ACTINIDE RESEARCH QUARTERLY

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Los Alamos

NATIONAL LABORATORY

— EST. 1943 —

CONTENTS

Plutonium science by the bay

THE VIEW FROM ASILOMAR

The waters of the Pacific Ocean off the Monterey Peninsula in California made a dramatic backdrop for the 2006 Plutonium Futures—The Science Conference, which took place July 9–13 at the Asilomar Conference Grounds in Pacific Grove. This conference was the fourth in a series of important international conferences focused on plutonium and other actinides that was initiated in 1997 to enhance the international dialogue among scientists on the fundamental properties of plutonium and their technological consequences. This series was also intended to recapture the spirit of cooperation that was originally established in the "Plutonium" conferences that started in 1960 following President Eisenhower's "Atoms for Peace" speech.

Co-organized by Los Alamos and Lawrence Livermore National Laboratories, the Plutonium Futures Conference was cosponsored by the American Nuclear Society, Elsevier, Quantum Design, and the FEI Company. The conference attracted 282 presentations from nearly 400 participants from 26 countries and covered the latest results in plutonium science and technology.

A popular aspect of the conference was the tutorial session on Sunday afternoon, which was well attended by novices and veterans alike and featured such diverse topics as plutonium metallurgy, plutonium in the environment, and international arms control and nonproliferation. During the week, two plenary lectures began each morning and afternoon session and highlighted the breakout sessions on coordination/organometallic chemistry, solid-state physics, environmental chemistry, materials science, separations and reprocessing, advanced fuels and waste forms, phase transformations, solution and gas-phase chemistry, compounds and complexes, electronic structure and physical properties, and more.

Lively roundtable discussions were held on Monday and Tuesday evenings and centered on Legacy Issues and New Strategies for Advanced Nuclear Fuel Cycles. Three poster sessions with a total of 185 presentations were held on Monday and Tuesday evenings and Wednesday afternoon and added greatly to the technical exchanges among the conference participants.

The Asilomar Beach and Conference Center, part of the California State Parks System, was itself one highlight of the conference. The name is derived from two Spanish words: "asilo," meaning refuge, and "mar," meaning sea. The Center encompasses 107 acres of coniferous forest separated from the ocean by sand dunes affording a significant ecological reserve. Conference participants walking through early morning fog encountered numerous birds, raccoons, deer, and warnings of mountain lions sighted in the area.
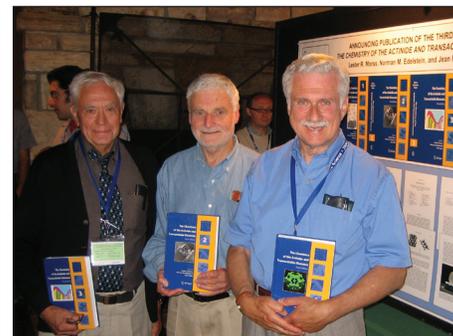
Jean Fuger (left), Norman Edelstein (center), and Lester Morss, editors of the third edition of The Chemistry of the Actinide and Transactinide Elements, *were at the conference for the premiere and release of the five-volume set.*
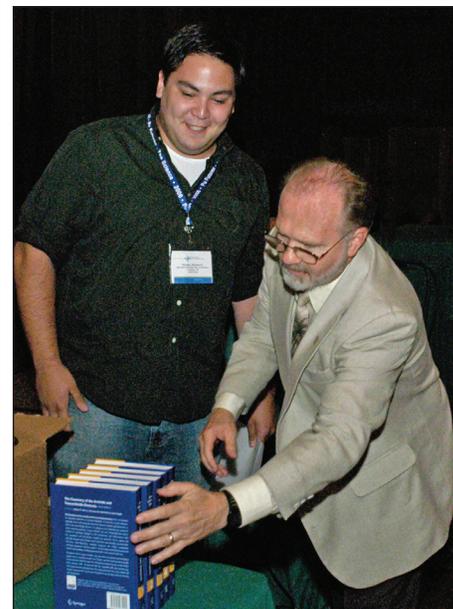
Conference cochair David Hobart (right) presents Student Poster Award-winner Mike Mrozik with a copy of the five-volume set of The Chemistry of the Actinide and Transactinide Elements. *Mrozik, a third-year graduate student at The Ohio State University, won the CATE volumes for his poster, "Calculation of Low-Lying Excited States of PaO$^+$ and PuO$^+$."*

An evening bonfire on the beach on Wednesday was followed by the Conference Banquet and then two thought-provoking lectures by Drs. Gerry Lander and Siegfried Hecker addressing "Plutonium Science Futures" and "Plutonium World Futures." Lander and Hecker were recognized for their outstanding contributions to plutonium science and their leadership in fostering this conference series.

After the talks, the conference committees and staff were recognized for their hard work and the Best Student Poster Awards were presented. The most coveted of the Student Poster Awards, sponsored by Springer Publishers, was a copy of the five-volume set of *The Chemistry of the Actinide and Transactinide Elements* (see *ARQ,* 1st/2nd Quarters 2006). The volumes were premiered and released at the Conference. The editors of this useful compendium were present as were numerous coauthors of the many chapters.

The next Plutonium Futures Conference will be in July 2008 in Dijon, France. It will be cosponsored by the Atomic Weapons Establishment (AWE), United Kingdom; the Commissariat à l'Energie Atomique (CEA), France; and Kernforschungszentrum Karlsruhe (KfK), Germany, in collaboration with Los Alamos and Livermore National Laboratories. We feel this is a further acknowledgement from our international colleagues of the value of this conference series. We look forward to working with them to prepare for another successful conference.

This issue of Actinide Research Quarterly *covers the recent Plutonium Futures—The Science Conference in Pacific Grove, Calif. Los Alamos' Vin LoPresti wore several hats at the conference: writer, photographer, and presenter. LoPresti is shown here in front of the poster he presented on research conducted with Steven Conradson and David Clark on X-ray absorption near-edge spectroscopy studies of plutonium speciation in samples from Rocky Flats. LoPresti's coverage of the conference begins on Page 3.*
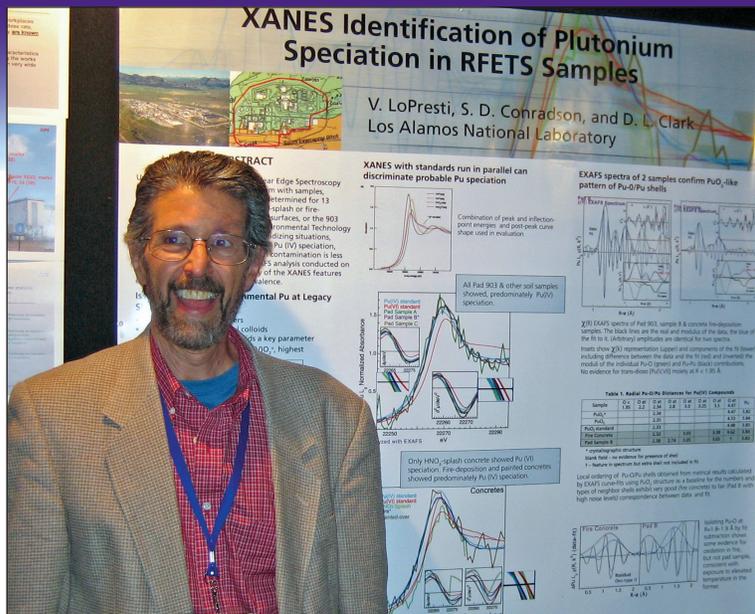
The actinyl chemistry of soft-donor ligands

The presentation by Stéphanie Cornet of The University of Manchester, England, was diverse in terms of the multitude of actinide compounds and synthesis routes described. The basis of the talk was the linear dioxoactinyl cation of the general structure $(O=An=O)^{n+}$ (where n = 1 or 2); for example, the plutonyl (V) cation $(O=Pu=O)^+$, and the plutonyl(VI) cation, $(O=Pu=O)^{2+}$. Generally, four to six additional ligands can coordinate in the equatorial plane.

Many of the synthetic procedures were based on the work of Carol Burns and co-workers at Los Alamos, who developed a simple one-pot dehydration of $UO_2Cl_2 \cdot xH_2O$ for the preparation of $UO_2Cl_2(THF)_3$ (THF = tetrahydrofuran); these compounds prove to be an excellent starting material for the synthesis of a variety of uranyl (VI) complexes. For example, the following are a few of the interesting structures that have been previously reported:

CORNET

Two examples of uranyl(VI) complexes prepared from $UO_2Cl_2(THF)_3$ are shown at left.
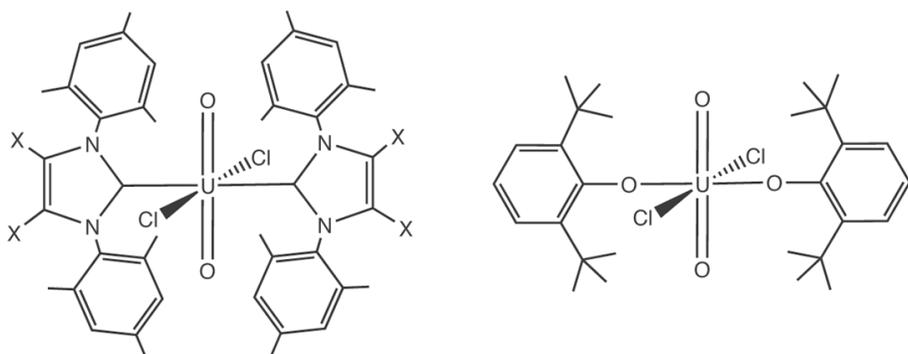
This talk was particularly focused on nitrogen- or phosphorus-containing soft-donor ligands. Cornet described the synthesis of phosphine oxide and phosphinimine complexes $[UO_2Cl_2(R_3PX)_2]$ (R=Ph or Cy, X=O or NH) by addition of two equivalents of the phosphine oxide or phosphinimine ligand to the uranyl–THF starting material. Moreover, the reaction with the N-donor phosphinimines (R_3PNH) to solutions of $UO_2Cl_2(R_3PO)_2$ resulted in the selective displacement of the P=O ligands and the formation of the phosphinimine complexes $UO_2Cl_2(R_3PNH)_2$. [1]H and ^{31}P nuclear magnetic resonance (NMR) spectra exhibited the presence of both *trans* and *cis* isomers in solution and the $UO_2Cl_2(Cy_3PNH)_2$ have been structurally characterized in both configurations. A short U–N bond length was also observed, suggesting a strong U–N interaction.
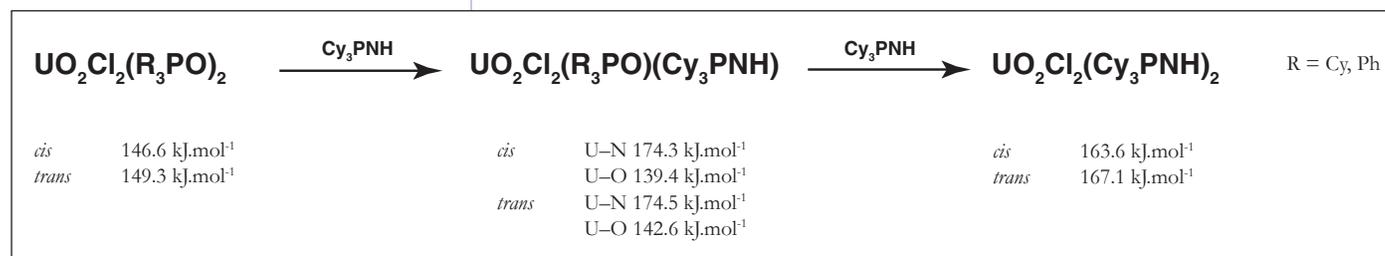
At right is an ORTEP (Oak Ridge Thermal Ellipsoid Plot) representation of trans-$UO_2Cl_2(Cy_3PNH)_2$.
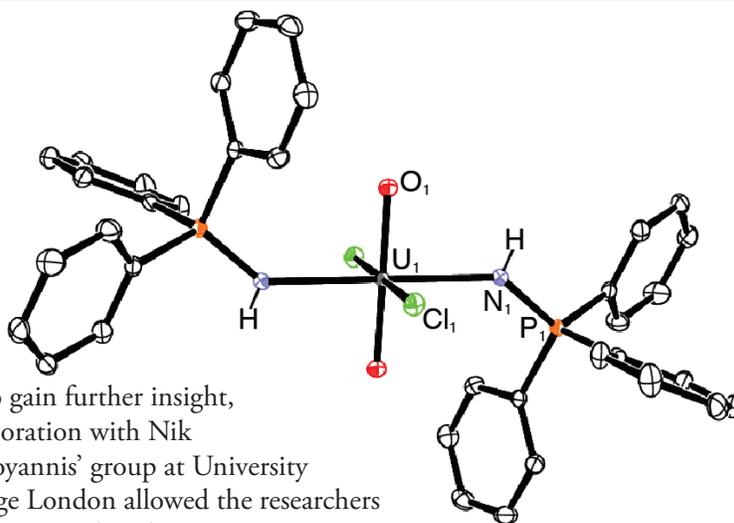
To gain further insight, collaboration with Nik Kaltsoyannis' group at University College London allowed the researchers to determine that the *trans* isomers were more stable and the major isomers in solution. Energy decomposition (using the fragment approach with ADF, the Amsterdam Density Functional quantum chemistry code) and Mayer bond-order calculations demonstrated that the U–N bond of the phosphinimine species is stronger and more covalent compared to the analogous U–O bond in the phosphine oxide complexes.


| $UO_2Cl_2(R_3PO)_2$ | $\xrightarrow{Cy_3PNH}$ | $UO_2Cl_2(R_3PO)(Cy_3PNH)$ | $\xrightarrow{Cy_3PNH}$ | $UO_2Cl_2(Cy_3PNH)_2$ | R = Cy, Ph |

cis	146.6 kJ.mol^{-1}	*cis*	U–N 174.3 kJ.mol^{-1}	*cis*	163.6 kJ.mol^{-1}
trans	149.3 kJ.mol^{-1}		U–O 139.4 kJ.mol^{-1}	*trans*	167.1 kJ.mol^{-1}
		trans	U–N 174.5 kJ.mol^{-1}		
			U–O 142.6 kJ.mol^{-1}		

A comparison of bond strength between the phosphinimine and phosphine oxide uranyl complexes is illustrated above.

This competition between the R_3PO and R_3PNH ligands enabled Cornet and co-workers to access nonaqueous neptunyl chemistry by using the phosphine oxide complexes as starting material to prepare $NpO_2Cl_2(R_3PNH)_2$.

Cornet also extended these studies by describing the synthesis of plutonyl chloride, PuO_2Cl_2, and its subsequent complexation to phosphine oxide. This work was done at the Commissariat à l'Energie Atomique (CEA), Marcoule, France, under an ACTINET collaboration (ACTINET is a consortium established in March 2004 of more than 25 European actinide research institutions). Crystals of this compound are awaiting X-ray diffraction studies. Studies are also under way on neptunyl– and plutonyl–amide species, and this diversity of work is producing numerous insights into the understanding of the actinyl bonding.

SOLUBILITY AND REDOX EQUILIBRIA OF PLUTONIUM

In this comprehensive plenary presentation, Thomas Fanghänel of the Joint Research Center of the European Commission at the Institute for Transuranium Elements, Karlsruhe, Germany, offered a plethora of information on the redox behavior of aqueous systems containing plutonium solids at the element's four environmentally common oxidation states (III, IV, V, and VI).
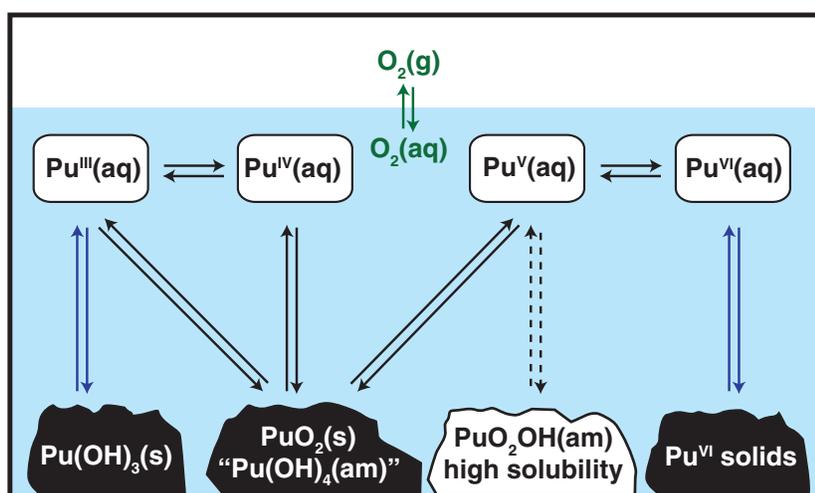
FANGHÄNEL

Equilibrium constant well-known (experimentally ascertained)

Equilibrium constant uncertain or unknown

The redox behavior of plutonium's four environmentally common oxidation states is shown at left.

Before plunging into the rather extensive substance of his presentation, Fanghänel reviewed the impressive plutonium chemistry initiative at Karlsruhe, where analytical methods for determining speciation of plutonium solids, aqueous species, and colloids encompass quite a large array of techniques. Presenting an equally large array of experimental findings, Fanghänel offered an updated view of plutonium's aqueous equilibria, one including a more-current view of this chemistry, with the inclusion of both superstoichiometric oxyhydroxides and of Pu(IV)-containing colloids.

His assertion was essentially that in this more-complete system, total plutonium solubility and distribution of oxidation states, can be explained solely in terms of equilibrium thermodynamics, somewhat downplaying processes such as radiolysis. Establishing the parameters for this system required, of course, accurate experimental determination of concentrations of the various species, using techniques such as laser-induced breakdown detection (LIBD) for colloid quantification (see *ARQ,* 3rd/4th Quarters 2003).
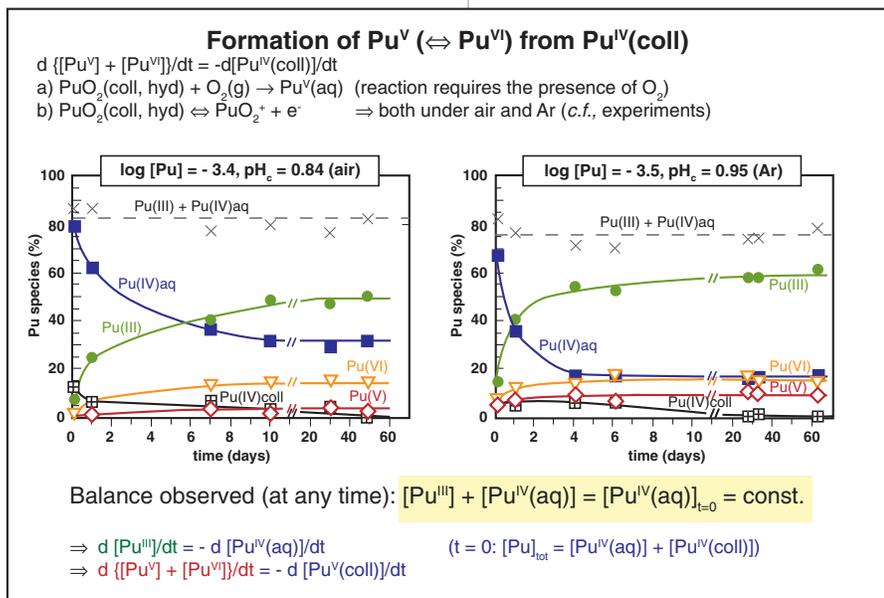
Solid–liquid and redox equilibria of plutonium are shown in the figure at right. New findings are highlighted by the red arrows.
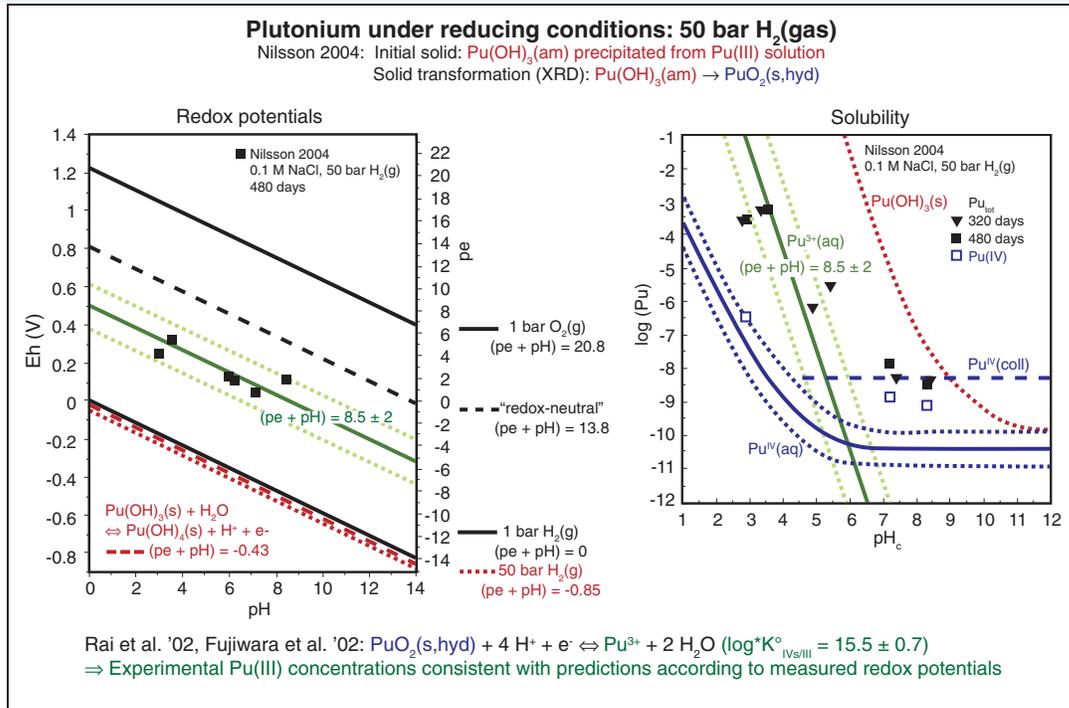

Equilibrium constant well-known (experimentally ascertained)

Equilibrium constant uncertain or unknown

Equilibrium constant derived in the present work (from exp. data)

Editor's note: *ARQ* has written about PuO_{2+x} since its original reports in 2000. This was viewed by many people with some skepticism. Subsequent research has firmly established the identity of this material. *ARQ* devoted a thematic issue to the topic (see 2nd Quarter 2004).
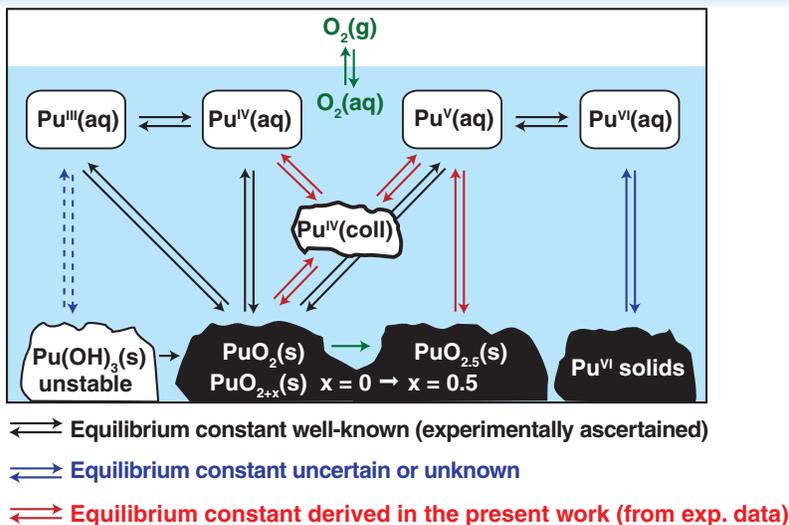
One of the several interesting findings of these experiments is that the reaction mechanism of the disproportionate reactions, $2Pu(IV) \rightarrow Pu(III) + Pu(V)$ and $3Pu(IV) \rightarrow 2Pu(III) + Pu(VI)$ appear to be two-step processes with the first step involving the oxidation of Pu(IV) colloids and the dissolution of the much-more-soluble Pu(V) species, and the second step entailing equilibration of the redox couples, Pu(IV)/Pu(III) and Pu(V)/Pu(VI). Essentially, this implies that the increase in [Pu(III)] (plutonium concentration) during diproportionation would result from a decrease in [Pu(IV)], but that increases in [Pu(V)] and [Pu(VI)] actually derive from the Pu(IV) in colloids. (The brackets indicate aqueous concentration.)

This finding was part and parcel of Fanghänel's ongoing emphasis on the key role of colloids—that the colloids were necessary to explain the redox properties of the system. Additionally, the experimental results suggest focusing the spotlight on the role of PuO_{2+x}, where, in his system, under argon with "trace O_2" concentration, consumption of the oxygen in reaction with PuO_2 was found to produce the superstoichiometric $PuO_{2.27}$; whereas in a system where oxygen was not limiting, the reaction proceeded to the formation of $PuO_{2.5}$.

Formation of Pu^V ($\Leftrightarrow Pu^{VI}$) from Pu^{IV}(coll)

$d\{[Pu^V] + [Pu^{VI}]\}/dt = -d[Pu^{IV}(coll)]/dt$

a) $PuO_2(coll, hyd) + O_2(g) \rightarrow Pu^V(aq)$ (reaction requires the presence of O_2)

b) $PuO_2(coll, hyd) \Leftrightarrow PuO_2^+ + e^-$ $\Rightarrow$ both under air and Ar (*c.f.,* experiments)

Balance observed (at any time): $[Pu^{III}] + [Pu^{IV}(aq)] = [Pu^{IV}(aq)]_{t=0} = $ const.

$\Rightarrow d[Pu^{III}]/dt = -d[Pu^{IV}(aq)]/dt$ $\qquad$ (t = 0: $[Pu]_{tot} = [Pu^{IV}(aq)] + [Pu^{IV}(coll)]$)

$\Rightarrow d\{[Pu^V] + [Pu^{VI}]\}/dt = -d[Pu^V(coll)]/dt$

Plutonium under reducing conditions: 50 bar H$_2$(gas)
Nilsson 2004: Initial solid: Pu(OH)$_3$(am) precipitated from Pu(III) solution
Solid transformation (XRD): Pu(OH)$_3$(am) → PuO$_2$(s,hyd)

Redox potentials / Solubility

Rai et al. '02, Fujiwara et al. '02: PuO$_2$(s,hyd) + 4 H$^+$ + e$^-$ ⇔ Pu^{3+} + 2 H$_2$O (log*K°$_{IVs/III}$ = 15.5 ± 0.7)
⇒ Experimental Pu(III) concentrations consistent with predictions according to measured redox potentials

In total, Fanghänel maintains that his results suggest that O$_2$ is "scavenged" by PuO$_2$ to form mixed-valent PuO$_{2+x}$ with the composition (Pu^V)$_{2x}$(Pu^{IV})$_{1-2x}$O$_{2+x}$.

Fanghänel presented a number of results from the literature to support his proposition that experimentally determined concentrations of plutonium species under various conditions appeared to be consistent with predictions based on measured redox potentials. These results included a Pu(OH)$_3$⇔PuO$_2$ equilibrium under several types of reducing conditions (iron powder, hydrogen gas under pressure, for example) and a variety of data indicating PuO$_{2+x}$ as the key species in controlling solubility in aqueous systems.

This talk was an enlightening and a challenging one, prompting Fanghänel's audience to evaluate the ideas and the underlying data presented and to think deeply about preconceived notions regarding aqueous plutonium chemistry.

The solubility and pe-controlling equilibria of plutonium are shown below. The pe value is defined as the negative decadic logarithm of the apparent electron activity in a solution: pe = -log a(e-). This is analogous to the definition of pH as the negative decadic logarithm of the proton activity in a solution: pH = -log a(H$^+$).
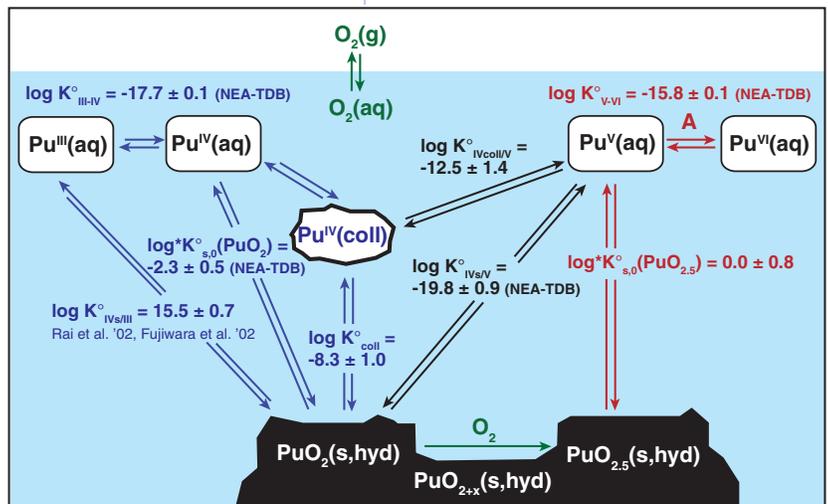
SUPERCONDUCTIVITY IN ACTINIDES AND RELATED MATERIALS
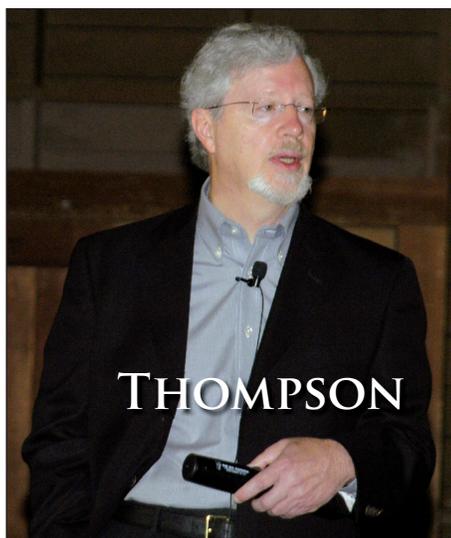
THOMPSON

The difference in the critical temperature (T_c) between plutonium- and uranium-based superconductors is shown at right.

In his plenary talk on actinide superconductors, Los Alamos' Joe Thompson used the exciting discovery of $PuCoGa_5$ as a jumping-off point for a more general review of superconductivity mechanisms and potential insights into the mechanism of so-called unconventional superconductivity.

The basis for the presentation was immediately apparent in Thompson's opening slide, which presented the now well-known nearly order-of-magnitude difference in the critical temperature (T_c) for superconductivity between the plutonium superconductor, $PuCoGa_5$, and 12 uranium-based superconductors, all of which show T_cs of less than 2.5 kelvin (K)—while the two known plutonium superconductors show T_cs of 18.7 K ($PuCoGa_5$) and 8.5 K ($PuRhGa_5$). As Thompson framed it, these discoveries motivate us to better understand the complexity of plutonium's solid-state physics, particularly the ongoing mysteries of the behavior of its arguably both itinerant and localized 5f electrons.

A fundamental question posed in this talk was that of the mechanism of superconductivity for these plutonium compounds, i.e., are they conventional or unconventional superconductors? In the current understanding of so-ca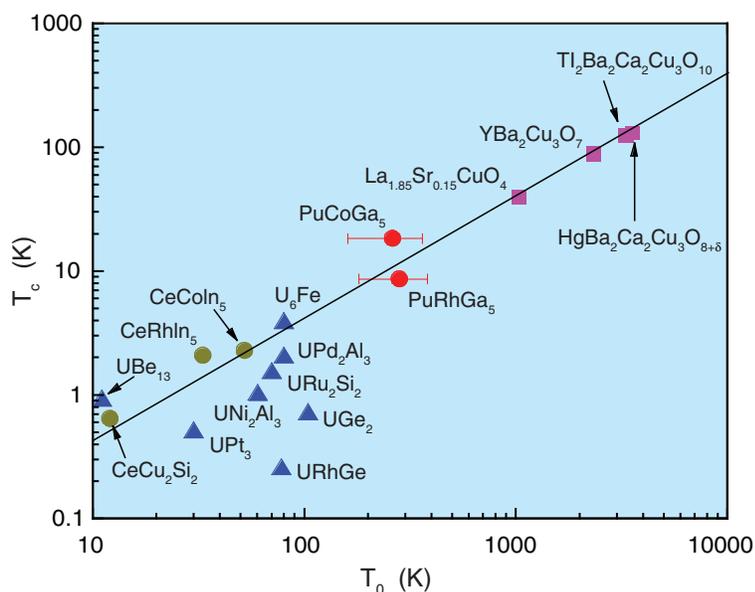lled conventional superconductivity, a temporary lattice distortion provides an attractive interaction between conduction electrons of opposite spin and momentum, forming a so-called "Cooper pair," which then behaves as a unit at temperatures below the T_c, condensing into a macroscopic quantum state that is energetically separated from that of all unpaired electrons in the solid by an energy gap that is finite over the entire Fermi surface. It requires only a small number of magnetic moments in a conventional superconductor to destroy superconductivity (essentially driving the T_c to 0 K).

But superconductivity in $PuCoGa_5$ has proven to be robust against the application of a magnetic field, hence arguing against conventional superconductivity. By contrast, electron pairing in unconventional superconductors comprises an attractive interaction between itinerant electrons mediated by an exchange of spin fluctuations. As a consequence, the superconducting energy gap between the Cooper pairs and the other electrons in the solid goes to zero at gap nodes on the Fermi surface.
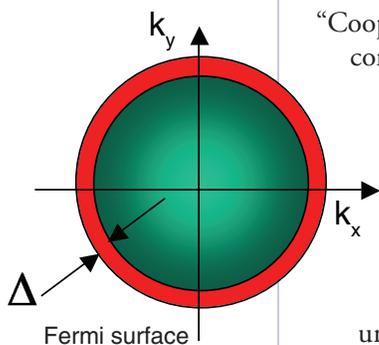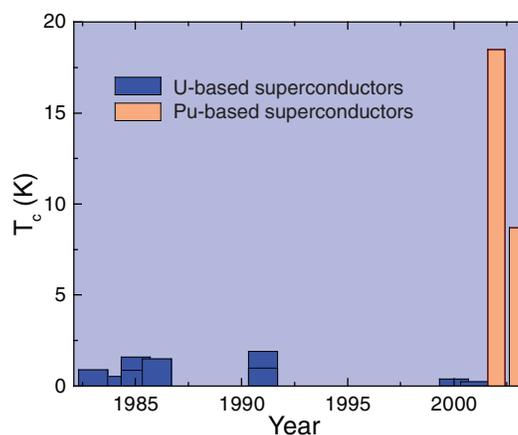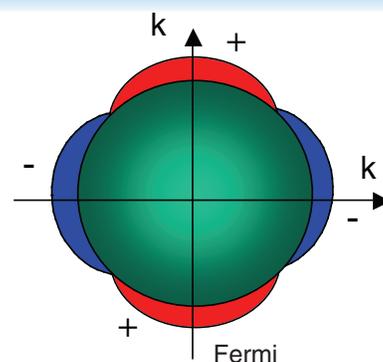

An illustration of the finite energy gap (Δ) in the Fermi surface of a conventional superconductor.

Thompson reviewed a variety of data for the plutonium superconductors, particularly a normalized-temperature-dependent relaxation rate dominated by the occurrence of antiferromagnetic spin fluctuations. He showed that the same characteristics occurred in the unconventional superconductors, $CeCoIn_5$ (with a relatively low T_c of 2.3 K) and $YBa_2Cu_3O_7$, a so-called high-T_c cuprate superconductor (T_c = 92 K). On the other hand, this is qualitatively different from the situation in conventional superconductors such as Al (T_c = 1.178 K) and MgB_2 (T_c = 39 K) in which such fluctuations are excluded by the requirement that there be a finite energy gap over the entire Fermi surface.

An illustration of the zero energy gap in the Fermi surface of an unconventional superconductor.

A representation of critical temperature (T_c) versus a characteristic spin-energy scale (T_0) for unconventional superconductors is shown at left.

In a representation of T_c versus T_0 (a characteristic spin-energy scale) for unconventional superconductors, Thompson reiterated the notion that plutonium superconductors appear to form a critical bridge between uranium- and cerium-based systems and high-T_c cuprates. He discussed an interesting model of hybridization that would broaden an f-electron contribution to magnetic fluctuations, perhaps accounting for the observed properties of the plutonium superconductors, including their T_c much higher than that of their cerium- and uranium-based cousins.

Although Thompson admits that there is no proof that superconductivity is mediated by magnetic excitations, his simple model of f-electron hybridization does qualitatively capture trends in unconventional superconductivity and offers an interesting path forward for further investigation. He suggested a number of these experimental paths, including systematic bandwidth tuning by varying chemical/structural environments and pressure; Fermi surface studies and angle-resolved photoemission to test electronic structure calculations; and inelastic neutron-scattering, optical spectroscopies, and lower-temperature experiments with plutonium-242 to explore low-lying spin, charge, and lattice excitations.

STRUCTURES AND BONDING IN TRIATOMIC COMPOUNDS
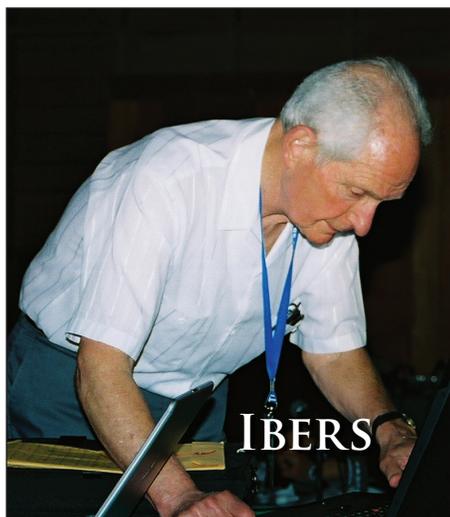
IBERS

Flowing within one of the major intellectual streams of the conference—nonintegral stoichiometry—James Ibers of Northwestern University reported on the structure and bonding in several triatomic compounds containing an alkali metal (A), an actinide metal (An), and a chalcogen (Q) and having the standard stoichiometry, AAn_2Q_6. Such compounds fall into two general crystal types: designated Cmcm and Immm. In both cases, the crystals are remarkably interesting architecturally, each formed by an alternation of layers in which the actinide's complexation ability plays a key role.
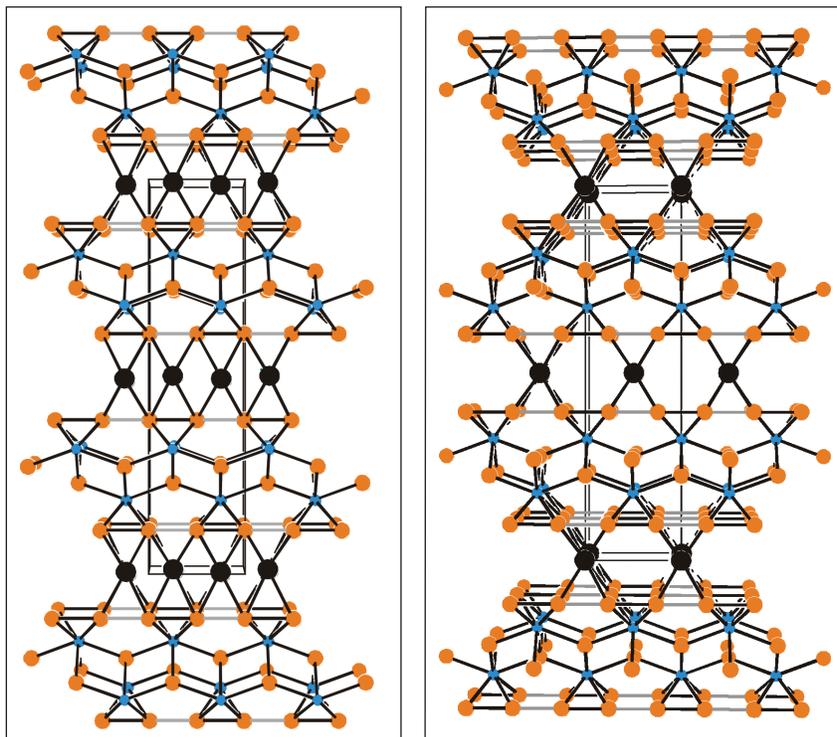
Cmcm and Immm crystal structures are shown at right. A uranyl sulfide crystal structure is shown below.
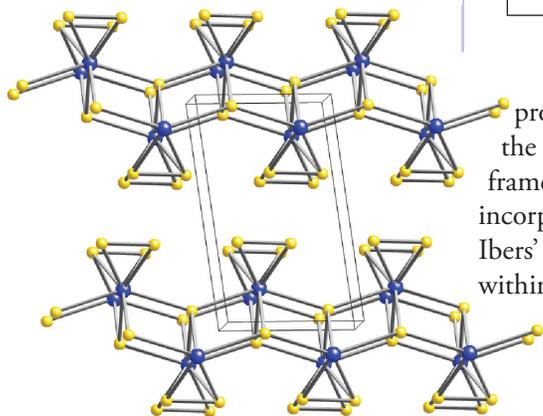
Ibers first described the synthesis of uranium sulfides, a multistep process that initially forms uranium(IV) chloride, (UCl_4) and subsequently the layered crystal structure of the sulfide, which ultimately serves as the framework for building the larger layered crystals when the alkali metal is later incorporated. The electronic structure of the sulfide is such that, according to Ibers' data, both 6d and 5f electrons of the uranium participate in bonding within the uranium sulfide crystal.

Progressing from the uranium sulfide (or selenide) to the triatomic compounds with potassium incorporated entails single-step reactions at high temperature (900-1000 degrees Celsius), and the resulting crystal can have a nonintegral stoichiometry. Within the crystal, the uranium site occupancies are fixed, but significant variation is tolerated for the chalcogen and alkali metals. Hence, both the stoichiometric KU_2Se_6 and the nonstoichiometric $K_{0.91}U_{1.79}S_6$ are observed to form in the synthesis reactions.

Crystal structures of these compounds appear to form around the framework of linear chains of the chalcogen in its c-paired divalent anionic form $(Q–Q)^{2-}$, and Ibers characterized these Q–Q chains in terms of their bond distances for the chalcogens, sulfur (S), selenium (Se), and tellurium (Te). Potassium (K) presumably donates an electron to the chalcogen pair in the selenide, and the bonding between the chalcogens is such that there no longer appear to be discrete single bonds. By contrast, in the sulfide, the $3p$ σ^* orbital is of higher energy compared with $4p$ σ^* in the selenide; therefore K cannot donate its lower-energy electron to reduce the stronger S–S single bond. The structural difference between the sulfide and selenide is a function of the observation that the S valence states are more localized (anionic) than for Se. Therefore, the research suggests that charge compensation takes place via the formation of cationic vacancies, which accounts for the formation of the nonstoichiometric compound $K_{0.91}U_{1.79}S_6$.

Ibers expressed the hope that theoretical studies would assist in validating his experimental work. One 2006 publication appears in *Inorganic Chemistry,* another is in press.
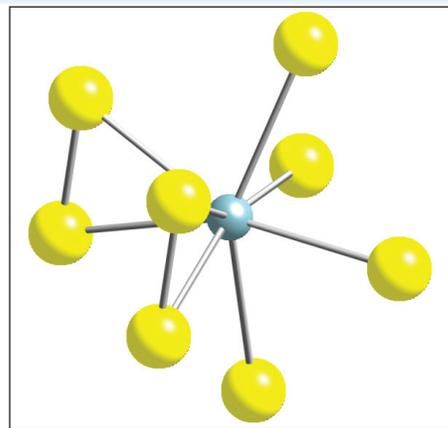
An illustration of coordination around uranium (blue) in $K_{0.91}U_{1.79}S_6$.
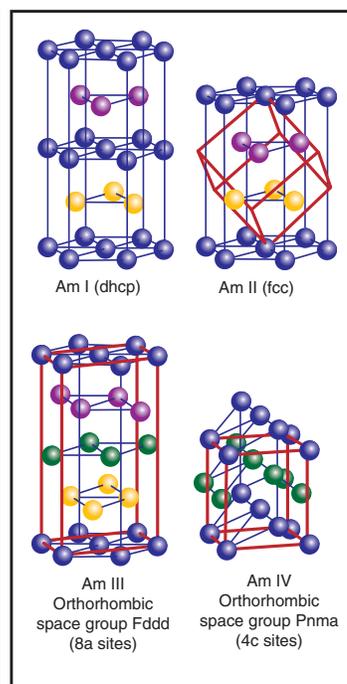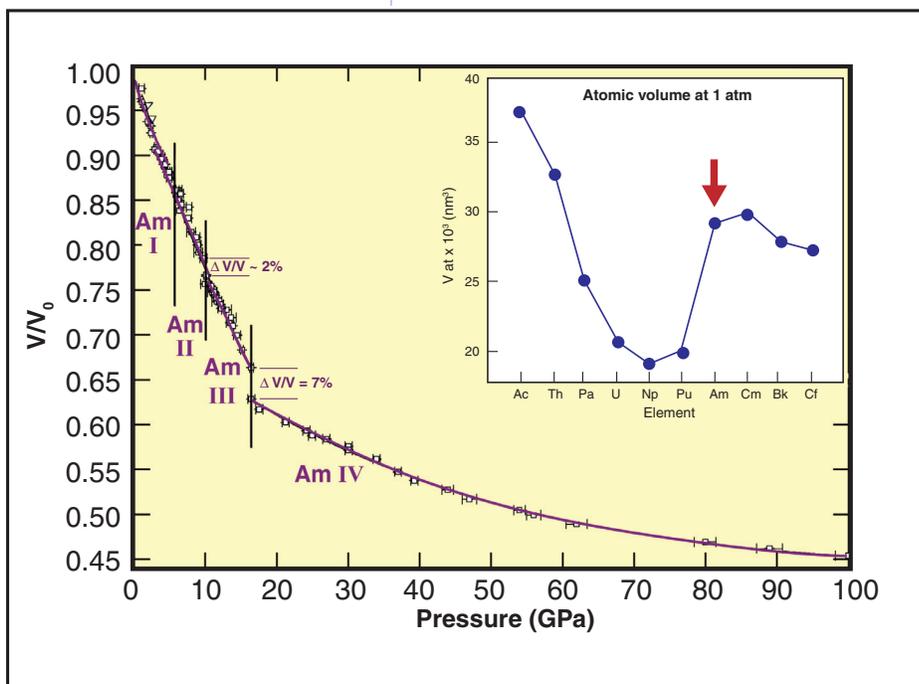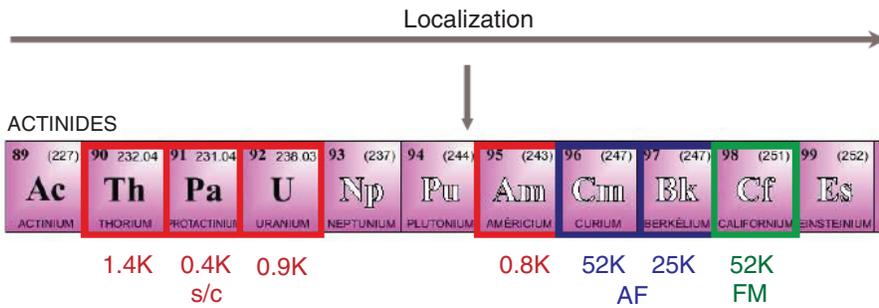
AMERICIUM UNDER PRESSURE

GRIVEAU

A plot of atomic volume versus number of f electrons in the actinide series, relative to those of alpha and delta plutonium, is shown in the inset below. A plot of changes in volume versus applied pressure (below) shows how pressure affects atomic volume and subsequent properties.

This interesting investigation into 5f-electron behavior presented by Jean-Claude Griveau of the Joint Research Center of the European Commission at the Institute for Transuranium Elements, Karlsruhe, Germany, built upon the seminal work of Los Alamos' Jim Smith and co-workers, which had verified superconductivity in americium (Am). In this instance, Griveau and his collaborators from Oak Ridge National Laboratory and Rutgers University investigated the effects of subjecting the element to high pressures—in the gigapascal (GPa) range, a clever notion underpinned by the hypothesis that one could influence atomic volume and, as a correlate, electronic behavior through this methodology.

Beginning from a plot of atomic volume against the number of f electrons in the actinide series and the classic chart of the itinerant-to-localized f-electron series of the actinides (with plutonium at the transition point), the jumping-off point was the observation that americium's six 5f electrons are localized at zero applied external pressure.

Editor's note: Pressure is an important variable in the chemistry and physics of materials, and Richard Haire of Oak Ridge National Laboratory reported on atomic-volume changes in americium in an earlier issue of *ARQ* (see 3rd/4th Quarters 2003). The plot of $\Delta V/V_0$ for americum metal (below) was adapted from S. Heathman et al. PRL 85 (2001) 2961.

Localization

ACTINIDES

89 (227)	90 232.04	91 231.04	92 238.03	93 (237)	94 (244)	95 (243)	96 (247)	97 (247)	98 (251)	99 (252)
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMÉRICIUM	CURIUM	BERKÉLIUM	CALIFORNIUM	EINSTEINIUM

	1.4K	0.4K	0.9K			0.8K	52K	25K	52K	
		s/c					AF		FM	

In plotting the ratio of atomic volume under applied pressures up to 100 GPa to volume at zero applied pressure (V/V_0) against applied pressure, one can follow both oxidation-state transitions and the accompanying phase-transition changes in crystal structures for Am(I, II, III, and IV). In addition, a plot of changes in resistivity versus applied pressure clearly showed how pressure affects electronic properties as atomic volume is altered.

As final evidence, Griveau showed measurements building on the work of Link et al., which illustrated a change in americium's critical temperature (T_c) for superconductivity with changing applied pressure, a thought-provoking demonstration of the significant change in electronic structure induced by this modality, both the T_c and the critical field (H_c) peaking in Am(II).

Referring to a sharp change in both the T_c and H_c patterns of change at the Am(III)-Am(IV) transition—a sudden pattern of increase with additional applied pressure after a gradual decrease with pressure in Am(III), Griveau pointed to these and other indicators as provoking the speculation that this transition might possibly mark a change in the mechanism of superconductivity in Am(IV), by comparison to Am(I–III). He left this question open for future studies.
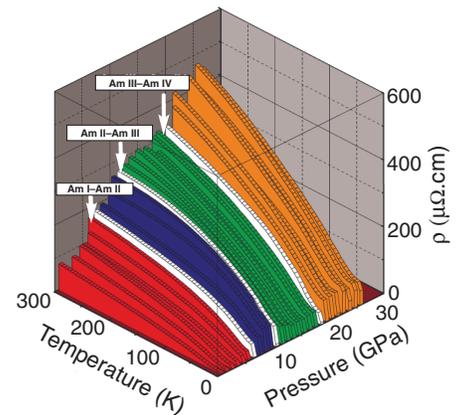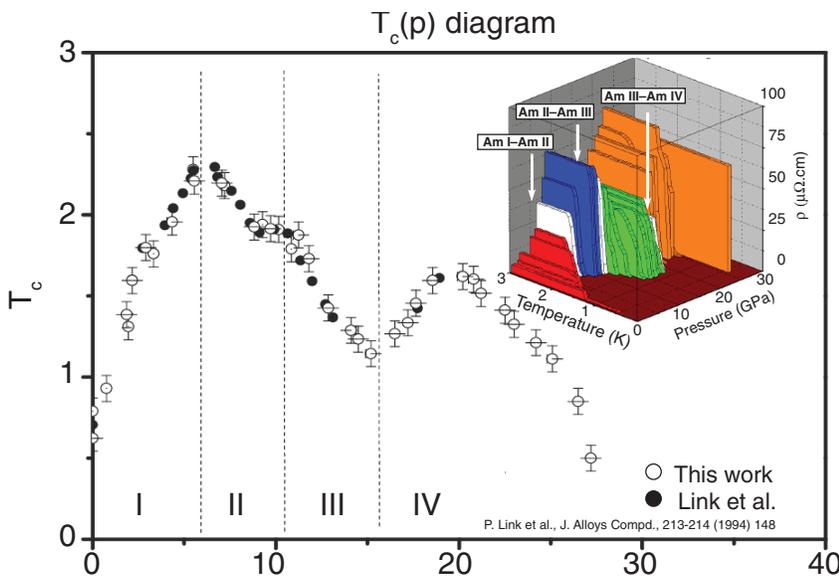
Griveau's measurements (above) of the change in americium's critical temperature with changing applied pressure build on the earlier work of Link et al. (at left).
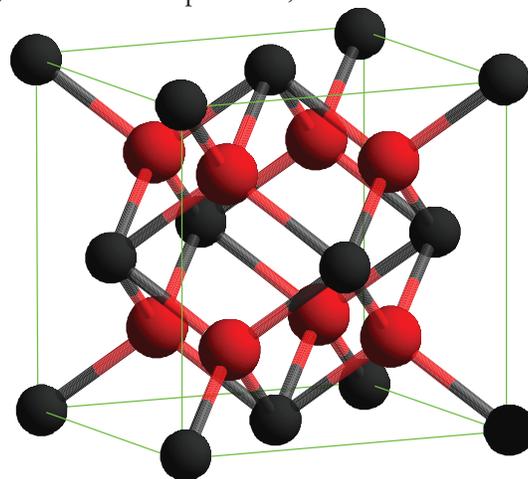

$T_c(p)$ diagram

P. Link et al., J. Alloys Compd., 213-214 (1994) 148

○ This work
● Link et al.

Oxygen exchange and diffusion in uranium dioxide single crystals
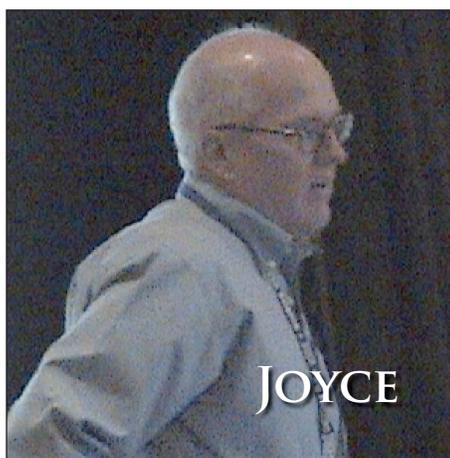
Joyce

In a talk that promised possible insights into the recent flurry of interest over PuO_{2+x} (superstoichiometric plutonium oxyhydroxides), Steve Joyce of Los Alamos discussed the issues inherent in the diffusion and incorporation of oxygen into uranium dioxide (UO_2) crystals. These issues included changes in volume and conduction properties in addition to the obvious alterations in stoichiometry, both stoichiometric (U_4O_9, U_3O_7, U_2O_5, and UO_3) and superstoichiometric ($UO_{2\pm x}$). Joyce emphasized that in its UO_2 fluorite crystal structure, the compound is quite amenable to additions of oxygen with shifts in the oxygen positions, even as the uranium lattice is maintained. He offered data that tended to support those contentions.
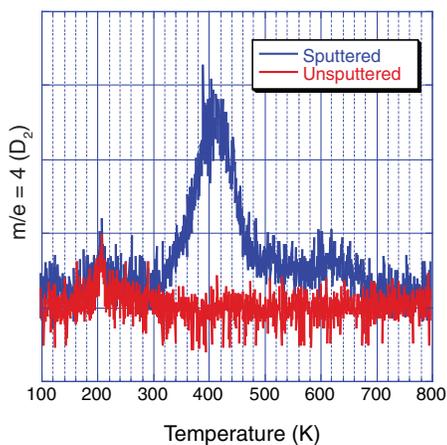
The basis of these experiments was the exposure of UO_2 crystal surfaces to both molecular oxygen and water, at different temperatures, to assess both diffusional penetration and the effect of the diffusing species on the crystal. The temperature variation is important because while UO_2 can be oxidized by water at lower temperatures, O_2 is only reactive to the UO_2 at higher temperatures, and all previous research has studied the system at temperatures of 950 kelvin (K) and above.

An additional experimental procedure was the use of electric sputter damage to the crystal surface, thereby creating oxygen vacancies within 10 nanometers (nm) of that surface and leading to the evolution of hydrogen gas, H_2. Since each successive exposure to sputter reduced H_2 evolution, the conclusion, confirmed by X-ray photoemission spectroscopy, was that the sputter was accompanied by the dissociation of water molecules. Oxygen was "left behind" to heal those crystal vacancies, and H_2 evolved as a product of that dissociation of water.

Joyce noted that previous studies had indicated that below 1500 K oxygen was found to be the only diffusing species and that uranium diffusion was unimportant. To better assess these processes, water was labeled with ^{18}O so that the crystal's surface could be nondestructively labeled with a heavier oxygen isotope. Prior attempts to use isotopically labeled molecular oxygen ($^{18}O_2$) had not been very successful without sputtering and its concomitant damage, which was undesirable in this instance.

The uranium dioxide (UO_2) fluorite structure is shown at right. Uranium atoms are red and oxygen atoms are black.

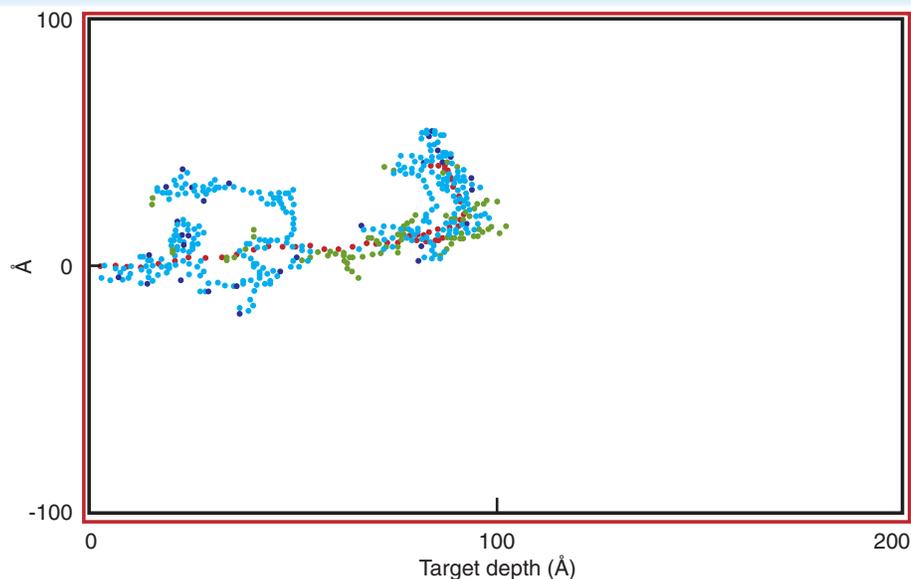*Hydrogen evolution from sputtered versus unsputtered crystals.*

The creation of oxygen vacancies in a uranium dioxide (UO$_2$) crystal as a function of depth from crystal surface, shown in a slice through the crystal.

Oxygen isotopes were subsequently detected with electron-stimulated desorption, a technique that uses electron irradiation of a surface to promote desorption of adsorbed surface species, which are then detected through mass spectrometry. Essentially, this technique creates electron core holes in metal atoms that are subsequently filled interatomically by electrons from other atoms—such as oxygen—in the crystal. Auger emission of electrons from those oxygens can create positive (O$^+$) ions released from the crystal and detected by mass spectrometry. This technique detected both ^{16}O and the more massive ^{18}O at the surface of the crystal, even at 250 K (below room temperature), with ^{18}O disappearing from the surface and diffusing into the bulk of the crystal.

These studies draw a picture of a significantly dynamical crystal structure with perhaps unexpected atomic mobility and flexibility that challenges the sometimes overly static view of such crystals derived from techniques such as X-ray crystallography.

Poster highlights I
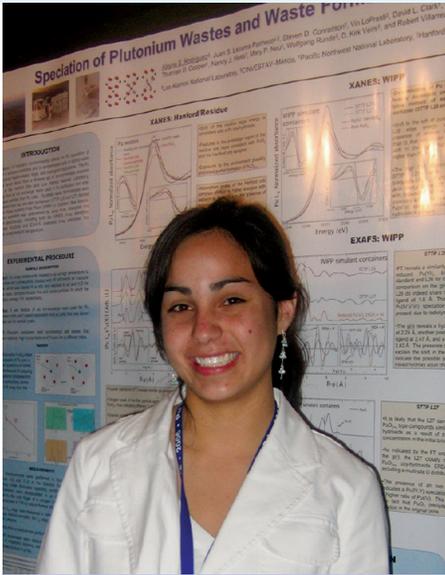
Los Alamos undergraduate student Alayna Rodriguez poses before her poster, "Speciation of Pu in Aged Wastes and Wasteforms." Rodriguez, now attending Harvard, conducted her research with Steve Conradson and Juan Lezama-Pacheco.
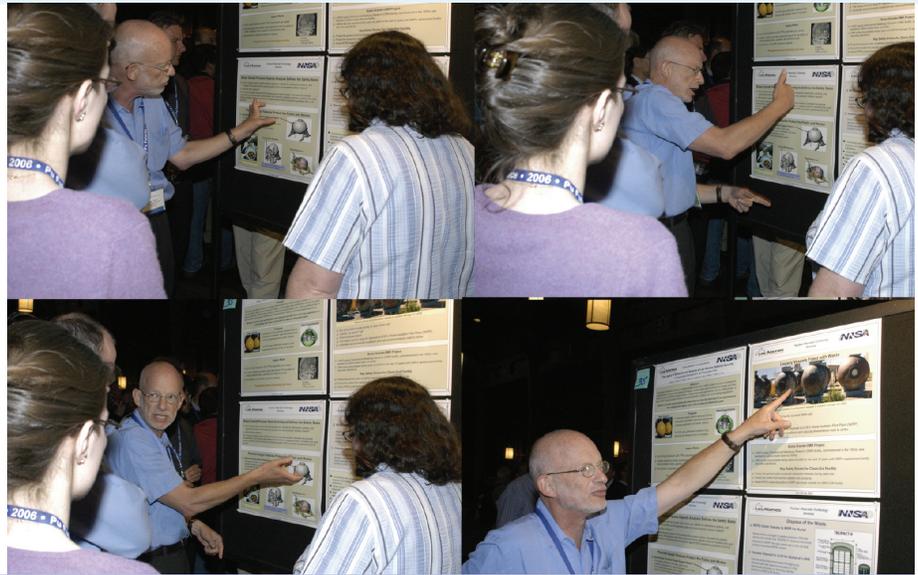
Working intensely to drive home a point to a group of listeners, Los Alamos' Joel Kohler displays an equivalent talent for elaborating the details of the Bolus Grande containment vessels as he did when occasionally entertaining conference attendees in the main registration area with his ad hoc piano recitals.
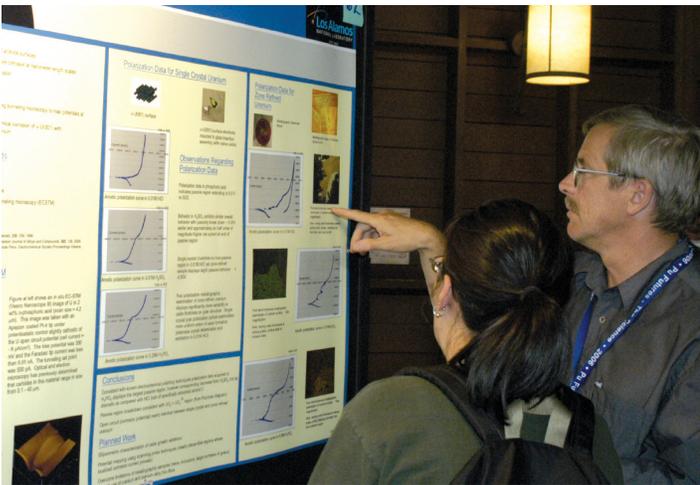
Angelique Diaz of the Colorado School of Mines receives a mini-tutorial from Los Alamos' Mark Paffett in some of Materials Science and Technology Division's electrochemical techniques.
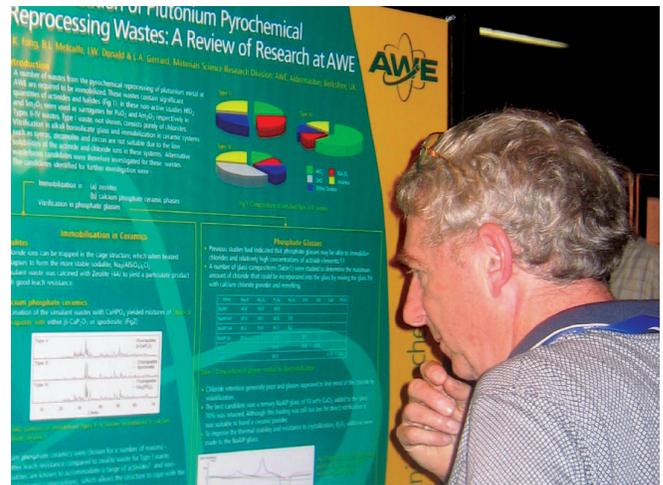
A conference attendee studies AWE's experiments aimed at discovering new techniques for the immobilization-storage of actinide and halide wastes derived from plutonium metal processing. The new techniques include immobilization using zeolites and calcium phosphate ceramics and vitrification in phosphate glasses.

X-RAY ABSORPTION SPECTROSCOPY STUDY OF SOLID SOLUTIONS

This talk, presented by Carol Valot for a team led by Philippe Martin, focused on characterization of the solid solutions generated by a new procedure for mixed-oxide (MOX) fuel manufacturing under development at Commissariat à l'Energie Atomique (CEA Atalante) in Marcoule, France.

Currently, MOX fuels are manufactured by cocrushing, palletizing, and sintering uranium oxide (UO_2) and plutonium oxide (PuO_2) powders, yielding a fluorite-type solid solution.

In the new CEA technique, oxalic acid ($H_2C_2O_4$) coprecipitation of uranium and plutonium with subsequent conversion to the oxides substitutes for mechanical mixing and is proposed to yield a better homogeneity of the uranium and plutonium in the solid. The goal is to obtain uranium oxide and plutonium oxide solid solutions with minimal impurities and an oxygen-to-metal ratio of 2:1.

To assess the success of their method, this CEA team used X-ray absorption fine structure (XAFS) spectroscopy as a local probe of atomic and electronic


VALOT
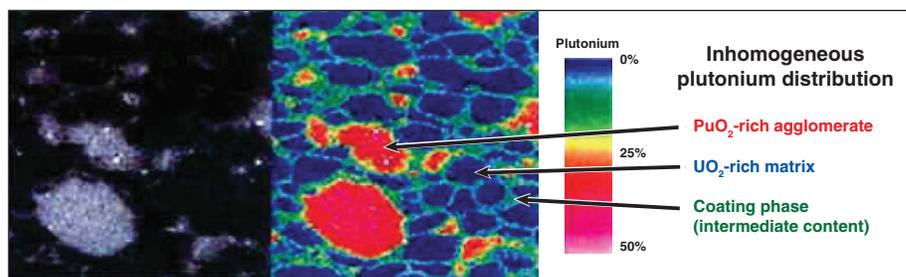
A mixed-oxide pellet as viewed under scanning electron microscopy (far left) and with electron probe microanalysis (left).

structure in the crystalline solid solution—in which the different chemical species occupy lattice points (characteristic of a solid) somewhat at random (characteristic of a solution). Four different molar ratios of Pu(III)/U(IV) were investigated (final plutonium atomic percents of 50, 30, 15, and 7).

A known feature of these MOX solid solutions, referred to as "Vegard's Law," is that the lattice parameter of $U_{1-y}Pu_yO_2$ changes linearly with y from pure UO_2 to pure PuO_2. In this case X-ray crystallographic data were consonant with the law's predictions.

On the other hand, the local atomic environments revealed by XAFS exhibited some distinct variations from prediction. For each of the four plutonium atomic percents, extended X-ray absorption fine structure (EXAFS) revealed a face-centered-cubic structure, and the deduced cell parameters suitably followed Vegard's Law. For the 50-percent plutonium solid solution, the correspondence was ideal—for both actinides, the overall shape of the spectra remaining the same

*Predictions of Vegard's Law correlated with data from X-ray crystallography.*
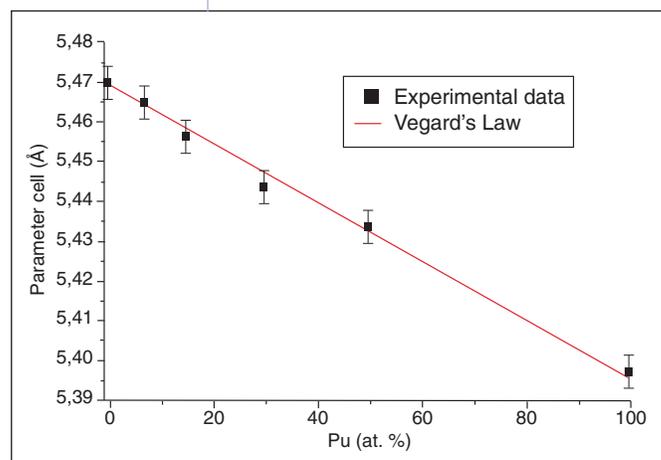
with two main peaks located at about 2.3 angstroms (Å) (corresponding to the first actinide–oxygen coordination shell) and about 4 Å (corresponding to the actinide–actinide shell and second actinide–oxygen shell). But a significant decrease of the second peak intensity was observed in samples with a plutonium content of less than 50 percent.

Additionally, in EXAFS spectra of samples with less than 50 atomic percent plutonium, actinide–oxygen first-coordination shells displayed unexpected behavior: for plutonium, an apparent decrease of the plutonium–oxygen bond length was observed; for uranium, a distortion of the peak was seen. These results suggested a more complex local environment for both actinides—a locally disordered structure by comparison to that described by Vegard's Law.

The variations in local structure revealed by EXAFS were paralleled by somewhat unusual findings regarding speciation in XANES spectra. For plutonium, regardless of atomic percent, XANES spectra remained identical to that of pure PuO_2, that is Pu(IV) in a cubic symmetry (fluorite structure). However, for uranium in the solid solutions with less than 50 atomic percent plutonium, a shift in white-line position to higher energy coupled with an increase in intensity of the shoulder at 17,190 electronvolt (eV) suggests the presence of a hyperstoichiometric structure, as delineated by Los Alamos' Steve Conradson and co-workers (see *ARQ*, 2nd Quarter 2004).

The researchers concluded that thermal treatment of the coprecipitation regimen must be optimized for the solid solutions of lower plutonium content and that further X-ray absorption spectroscopy characterizations must be performed at low temperature (10 kelvin). Despite what may be remaining issues in their MOX-fuel technique, Valot's presentation was yet another demonstration of the power of XAFS in revealing local structure that is often invisible to crystallographic methods.
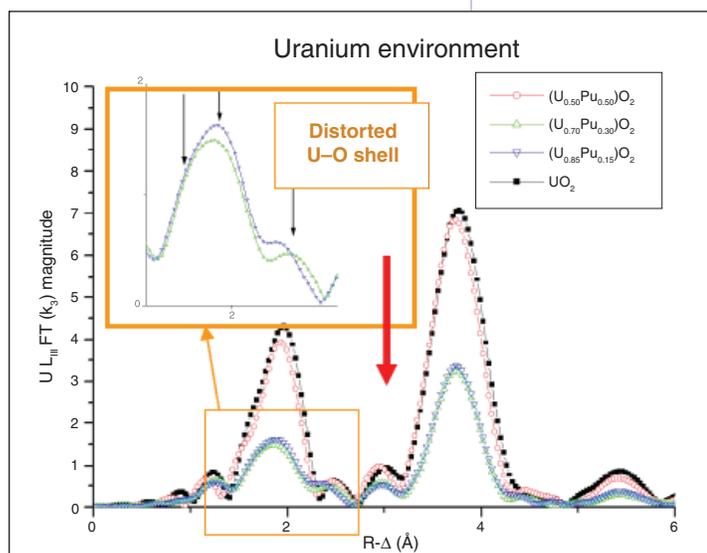
Fourier transform of uranium L_{III} edge EXAFS for the four different atomic percents of plutonium studied.

# Covalency in the f-element–chalcogen bond

In this presentation, Nik Kaltsoyannis of University College, London, offered a computational look at bonding between actinide or lanthanide metals (plutonium, uranium, cerium, or lanthanum) and imidodiphosphinochalcogenides, examining ligands containing the row-16 elements, oxygen, sulfur, selenium, and tellurium.

Kaltsoyannis emphasized the experimental observation that the uranium–chalcogen bond is significantly shorter than the equivalent lanthanum–chalcogen bond, despite the very similar ionic radii of the six-coordinate U^{3+} and La^{3+} ionic species; he cited recent Los Alamos work duplicating that finding for trivalent plutonium and cerium imidodiphosphinochalcogenides.

Using both Gaussian and Density Functional codes, Kaltsoyannis showed molecular orbital energy diagrams for both lanthanum and uranium and their bonding to the progressively less-electronegative chalcogens as one progresses from oxygen though sulfur to selenium and tellurium. The significant finding is that the increased degree of bond covalency—or decrease in ionicity—(which, strictly on this electronegativity basis might be expected to increase similarly from oxygen → tellurium) is not, in fact, equivalent for uranium and lanthanum. In reality, the studies show, the increased covalency is greater when uranium is the metal ion in the complex as compared to complexes containing lanthanum.

A computational analysis of the energy levels of 18 valence molecular orbitals indicates that the lanthanum and uranium d atomic orbitals contribute to these molecular orbitals to about the same extent. This finding implies that the difference between the actinide and the lanthanide must reside in the contribution of f electrons to bonding. This research in progress tentatively concludes that the 5f electrons in the actinide must make a larger contribution to covalency than the 4f electrons of the lanthanide.

Kaltsoyannis

A uranium phosphoimidochalcogenide with sulfur as the chalcogen.
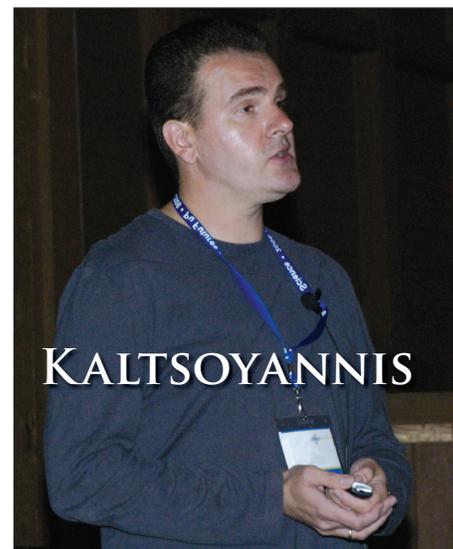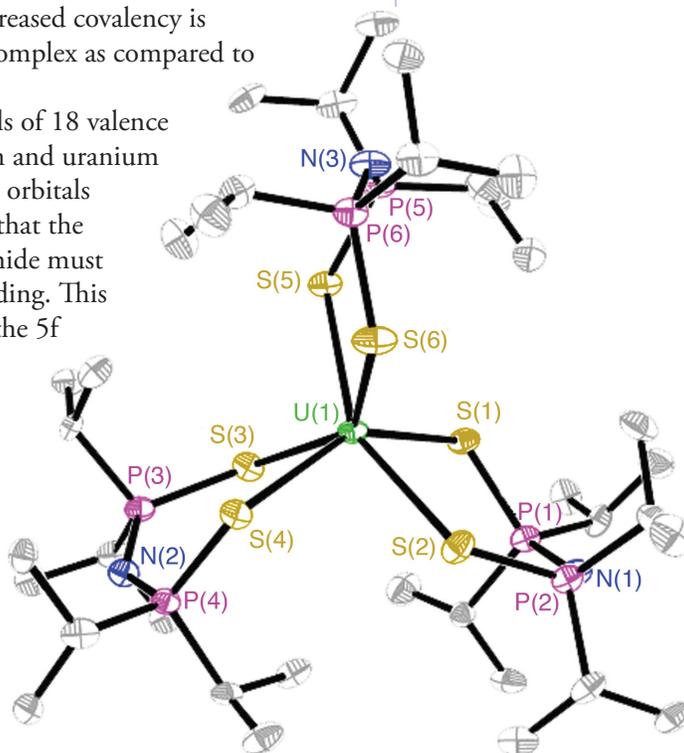
Poster highlights II

Matthias Graf (pointing) elucidates his work on electron-phonon coupling in delta plutonium to an inquisitive listener.

"Wonder if there's anything in this actinide stuff for me," perhaps muses a pensive Carson Hobart, as he supervises the table at which attendees perused a sample copy of the new (third) issue of The Chemistry of the Actinide and Transactinide Elements. Son of conference cochair David Hobart of Los Alamos, Carson's contributions as a volunteer to staff support were highly commended by all.

Underlining the international scope of the conference, discussants review a poster by actinide scientists from the Israeli Nuclear Research Center and Ben-Gurion University of the Negev (at left). To their right, two session attendees scan information describing neptunium behavior in citrate media.

SYSTEMATICS IN SUPERCONDUCTIVE COMPOUNDS

In about twenty minutes, Franck Wastin of the Joint Research Center of the European Commission at the Institute for Transuranium Elements at Karlsruhe, Germany, reviewed and discussed a range of compounds of the $AnTGa_5$ and $CeTIn_5$ groups and the factors postulated to "tune" the critical temperature (T_c) for superconductivity in heavy-fermion superconductors. The best known of these is Los Alamos' plutonium-cobalt-gallium superconductor, $PuCoGa_5$, with a T_c of 18.5 kelvin (K).

This research was prompted by the finding that $PuRhGa_5$ is also a superconductor with a T_c of approximately 9 K, but that the compound $CeCoIn_5$, essentially isostructural with $PuCoGa_5$, shows superconductivity only below 2 K. Hence, logic suggests that there is perhaps something about the electronic structure of the actinide-based superconductors that mediates a higher T_c.

Wastin reviewed a number of hypotheses to explain superconductivity and T_c in these compounds and succeeded in demonstrating flaws in each of them. In doing so, he considered the topics of lattice parameters, the effect of doping superconductive compounds with nonisoelectronic metals, and aging effects.

Wastin's main finding was a correlation between superconductivity and the total count of outer-shell electrons: specifically that, with few exceptions, all $AnMGa_5$ superconducting compounds fall within a narrow band at 32 ± 0.2 total electrons, with compounds showing higher or lower totals failing to exhibit superconductivity ($PuCoGa_5$ having exactly 32). The talk, of course, raised as many questions as it addressed since the significance of the study's finding remains to be investigated.
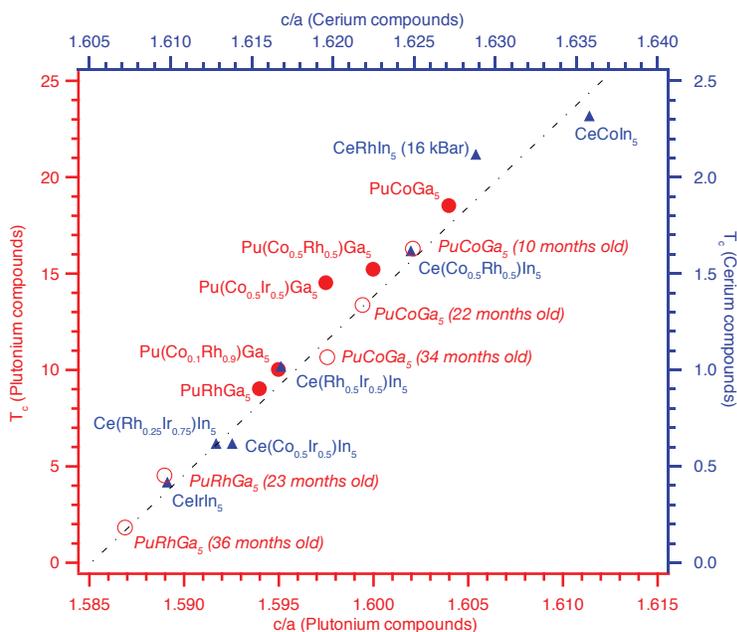
WASTIN

This plot of T_c versus c/a for superconducting compounds of plutonium (red circles and red axes) and cerium (blue triangles and blue axes) illustrates the contrast between triatomic crystalline materials, which despite being isostructural (for example, $PuCoGa_5$ versus $CeCoIn_5$), show markedly disparate critical temperatures for superconductivity (an order of magnitude higher in plutonium-containing materials). Aged plutonium compounds are indicated by open red circles. The parameters c and a represent tetragonal lattice constants for the crystals, which change slightly as crystals are placed under high pressure and, likewise, as crystals age.

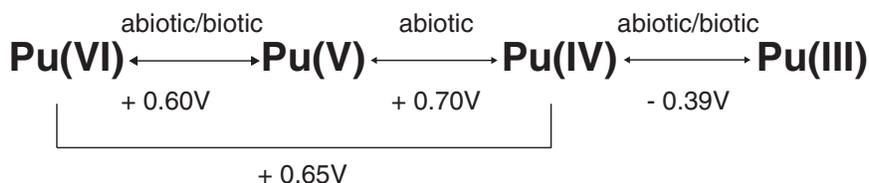# MICROBIAL TRANSFORMATIONS OF PLUTONIUM
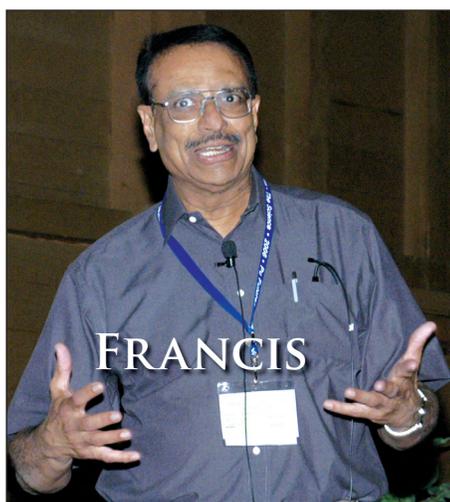
FRANCIS

Echoing one of the conference's up-and-coming areas—and a research topic that was more subtext than theme at the 2003 conference in Albuquerque—A.J. Francis of Brookhaven National Laboratory gave an enlightening talk on aspects of the metabolic processes by which soil microbes—bacteria and fungi—can become a key factor in environmental actinide chemistry. Sponsored by DOE's Environmental Remediation Sciences Program, this research complemented studies by Annie Kersting, Mary Neu, and other investigators—some presented in poster format—who have begun to carve out a better understanding of what may well be the next frontier in actinide environmental remediation: actinide biogeochemistry.

Francis' presentation springboarded from the issue of waste-repository remediation: the complex abiotic soil chemistry of various DOE waste sites further complicated by the presence of diverse colonies of microbes, most of which seem to thrive regardless of the presence of alpha- and gamma-emitting radionuclides. By sampling soil at Los Alamos' transuranic waste burial site at TA-54, Francis and his coinvestigators studied both aerobic (employ molecular oxygen [O_2] as the primary electron-acceptor in their metabolism) and anaerobic (metabolize carbohydrates and fats in the absence of O_2) bacteria, to assess the effect of their metabolisms on the changes in actinide soil chemistry provoked by biotransformation.

The inclusion of both metabolic types is important because it tends to account for processes at different soil depths; aerobes more likely to be found in superficial soil layers where oxygen is more available, anaerobes somewhat more prevalent in deeper soil layers. When one considers that there are on the order of several million of each type of bacterial cell per gram of soil (plus abundant fungal cells per gram), the notion that "life matters" in actinide soil chemistry is difficult to ignore.

Given that such microbial numbers are also characteristic of sites such as the Waste Isolation Pilot Plant in New Mexico and Yucca Mountain in Nevada, the group's experiments attempted to characterize the interactions of a number of bacterial species with a variety of plutonium (Pu) oxidation states, and their results suggest not only that bacteria should be counted but also that bacteria count.

Biotic and abiotic redox transformations of soil plutonium.

$$\text{Pu(VI)} \xleftrightarrow{\text{abiotic/biotic}} \text{Pu(V)} \xleftrightarrow{\text{abiotic}} \text{Pu(IV)} \xleftrightarrow{\text{abiotic/biotic}} \text{Pu(III)}$$

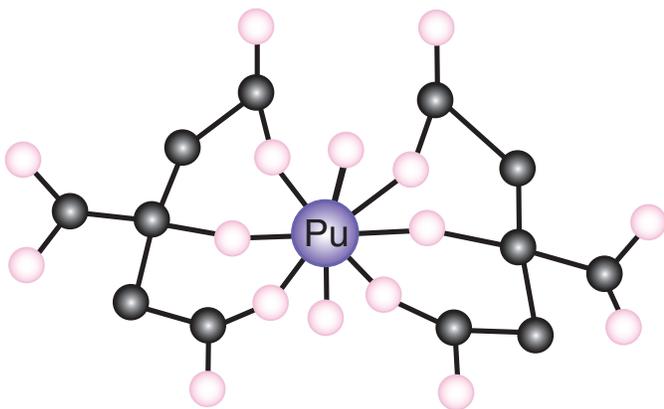+ 0.60V   + 0.70V   - 0.39V

+ 0.65V

This research group's results indicate that beginning from the known thermodynamics of Pu(IV) as the most stable form under environmentally relevant conditions, bacteria can facilitate both oxidative and reductive processes that affect soil speciation, as well as altering soil pH and perhaps plutonium solubility through secretion of organic acids such as citric, acetic, and butyric acids.
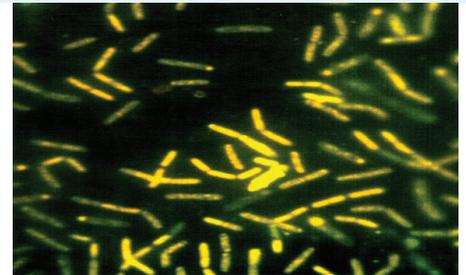
For example, growth of the anaerobic bacterium, *Clostridium,* in a plutonium-inoculated growth medium was found to lower both the medium's pH and its Eh, thereby solubilizing a significant fraction of previously solid plutonium. X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) analysis of the solubilized plutonium confirmed its predominately Pu(III) speciation. The results therefore suggest the reduction of Pu(IV) to Pu(III) by *Clostridium.* Given that the (III) oxidation state has, under most environmental conditions, higher mobility than Pu(IV), this bioreduction has the potential to influence plutonium dynamics.

In a related study employing electrospray ionization mass spectrometry, Francis and co-workers examined the growth of *Pseudomonas* bacteria in the presence of 10^{-5} moles per liter plutonium-242(IV) citrate (citric acid) complexes. In a situation where the plutonium citrate complex is relatively stable in solution, the investigators found that bacterial metabolism was able to alter that stability such that new bi-citrate complexes formed.
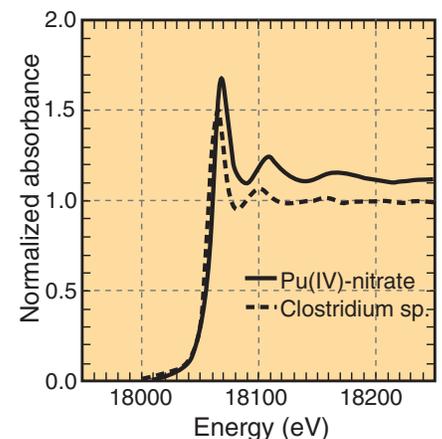
From such work, environmental remediators should consider the mechanisms by which microorganisms can influence speciation, specific chemical complexation and hence environmental mobility of plutonium, which all echo the conference theme that biology should be considered in assessing legacy site status.

Optical micrograph of cells of the bacterium Clostridium *sp.*

XANES reveals a -3-eV shift in peak soil plutonium absorption, indicating a change in predominant oxidation state from (IV) to (III).
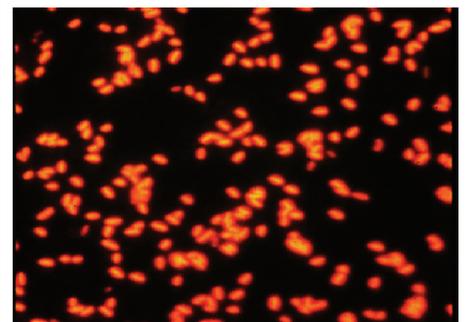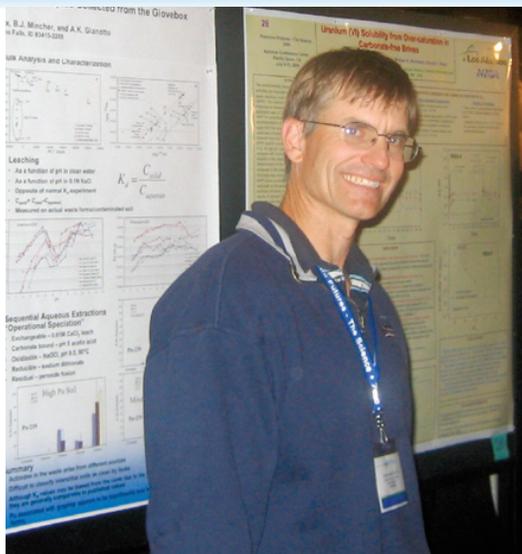

Plutonium bi-citrate: a complex of plutonium and two citrate molecules, showing only carbon (black) and oxygen (white) and omitting hydrogen in the citrates.

Optical micrograph of cells of the bacterium Pseudomonas fluorescens.

Poster highlights III

A poster from a group at Idaho National Laboratory details a procedure for the efficient collection of transuranic (TRU) waste samples and associated soils from gloveboxes (referred to as the "Glovebox Excavator Method") and the methods used to subsequently characterize those samples. A major stated purpose of the project is to demonstrate retrieval, characterization, packaging, and interim storage of waste contaminated with transuranics.

Peter Aryasov of the Ukraine explains aspects of his poster to several interested inquirers. The poster outlined details of the aerosol-monitoring operations at the Radiation Protection Institute of the Ukraine, where Aryasov is head of the dosimetric laboratory.

Bruce Bursten, Darleane Hoffman, and Boris Myasoedov pose at the Monday evening poster session, before the display announcing the publication of the new (third) edition of The Chemistry of the Actinide and Transactinide Elements, *the seminal and now classic text in the field.*

Eyes aglow in anticipation of the final Wednesday night poster session, a raccoon is forced to resort to other activities to release the frustration associated with the conference committee's inability to recognize its registration credentials.

Roundtable: new strategies for advanced nuclear fuel cycles

Chaim Braun and M.R. Srinivasan (left) and Burton Richter and Sig Hecker (right).

The shadow cast over this after-dinner discussion was clearly the issue of global warming, and after some brief but poignantly cautionary remarks by moderator Sig Hecker (director emeritus of Los Alamos National Laboratory), panelists Burton Richter, Chaim Braun, and M.R. Srinivasan each further shaded that shadow based on his own perspective. But in all cases, the panel's overall thrust was unambiguous. Given the world's burgeoning energy needs, the limited fossil-fuel supply, and the probable reality of greenhouse gas effects on the environment, nuclear power should form a key component of the planet's energy future.

Speaking first was Richter, of the Stanford Linear Accelerator Center. He took the historical path, hearkening back to President Carter's "once-through" fuel strategy, one that according to the Carter presidential library documents would have been abandoned had he been elected to a second term. When viewed against the fact that the United States has not ordered a new nuclear reactor for several decades, Richter's thrust was clear: the once-through fuel cycle is a dead end, one requiring enormous spent-fuel repository capacity even were the United States to not expand nuclear-energy-generating capacity beyond its existing array of more than 100 reactors.

Clearly advocating for spent-fuel reprocessing and actinide transmutation in fast-spectrum reactors, Richter estimated that one of the latter for every seven to eight light-water reactors would be sufficient for U.S. needs.

Returning to reality, Richter emphasized that no proliferation-proof fuel cycle exists, and therefore, he advocated internationalizing the fuel cycle (as in the Global Nuclear Energy Partnership, or GNEP), with nuclear nations delivering leased fuel via "just-in-time" delivery and retrieval of spent fuel, which would then be reprocessed. In this scheme, so-called "supplier states" would enrich uranium, recover spent fuel, reprocess the spent fuel to separate actinides, then burn the actinides in the fast-spectrum reactors.

World nuclear expansion: U.S. role

- More than 130 reactors are being built, planned, or under consideration worldwide

- U.S. has not ordered a reactor for decades, despite an existing fleet of more than 100 reactors

- U.S. should be in a position to influence how these facilities are designed, constructed, and operated
  - Safety
  - Waste disposal
  - Proliferation-resistance

Legend:
- Under Construction
- Planned and Approved
- Under Consideration

Countries: India, Russia, Japan, China, Taiwan, Canada, Iran, North Korea, Romania, Argentina, South Korea, Ukraine, Pakistan, Finland, Brazil, Turkey, Vietnam, Slovakia, Indonesia, Czech Rep., South Africa, Israel, France, Egypt, Bulgaria
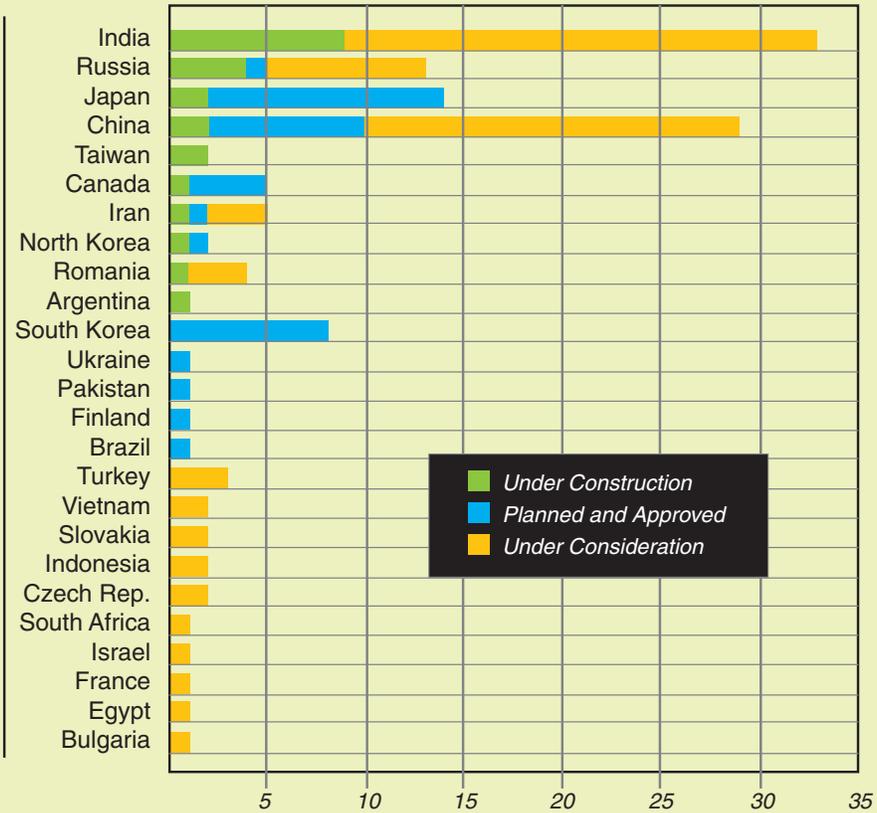
In turn, so-called "user states" would pay for the reactors and enriched fuel, as well as for the spent-fuel reprocessing.

Unfortunately, Richter admitted, more research and development are necessary, given that it is not yet clear what is the best fast-reactor system to attract the interest of commercial energy producers. His disposition in this regard was nothing if not consistent, in that he was clearly interested in discovering and taking whatever steps would be necessary to engage U.S. energy corporations.

Former Atomic Energy Commission Chairman Srinivasan essentially narrowed the view from Richter's global perspective and focused largely on India's burgeoning electricity needs and its projections for nuclear-power growth; his projections included a better-than-6-percent annual growth rate for Indian electricity generation over the next 20 years. Srinivasan's scenario featured a three-stage program: Stage II adds fast breeder reactors to an already impressive collection of heavy- and light-water reactors; Stage III adds thorium-based reactors to the mix. India has already built a pilot plant for reprocessing carbide fuels, which has already successfully reprocessed high-burnup carbide.

Slightly in contravention to Richter's plea for internationalization, Srinivasan emphasized India's need for its own fuel-cycle services, but he also envisioned India as a supplier of fuel-cycle services to what he characterized as friendly countries. His rollout of his country's specific plans for new reactor construction was nothing if not impressive. Indian scientists are actively pursuing a diversity of research and development areas, including sodium bonding in fuel fabrication, development of cladding materials, pyrochemical fuel reprocessing, and the development of technologies for waste management.

In addition, India (which has been reprocessing fuel since the 1960s) has just set up a second reprocessing plant, and has even set up a pilot plant at the Bhabha Atomic Research Centre to reprocess thorium oxide fuel. Srinivasan outlined several attractive features of thorium oxide over uranium oxide, including proliferation-resistance and less minor-actinide residue with reduced waste stream. All in all, the emphasis was on India's plans for growth based on its experience with nuclear technology and its anticipation that it can successfully accomplish its goals.

Stanford's Braun returned to the topic of the U.S. reactor dilemma, reminding his audience that his country was once the world leader in fast-breeder-reactor technology. He opined that most utilities were awaiting government signals to reactivate their fast-reactor programs and was even more emphatic than Richter in calling for that to occur, given the long lead time in nuclear programs.

Nor was Braun bereft of solutions as he reviewed GNEP, an initiative to roll out several elements of a cleaner nuclear technology, including advanced burner reactors (ABRs), proliferation-resistant recycling, and the minimization
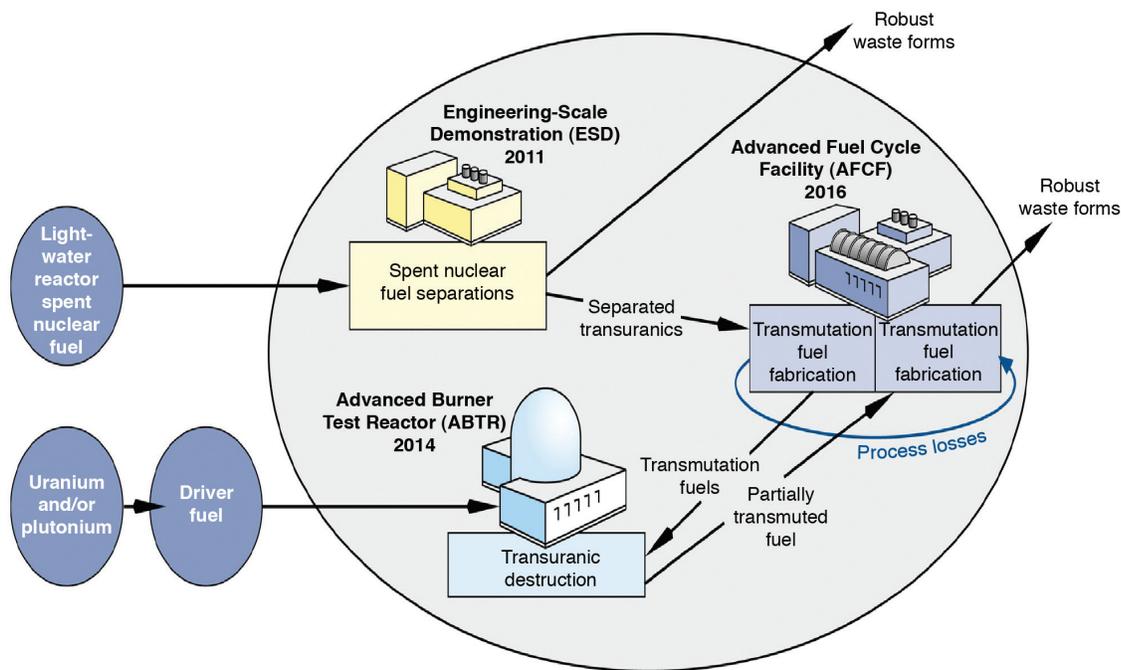
of nuclear waste. Specifically, this initiative would include spent-fuel separation with transmutation and ultimate destruction of transuranics, and the formulation of more storage-friendly waste forms.

Unfortunately, Braun emphasized, the time to begin implementation is immediately, particularly since ABRs are considered a near-term solution on the way to fast-breeder reactors, and he was explicit in offering a view that the U.S. fast-reactor program was largely permitted to atrophy in the 1990s.

Unfortunately for both the panelists and the audience, the time allotted was inadequate to complete the discussion or to engage the audience in crosstalk, a poster session stacked up behind the after-dinner panel. Moreover, given the pessimistic tone of both Richter's and Braun's presentations, one departed this discussion with the bitter taste of disappointment. In an age of diminishing fossil fuels and rising gas prices, while other nations like India are upgrading their nuclear-based electricity generation, the nuclear power initiative appears to have ground to a halt in the United States. In addition, one is left to wonder whether recent U.S. initiatives to close the nuclear fuel cycle have foundered, or whether programs in this area will regain their momentum.

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LALP-06-104

$$Pu(VI) \xleftrightarrow{\text{abiotic/biotic}} Pu(V) \xleftarrow{\text{abiotic}} Pu(IV) \xleftrightarrow{\text{abiotic/biotic}} Pu(III)$$

+ 0.60V   + 0.70V   - 0.39V

+ 0.65V