interest in the coordination chemistry of lanthanides and actinides, we have recently described the design and synthesis of an octameric lanthanum pyrazolonate cluster.[1] Out of this same work we have also synthesized the first supramolecular actinide complex with Th(IV). Studies with tetradentate hydroxypyridinone(HOPO) ligands and Ce(IV) as a model for Pu(IV) have shown that these cations have a high stability with these ligands.[2]

Actinide decorporation studies in our group have recently focused on uranium(VI), plutonium(IV) and neptunium(V) ion. We have focused on the toxicity and efficacy of catecholate and HOPO ligands for the decorporation of uranyl.[3] Additionally, a study of *in vivo* decorporation of Pu(IV) compared structural isomers of multidentate hydroxypyridinonate ligands for efficacy and toxicity.[4]

The removal of actinides from waste streams presents challenging separations problems due to the unique mixture of radioactive and non-radioactive components in each stream. In collaboration with researchers at LANL, we are examining polymer filtration and water soluble chelating polymers used in combination as an effective way to remove and concentrate Pu(IV) from dilute waste streams. The scaffold for the WSCP is polyethyleneimine (PEI), a soluble polymer with a molecular weight $\geq 30{,}000$ Da, with terephthalamide (TAM) ligands attached to the PEI as the Pu(VI) chelating agents. In Pu(IV) uptake experiments, we found these functionalized polymers work extremely well through a large pH range: K_d values of 4.8×10^6 (pH 11.4, 99.8% extraction) and 1×10^5 (pH 2.9, 91.1% extraction). Also examined was the uptake of Am(III), a potential competitor, which binds tightly at higher pH, comparable to Pu(IV), but is disfavored at lower pH. Competition experiments with excess EDTA or Fe(III) demonstrated that neither interfered significantly with the uptake of Pu(IV).

Future work will continue to focus on structural and solution coordination chemistry of the actinides. Included are plans for 'in house' experiments with Pu and Np, using custom built solution cells and control equipment inside an approved radiological glovebox. Incorporation of HOPO ligands into sensors for uranyl (UO_2^{2+}) is also currently being explored.

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METAL ION RECOGNITION IN CHEMICAL SEPARATIONS: STEREOCHEMICAL, SYNERGISTIC, AND SOLVENT EFFECTS IN METAL ION SEPARATIONS USING CROWN ETHERS

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Recently, the need for new and improved separations technologies, particularly for metal ions, has grown significantly. Solvent extraction (SX) is frequently the method of choice for both process-scale and (with suitable modifications) analytical-scale metal ion separations, a direct result of its physical simplicity and versatility. Although there are a number of both physical and chemical parameters in any liquid-liquid system that can be varied to enhance the efficiency and selectivity of the system for extraction of a particular ion, in the final analysis, the success of a given extraction process is frequently governed by the efficiency and selectivity of the extractant itself. For this reason, there has long been considerable interest in the design and synthesis of extractants of improved specificity for selected metal ions.

Recent work in our laboratory has focused on the use of macrocyclic polyethers (crown ethers) for the separation and preconcentration of various metal ions, both in liquid-liquid extraction and in ion-exchange and chromatographic systems. Of particular interest in our work has been the elucidation of the factors governing metal ion extraction from acidic media by crown compounds and the exploitation of these factors in developing improved methods for the separation of selected fission product (*i.e.*, alkali and alkaline earth) cations. Previous work has established that a number of structural features of a crown molecule determine the strength and selectivity of its interaction with a given metal ion and thus, its usefulness as a metal ion complexing agent / extractant. Although the effect of many of these parameters has been thoroughly investigated, the influence of crown ether stereochemistry has received relatively little attention. In collaboration with Pacific Northwest National Laboratory, we have recently demonstrated the utility of molecular mechanics methods in establishing the relative extraction efficiency of various crown ether stereoisomers, identifying appropriate synthetic targets, and understanding the often substantial differences in extraction behavior observed for commercially available crown ethers. In conjunction with these studies, we have sought improved methods by which selected stereoisomers can be either synthesized or isolated from commercial preparations, and these efforts have led to both improved routes to the preparation of several isomers of dicyclohexano-18-crown-6 and to a combined chromatographic/ selective precipitation approach to the isolation of several stereoisomers of its di-t-butyl-substituted derivative.

In an effort to avoid stereochemical influences on complexation/extraction behavior, we have also been examining the application of simple, unsubstituted crown ethers (*e.g.*, 18-crown-6), compounds generally regarded as having little utility in SX systems due to their significant water solubility, in metal ion separations. Certain of these compounds have been found to have a significant effect (*i.e.*, selective enhancement of retention) on the elution behavior of alkaline earth cations on strong-acid cation-exchange resins, and it has been demonstrated that these effects can be exploited to devise improved methods for their separation. Follow-up studies using the same crown ethers in an SX system employing lipophilic sulfonic acid cation exchangers in o-xylene indicate that selective synergistic enhancement of cation extaction is also possible in these systems. Both of these observations offer additional opportunities for the design of efficient and selective metal ion separation schemes. The application of solvent effects offers a similar range of opportunities for the development of novel systems for metal ion separations.

RELATIVISTIC DENSITY FUNCTIONAL STUDIES OF THE STRUCTURE AND BONDING OF EXPERIMENTALLY-RELEVANT ACTINIDE SYSTEMS

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Density functional theory (DFT) with scalar relativistic corrections (and, when appropriate, spin-orbit relativistic corrections) has become a remarkably useful tool to assist experimental efforts in actinide chemistry. We have used relativistic DFT, generally with the Perdew-Wang (PW91) generalized gradient functional, to address a number of disparate questions about structure, bonding, and spectroscopy of actinide systems that are under active experimental investigation. In particular, the ability to calculate the structures, relative energetics, and vibrational frequencies of actinide-containing systems via *a priori* electronic structure calculations is increasingly becoming an important tool in the further development of experimental actinide chemistry.

This presentation will highlight three recent investigations of this sort: (1) The structures of bis-arene complexes of the type $(\eta^6\text{-}C_6H_3R_3)_2An$ (R = H, Me, ^{t}Bu; An = Th, U, Pu) are predicted as a function of the arene substituent and actinide center. These calculations relate to nascent investigations of the syntheses of this largely unknown class of organoactinide complexes. (2) In collaboration with Andrews and coworkers at the University of Virginia, we are exploring the structure and bonding of small actinide-containing molecules that are generated via laser ablation of actinide metals in the presence of small reactive molecules, such as CO and CO_2. Calculated vibrational frequencies of the An + CO and An + CO_2 adducts are used to help identify the species that are isolated in frozen noble-gas matrices of the reaction products. (3) In collaboration with coworkers at Argonne National Laboratory, we have explored the speciation of ions of plutonium and neptunium ions in water. The DFT-calculated structures correlate well with the available EXAFS and XANES data on these species.

SOFT X-RAY SYNCHROTRON RADIATION INVESTIGATIONS OF ACTINIDES

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To fundamentally understand the chemical and physical properties of actinide systems, it is necessary to have knowledge of electronic ground state and low-energy excited states. Nowhere is this complex behavior of the actinides more evident than at the transition from itinerant to localized 5*f* states in the actinide metals that occurs between plutonium and americium. The complementary soft x-ray synchrotron radiation (SR) methodologies of photoelectron spectroscopy (PES), resonant PES, near-edge x-ray absorption fine structure (NEXAFS), and x-ray emission spectroscopy (XES) provide ideal avenues for the investigation of actinide electronic structure and surface chemistry/physics in the energy regime that directly involves the valence electrons. Furthermore, light elements such as boron, carbon, nitrogen, and oxygen may be directly investigated at the K-edges in this energy region (which are often key constituents in actinide materials systems). Recently, meaningful soft x-ray PES and XES experiments have been safely performed at the Advanced Light Source (ALS) at LBNL stemming from the capability to use small amounts of actinide material.[1-2] Significant improvements in theoretical calculations are providing valuable support to assist in the interpretation of the results from these experiments. The results of these investigations will help characterize the behavior of 5*f* electrons in chemical bonding that is vital for understanding the chemistry/physics of actinide materials as well as providing a more comprehensive view of chemical bonding throughout the periodic table.

The research capabilities that will form the foundation for soft x-ray SR investigations at the ALS in the near future are currently under development. An important component is the development of an end station to regularly handle and clean actinide sample surfaces. A dedicated actinide electron spectrometer end station for use at the ALS is nearing completion as part of a collaborative effort by the three University of California National Laboratories. The end station will be used for high resolution PES and NEXAFS spectroscopic investigations of plutonium metals, alloys, compounds, and other actinide materials. The current XES studies will be extended to include transuranic materials and combined with the use of liquid cells, will begin to investigate simple actinide solution chemistry. The soft x-ray SR scientific efforts will make use of the ALS-Molecular Environmental Science Phase I Beamline (75-2000 eV) that will become available in the fall of 2002.

A crucial element of the soft x-ray SR effort is the preparation of high quality actinide materials for use in conjunction with the actinide end station. Although the actinide end station will have sample cleaning capabilities compatible with the use of actinide millicrystals, the ability to prepare pristine thin films of actinide materials *in situ* will provide tremendous opportunities in the future. Thus, both actinide small crystal and thin film growth capabilities will be developed. The thin film growth capability and spectroscopy on the actinide thin films will be collaborative with T. Gouder.[3] The ability to frequently prepare fresh surfaces via thin film growth will open a new realm for the investigation of chemistry/physics at actinide surfaces, especially with molecules containing the light elements mentioned above. The growth of actinide thin films on different substrates also provides a number of interesting possibilities to explore actinide interfacial chemistry as well.

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MULTI-PIXEL MONOLITHIC Ge FLUORESCENCE DETECTOR, PULSE SIGNAL PROCESSING ELECTRONICS, AND A REAL TIME DIGITAL DATA ACQUISTION SYSTEM FOR XAFS STUDIES.

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It is apparent that over the last decade x-ray absorption fine structure (XAFS) spectroscopy has become an increasingly useful experimental technique for heavy element research. Other groups in other fields have also certainly recognized the value of XAFS experiments. As a result, experimental time on synchrotron beam lines is increasingly precious. Thus, effective use of the beam time is essential, especially for dilute samples and samples with highly scattering matrices. Better performing instrumentation is needed.

The Instrumentation Engineering Groups at LBNL have been at the forefront of design, development, fabrication, and implementation of state-of-the-art pulse counting electronic modules and fabrication of novel solid-state detectors for more than forty years. These groups have contributed significantly to the success of DOE accelerator-based science programs and have served to stimulate useful interactions between the DOE laboratories. Furthermore the LBNL Engineering Groups through indirect competition and or collaboration with private instrumentation companies (via direct technology transfer agreements or demonstrating the enhanced performance of working examples) have provided much of the technological foundation for the commercial products manufactured by several companies.

The LBNL Actinide Chemistry Group (ACG) XAFS program recognized the necessity to have routine access to a high performance multi-element x-ray fluorescence detector at SSRL. The few detector systems available from SSRL were usually in use by other groups. This condition stimulated collaboration between the LBNL Detector groups and ACG to fabricate a detector/data acquisition system for the ACG XAFS program. It was recognized after identifying the performance limitation of each detector/acquisition system component that only an optimized custom system, tailored to the requirements of the LBNL ACG for x-ray fluorescence detection, would give the best performance.

The fabrication of the LBNL multi-pixel monolithic Ge detector element along with the advantages and disadvantages of the configuration will be presented. The preamplifiers, pulse shaping amplifiers (250 and 500 ns peaking times), and dead-timeless single channel analyzer (SCA) modules that comprise the optimized fluorescence detection system also will be presented in detail. The issue of "counter dead-time" and the correction needed as a function of detector total incoming count rate (ICR) will be discussed. Related to the choice of count pulse processing peaking-times, the LBNL detection system is correctable, with a single dead time constant, up to an ICR of 1 million events per second per detector pixel. For each individual detector channel preliminary results from testing a real time pulse height analyzer (PHA) data acquisition system will be described as well. This PHA system has “nuclear grade” 12-bit resolution and can operate without bit loss at rates exceeding 1 million counts per second per detector element. It is believed that the performance of the detector, electronics, and developmental data-acquisition system is close to the limit of analog-based XAFS detection schemes. Further signal detection enhancements will stem from developing and using specialized specific x-ray energy filtering techniques.

THE USE OF HIGH-ENERGY X-RAY SCATTERING TO PROBE THE SOLUTION STRUCTURE OF PU "POLYMER"

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Crystalline solids are viewed conceptually as ideal, infinite lattices onto which are arranged the atoms that form the basis of the material. The symmetry that results from this atomic arrangement greatly simplifies the analysis of diffraction data. Thus, the data analysis of a diffraction pattern is not computationally intensive because it inherently assumes perfect symmetry. In reality, any deviation from a symmetric atomic arrangement contributes to the diffuse background and is ignored or discarded in most standard structural refinements. It has recently been recognized that this simple picture of a crystalline solid can overlook a large amorphous component or defected fraction that can exert an important influence on the properties exhibited by the bulk material.

In contrast to crystalline solids, ideal amorphous systems such as glasses and liquids assume a perfectly homogeneous environment over a wide variety of length scales. Diffraction techniques, which rely on long-range order, provide comparatively little insight into structural aspects of these systems. The absence of any inherent symmetry has largely limited structural modeling in amorphous systems to near neighbor interactions. Single-ion probes such as NMR and EXAFS are often used to assess short range, near-neighbor interactions in such materials but little exists in the way of a broader picture.

We use a solution of tetravalent Pu "polymer" to demonstrate the utility of high-energy x-ray scattering for structural characterization. Technically these experiments are done in essentially the same manner as are diffraction experiments, with some minor differences. These differences include the need to obtain data over an expanded Q-range and to take more care in limiting sources of background. However, the data treatment is very different from a conventional diffraction experiment. A more general scattering treatment is utilized in which the data are Fourier transformed to obtain a pair distribution function (PDF). The PDFs contain information about the environments of all the ions in the system.

This approach to data treatment previously has been used to probe homogeneous glass and liquid structures and, very recently, to look at short range superstructure ordering in crystalline materials. Historically, these experiments have been largely limited to neutron scattering data. X-ray data have suffered from inadequate counting statistics or limited Q range. This picture is changing as the third generation synchrotrons are coming on line. There is a clear opportunity for the actinide community to gain new structural and chemical insights from some of these developments. From our perspective, an added advantage of high-energy x rays is that they are very penetrating, so that many of the standard x-ray absorption problems that are encountered when studying actinide-containing materials with lower energy photons will be significantly reduced or eliminated.

BESSRC, the CAT to which the M-Wing staff belong, is commissioning a high-energy x-ray scattering line that will provide data to very high Q. The high flux of high energy x-rays (>100 keV) available on 11-ID-C represents the state-of-the-art. Combined with our new ideas for background reduction, PDF analyses may well provide resolutions and data ranges not seen previously. It is this opportunity that we intend to exploit.

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LASER SPECTROSCOPIC INTERFACIAL STUDIES OF ACTINIDES ON BACTERIA AND MINERAL SURFACES

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In addition to experimental determinations of sorption coefficients and sorption kinetics for actinides on mineral or bacterial surfaces, the speciation of the chemical interactions of the actinides and the understanding of sorption mechanisms and related processes is essential. Only a few analytical methods can give information about the chemical environment of actinides at low concentrations in aqueous suspensions containing mineral particles or bacteria. Especially suitable for studying interfacial processes are time resolved laser-induced fluorescence spectroscopy (TRLFS) and surface enhanced Raman spectroscopy.

Our TRLFS-studies of U(VI)-complexes with freshly grown, aged, and genetically engineered bacteria show that a variety of processes can occur with different biomasses. Depending on the biomass, the U(VI) interaction with organic or inorganic phosphate that is expressed by the cells can range from pure sorption to pure precipitation. These complex processes need to be fully understood, quantified and considered in the interpretation of laboratory sorption data.

We monitored the expression of phosphate on the bacterial surfaces' of dying and decomposing bacteria by surface enhanced Raman spectroscopy. We conclude from our findings that actinide sorption on fresh or dead bacteria differ significantly. This needs to be taken into account for the prediction of the actinide migration in natural environments where a mixture of living and dead biomass is present.

We are investigating the sorption and interfacial behavior of trivalent Cm on minerals, soils and bacteria by TRLFS. The extremely low limit of detection for Cm fluorescence ($5 \cdot 10^{-11}$ mol/L) and the use of a newly installed Nd-YAG – MOPO laser system will give us insight into the complex interfacial interactions of trivalent actinides.

Furthermore, Raman spectroscopy can detect functional groups on bacterial surfaces and perform speciation of non-fluorescent actinides in oxidation states V and VI. Because conventional Raman spectroscopy has low sensitivity, we resonance Raman spectroscopy to lower the detection limit. We have successfully applied this technique for the characterization of Tc(V,VI) complexes. Our Nd-YAG – MOPO laser system, tunable in the wavelength range 200-2000 nm, will enable us to reach resonance frequencies of actinides and of defined functional groups on surfaces of minerals or bacteria. Additionally, we investigate the effect of surface enhanced Raman spectroscopy and will apply this technique to determine the speciation of actinides on geological and bacterial interfaces.

SURFACE INTERACTIONS OF ACTINIDE IONS WITH GEOLOGIC MATERIALS*

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Knowledge at the molecular level of the factors governing radionuclide speciation is vital for assessing the risks imposed by long-term storage of nuclear waste and by radionuclides already present in the environment. Two sites of particular concern are the Nevada Test Site (NTS), the site of numerous underground nuclear tests, and the Yucca Mountain Project (YMP), currently the site of the proposed U.S. designated storage facility for high level nuclear waste.

Over a 41 year period, 828 underground nuclear tests were conducted on the grounds of the NTS leaving as a legacy $>10^8$ Ci of radioactive material in the geosphere of the site. Much of this material is incorporated into the melt glass that forms at the bottom of the cavity after a blast. No barrier exists between these radionuclides and the geosphere to prevent their slow dissolution and migration from the immediate area of the blasts out into the far field environment.

More recently, mineral colloids were found to be an important vector for facilitating radionuclide migration in the environment at the NTS [1]. Plutonium, positively identified as coming from a test conducted at the end of 1968, was found in mineral colloid fractions of groundwater samples taken 1.3 km away from the blast site. Greater than 99% of the total plutonium in the sample was associated with filtered colloidal materials (>7 nm dia.) composed of a mixture of clays and zeolites.

In addition to the radionuclides present in the environment at the NTS, there is concern for the potential release of radionuclides into the geosphere at Yucca Mountain. The radioisotopes of primary concern in the high lever reactor waste to be stored at Yucca Mountain include the long-lived isotopes of U, Np, and Pu and their shorter-lived fission products. Yucca Mountain will also be used as the storage site for an estimated thirty-five metric tons of weapons-grade plutonium from decommissioned warheads, which will most likely be converted to a stable waste form material (i.e. ceramic or glass) containing the neutron poison gadolinium before final storage.

This presentation will discuss XAFS characterization results from a variety of LLNL research efforts that focus on actinide interactions with geologic materials relevant to the NTS and YMP. Specific examples will include: Pu interactions with zeolite colloids, UO_2^{2+} sorption onto silica, alumina, and montmorillonite [2], and Np in cementitious materials [3]. A molecular level determination of the speciation (oxidation state and structure) for U, Np, and Pu in the near field (man-made) and far field (geologic) environments is necessary to successfully predict rates of migration of radionuclides at these sites. XAFS spectroscopy, including XANES and EXAFS, provides an ideal tool for these determinations, since it is an *in-situ,* element-specific probe which eliminates most sample pretreatment requirements and allows one to examine the actinides in complex heterogeneous environmental matrices.

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THE ACTINIDE FACILITY

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The Advanced Photon Source (APS), located at Argonne, is in a unique position to perform experiments on actinide-containing materials because it is situated on a site with facilities and expertise for handling radioactive samples. The Actinide Facility is mandated to assist with experiments at the APS that involve samples containing these elements. The Actinide Facility is not a beam line, but is instead an infrastructure for handling active samples, developing safety protocols and sample containment, and advising experimenters. The Facility includes hot laboratories located in M-Wing of Argonne's Chemistry Division. These laboratories are purpose built for handling and manipulating radioactive samples. M-Wing, together with the Facility, have personnel familiar with the handling of radioactivity, administrative protocols, and many of the technical requirements for the wide variety of synchrotron-based experiments available at the APS.

In addition to these administrative roles, the staff are developing capabilities for doing unique experiments at a synchrotron. For example, in collaboration with M-Wing staff, we have recently designed, built, and demonstrated an electrochemical cell for in-situ spectroscopy experiments. Using this cell, it has been demonstrated that thermodynamic formal potentials can be obtained from XANES data on samples that have more than one redox-active species, and are opaque to UV/visible radiation. Using the same cell, we have also stabilized Np(VII) in alkaline solution and determined its coordination environment. Other recent developments include the design and implementation of electron-yield detection for actinide samples. We have also begun to take advantage of the high-energy scattering beam line at BESSRC CAT, of which the Chemistry Division is a member, to obtain radial distribution functions from a variety of solid, solution and amorphous actinide-containing phases. The information obtained from these experiments is of programmatic interest to the M-Wing staff as well as to the actinide community in general.

We will present an overview of the current capabilities developed by Actinide Facility and give scientific examples of their implementation. All equipment and protocol designs are available to APS CAT members or Independent Investigators wishing to take advantage of these developments.

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Heavy Element Chemistry Contractors' Meeting

November 19 - 21, 2000

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Burns, Carol J.	Chemistry Division, Los Alamos National Laboratory	P4-10 P4-11

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Shuh, David K.	Chemical Sciences Division, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory	P6-2
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Smith, Paul	Department of Energy, Germantown	
Soderholm, L.	Chemistry Division, Argonne National Laboratory	P6-7
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