



**A Los Alamos  
power source,  
developed and manufactured at the Laboratory,  
has enabled Curiosity,  
a rover equipped with sensing devices, exploratory  
equipment, computers, and cameras,  
to explore Mars.**



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**This issue of the Actinide Research Quarterly (ARQ)** marks the beginning of a broader partnership of the ARQ team with the Los Alamos National Security Education Center (NSEC). The ARQ has been published for the last several years with the support of the Plutonium Science and Manufacturing (ADPSM) Directorate and while this support will continue, the importance of actinide science at the Laboratory extends well beyond ADPSM. The NSEC seemed a logical home for the ARQ from an institutional perspective as it coordinates the activities of six scientific institutes and the student and postdoctoral programs at Los Alamos National Laboratory with the mission to do the following:

- Foster sustained excellence and enhanced external visibility of research at the Laboratory;
- Establish and coordinate broad communities among our staff in support of Laboratory missions;
- Develop and facilitate programs that provide staff revitalization, professional development, and critical skills development;
- Foster strategic partnerships with research universities, industry, and government agencies;
- Provide education and training opportunities to nurture a cohort of future Laboratory employees.

The Seaborg Institute leaders serve as the primary technical editors of the ARQ and seek to highlight progress in actinide science of importance to many Laboratory missions.

This issue certainly highlights the breadth of that mission. Its cover story celebrates the many successes of the Curiosity rover mission on Mars, all made possible by the plutonium-238 power source manufactured at Los Alamos. Next is an article about finding a solution to the long-standing theoretical problem of Mott insulators (including actinide oxides), because while many earlier theoretical approaches to calculating the electronic structure of actinide dioxides indicate that these materials should conduct electricity, they instead act as insulators, especially at low temperatures. Recent advances in the polymer assisted deposition (PAD) process invented and patented at LANL have allowed the first synthesis of epitaxially grown thin films of  $\text{NpO}_2$  and  $\text{PuO}_2$ . This important development has enabled much more detailed measurements of a very fundamental property, the optical band gap, and provided further checkpoints for theory development. The third article discusses the potential advantages of the development of a product-based certification for manufacture of weapon components compared with the current process-based certification. The last piece is a series of tributes to Robert A. Penneman, researcher and leader in actinide chemistry for more than four decades at Los Alamos, by friends and colleagues around the country and the world.

The National Security Education Center welcomes the enhanced partnership with the ARQ team and looks forward to helping highlight news from the many facets of actinide research.

David L. Clark  
Director, National Security Education Center

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Curiosity photograph  
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### **ACTINIDE RESEARCH QUARTERLY**

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#### *Address correspondence to:*

*Actinide Research Quarterly  
c/o Editor  
Mail Stop B260  
Los Alamos National Laboratory  
Los Alamos, NM 87545*

#### *ARQ can be read online at:*

*www.lanl.gov/arq*

*If you have questions, comments, suggestions,  
or contributions, please contact the ARQ staff at:  
arq@lanl.gov or (505) 667-0392*

*National Security Education Center  
David L. Clark  
Director*

*Scientific Advisors, Seaborg Institute  
Albert Migliori,  
Seaborg Institute Director  
Gordon D. Jarvinen,  
Seaborg Institute Deputy Director*

*Editor  
Sue King*

*Contributing Editor  
Eileen Patterson*

*Designers/Illustrators  
Kelly L. Parker  
Leslie A. Sandoval*

*Photo Support  
Leo J. Riedel  
Michael D. Greenbank*

*Printing Coordinator  
David Van Etten*

# Space and the Atom

## LANL Powers Mars Curiosity Rover



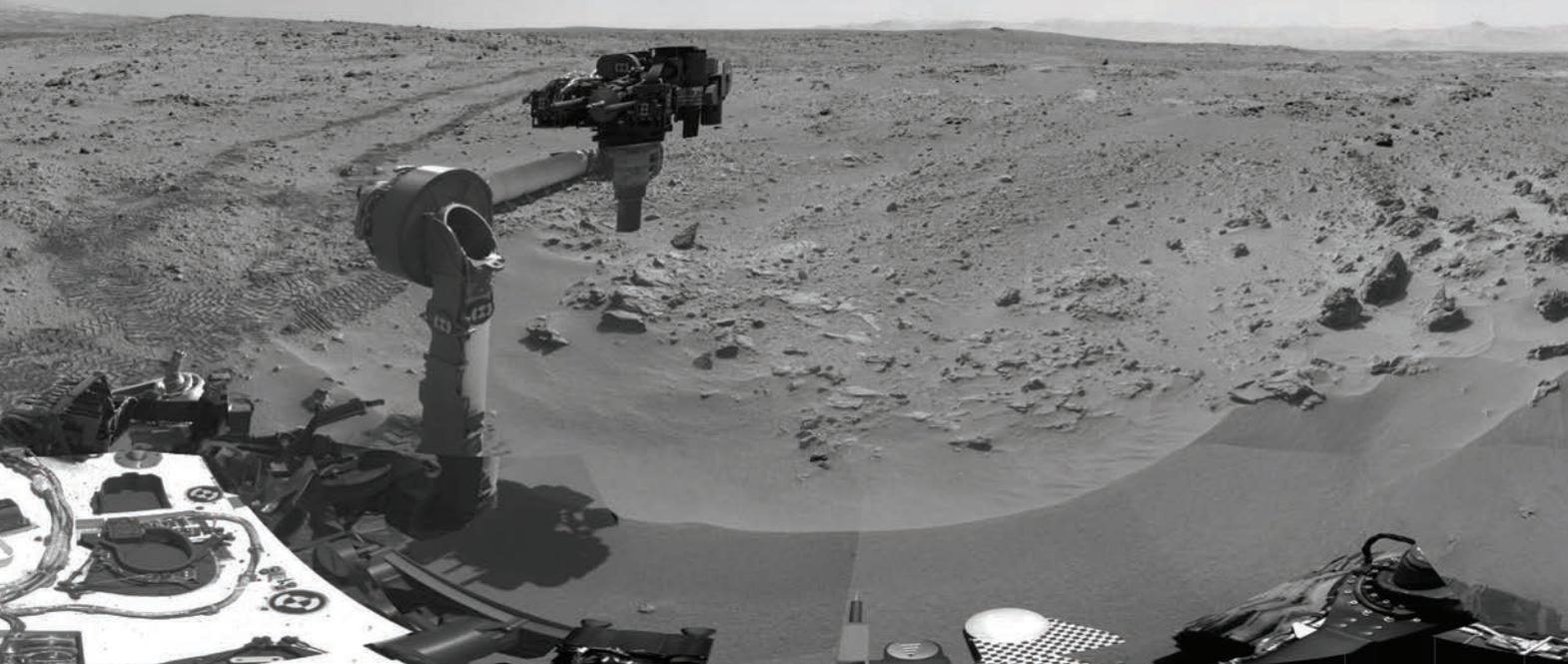
*This article was contributed by Amanda Bean, group leader of Nuclear Component Operations: Actinide Manufacturing and Technology (NCO-5). Amanda came to the Laboratory in 2001 as a graduate research assistant working in what is now C-IIAC (Inorganic, Isotope and Actinide Chemistry). She was awarded a Seaborg Institute Research Fellowship in 2002 to continue her studies of transuranic speciation using hydrothermal synthesis techniques. In 2003, Amanda was a LANL Director's Postdoctoral Fellow. During her fellowship, she investigated the synthesis of lanthanide and actinide compounds using molten salt-hydroxide fluxes and electrochemistry to produce complexes in high oxidation states.*

Once again, the marriage between space and the atom was realized when NASA's Mars rover Curiosity successfully descended upon the Red Planet's Gale Crater last August. Many across the United States had held their breath as they waited for the "seven minutes of terror" to pass as the most high-tech Mars rover to date maneuvered its complex drop through the thin Martian atmosphere from 13,000 mph to resting safely on the surface. This effort was made possible by many agencies across the United States, and none so close to home as Los Alamos' Plutonium Science and Manufacturing Directorate (ADPSM), whose engineers, staff, and technicians had hands-on experience with the power that made this mission possible.

What does "power" mean to a mission such as the NASA Mars rover Curiosity? To put it simply, it is a nuclear battery, a long-life, no-maintenance nuclear source of power. Electricity is generated from the natural decay heat of plutonium-238 and is exploited for use by means of solid-state thermocouples. An electrical current is produced when a closed electrical circuit is made with the two connections that are different temperatures. The difference between the natural heat of plutonium-238 and the cool temperature of the space environment or planetary atmosphere is the key to the workings of the radioisotope thermoelectric generator (RTG).

Thermocouples are found in common, everyday items such as air conditioners or refrigerators, and the general principle is best described using the Seebeck effect (see box on page 4).

The quest for the perfect source of heat and power for deep-space probes is long and fascinating. A power source must meet stringent requirements to be of



use for NASA missions; it must be impervious to cold, radiation, and other harsh effects of the space environment. It must operate continuously and require no maintenance because it can't be repaired after launch into space. The RTG was developed by Mound Laboratories in Miamisburg, Ohio, in the late 1950s. The first RTG was launched in 1961 for use in a navigation satellite (Glenn Seaborg's speech quoted in the margin at right celebrates that accomplishment). As NASA explains, more than 40 radioisotope power systems have been used over four decades on more than two dozen NASA spacecraft. The Apollo missions to the moon; the Pioneer, Voyager, Ulysses, Galileo, Cassini, and Pluto New Horizons missions to the outer solar system; and the Viking landers sent to Mars were all equipped with RTGs. "RTGs have never been the cause of a spacecraft accident, [though] they have been on board three space missions that did fail for other reasons," NASA says. "In all three cases, the RTGs performed as designed."

Inside the RTG is the actual radioactive heat source: the general purpose heat source (GPHS). The source of the heat is a pressed pellet of plutonium-238 oxide,  $\text{PuO}_2$ . The actual process of recycling the plutonium and producing the pellet happens within the ADPSM operations and engineering groups, NCO-5 and MET-1, respectively. Once material has been identified to be used for the final pellet product, it is sent through the aqueous nitrate process to remove any impurities and uranium-238 that grows in as the Pu-238 undergoes radioactive decay. The resulting powder is likely to have differing particle characteristics based on the previous history of the starting material. Therefore, after the aqueous process, there is a progression to normalize the granules by grinding to a powder and then ball milling, cold

“The presence of the “atomic battery” ... is a symbol of a “marriage” that was bound to occur—between Space and the Atom. We have known for some time that the two were made for each other. No one would be tempted, at the present time, to abandon other sources of energy for space. However, the atom has made greater strides toward coming of age for space application in the past few years than many of us could have hoped. The day is not far off when atomic energy will be available in many different packages for practical use in space vehicles.”

- Glenn Seaborg, 1961

\*Quote is from Nuclear Power and Space, a speech given in October 1961 by Dr. Glenn T. Seaborg, Chairman of the US Atomic Energy Commission, following the June launch of the TRANSIT IV-A, the first US atomic-powered satellite..

## The Seebeck Effect

This effect is the production of electricity through the use of temperature differences. A current loop is created when two metals respond to the temperature difference. Voltage can be derived from where  $S_A$  and  $S_B$  are the thermopowers (Seebeck coefficient) of metals A and B as a function of temperature, and  $T_1$  and  $T_2$  are the temperatures of the two junctions. The Seebeck coefficients are dependent on the conductors' absolute temperature, material, and molecular structure.



Thomas Johann Seebeck  
1770-1831

$$V = \int_{T_1}^{T_2} (S_B(T) - S_A(T)) dT$$

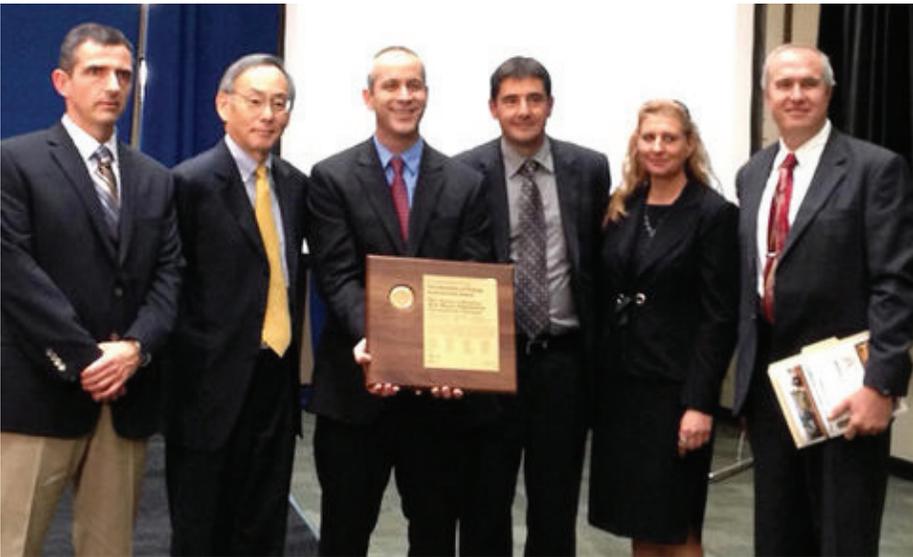
pressing, and screening the powder to produce granules of a desired size range. Once granules are of the desired size range and heated in an additional furnace treatment, they are loaded into a die and hot pressed. After the pellets have been pressed, they are sintered in flowing  $H_2^{16}O$ -saturated argon to reoxidize and reestablish stoichiometry from  $PuO_{1.88}$  to  $PuO_{2.00}$  and relieve mechanical stresses in the pellets to assist in transferring the pellet to the final cladding. The clad is then welded and decontaminated and ready for its final nondestructive testing and acceptance.

Currently for fiscal year 2013, 22 of the 28 heat sources to support potential future NASA missions have been manufactured. With the success of the landing of the Mars rover Curiosity, Los Alamos National Laboratory is excited and optimistic about future missions to Mars and to other locations in the solar system.

These successes do not come without a lot of hard work. The Plutonium Facility at Los Alamos has supported the heat source program since the beginning of its operation in the late 1970s. There are significant investments being made to the Plutonium Facility in order to assure a reliable facility infrastructure. The NE-75, Space Power/Pu-238 project of the Nuclear Nonproliferation and Security Program, is investing in preventive maintenance to further sustain reliability of equipment. Some more recent investments have been the installation and method development of a DC-Arc instrument, which was installed in the Plutonium Facility and will be used for isotopic analysis. The ability to obtain this data inside the Plutonium Facility reduces the need to ship samples to CMR, Chemistry and Metallurgy Research, and also will greatly reduce the turnaround time for data. NE-75 also participates in a cost-sharing



The 2012 NCO-5 team (alphabetical order):  
Lawrence Aragon, Anthony Archuleta,  
Jonathan Atencio, Amanda Bean, Lia Brodnax,  
John Brooks, Diana Brown, John Brown,  
Nash Esquibel, Jack Gower, Ronald Hart,  
Yvonne Herrera, Kent Kramer, Di Lamkin,  
Jesse Martinez, Connie Montoya,  
Richard O'Leary, Paul Richardson, Benny Rose,  
Rudy Salazar, Joey Sanchez, Edwin Serrano,  
Nathaniel Shanteau, John Stong, Adrian Trujillo,  
Daniel Valerio, Darryl Vigil, and Rodney Zamora.



Craig Van Pelt, DOE Secretary Steven Chu,  
John Matonic, Alejandro Enriquez,  
Diane Spengler, and David Armstrong during  
the ceremony honoring the LANL team with the  
Secretary of Energy's Achievement Award on  
October 4, 2012. The team was recognized for  
its work on the Curiosity rover power source.

model with other equipment such as the installation of a plutonium assay/  
radiochemistry glovebox and equipment, which was sponsored by the NNSA  
Plutonium Sustainment Program, but will be a benefit to both programs.  
With continued planning of preventive maintenance, Los Alamos National  
Laboratory is confident in its ability to continue to support the nation's  
mission needs.

*This article was contributed by Eve Bauer, Anthony Burrell, Robert Jilek, T. Mark McCleskey, Brian Scott, Quanxi Jia, Tomasz Durakiewicz, John Joyce, Miles Beax, Kevin Graham, Stosh Kozimor, Steve Conradson, Xiaodong Wen, Enrique Batista, and Richard L. Martin, Los Alamos National Laboratory; Lindsay Roy, Savannah River National Laboratory; Paul Bagus, University of North Texas; and Gustavo Scuseria, Rice University.*

# The Localization–Delocalization Dilemma:

## The Electronic Structure of *f*-element Oxides

The *f*-element oxides are of interest in a number of application contexts ranging from automobile exhaust catalysts (cerium sesquioxide, or Ce<sub>2</sub>O<sub>3</sub>) to nuclear fuels (uranium dioxide, or UO<sub>2</sub>). They are also of fundamental interest as members of the set of Mott insulators, a class of materials long problematic for theory because while they should conduct electricity, they instead act as insulators, especially at low temperatures.

What came to be known as the Mott insulator problem was first defined at a conference in 1937 in Bristol, England. The Dutch physicists Jan Henrik DeBoer and Evert Johannes Willem Verwey presented electrical conductivity data for a number of first-row transition metal oxides, including scandium, ScO (d<sup>1</sup>); titanium, TiO (d<sup>2</sup>); chromium, CrO (d<sup>4</sup>); manganese, MnO (d<sup>5</sup>); nickel, NiO (d<sup>8</sup>); and copper CuO (d<sup>9</sup>). The transition metal sites in these materials have a formal valence of +2, leading to the anticipated *d*-electron count given parenthetically above.

DeBoer and Verwey pointed out that because each of these materials had a partially filled *d*-band, according to the recently proposed band theory of solids they should all be metallic. In stark contrast, they were all insulators. A spirited discussion followed, but the problem waited to be addressed until after World War II, when it was revisited by British physicists Nevill Francis Mott and John Hubbard, who established that large electron-correlation effects not present in the band theory were responsible for the insulating behavior.

Perhaps the easiest way to understand the Mott problem qualitatively is through the potential energy curve for the diatomic hydrogen molecule, H<sub>2</sub> (Fig. 1). At equilibrium, we know that a molecular orbital description is a reasonably good approximation for the wave function. From two H 1s atomic orbitals, one on each hydrogen atom, we form bonding (in phase) and antibonding (out of phase) linear combinations. The bonding molecular orbital lies lower in energy and is occupied with two electrons; the corresponding antibonding molecular orbital is empty. It is easy to show that this wave function contains equal components of ionic (H<sup>+</sup>H<sup>-</sup>, H<sup>-</sup>H<sup>+</sup>) and Heitler–London (covalent, H:H) character. At long distances, however, the physical situation is best described by a wave function in which one electron is localized on the left atom and the other on the right; that is, only the covalent character remains.

We can understand this situation qualitatively within the Hubbard model. The model consists of a hopping term (*t*), which transfers an electron from one center to another and determines the electronic kinetic energy, and a repulsive term (*U*), which reflects the energy required to put two electrons

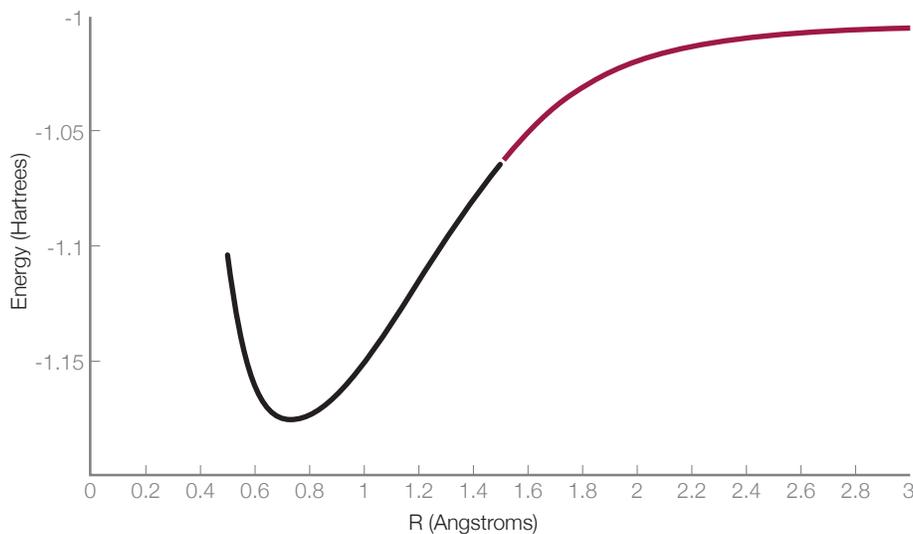


Figure 1: This is the potential energy curve for the diatomic hydrogen molecule,  $H_2$ .

in the same atomic orbital. Near equilibrium, the kinetic energy gained by delocalizing (hopping) the electrons easily overcomes the repulsion in the ionic component of the wave function associated with the double occupancy, and the molecular orbital approximation works well.

On the other hand, at long distances the orbital overlap is weak, the hopping term and kinetic energy are small, and the penalty associated with the double occupancy of the molecular orbital form dominates. The energy is minimized by eliminating the ionic piece, leaving only the Heitler–London component, reflecting the electron correlation. Here the electronic correlation is strong: when one electron is on the left, the other is on the right; the electrons localize, one to each nucleus. Most important, in this localized wave function the ionic terms are now absent; the covalent piece now dominates.

Consider now a long chain of equally spaced hydrogen atoms (Fig. 2). If the distances are typical of an  $H_2$  bond length, the molecular orbitals will form a continuous band of states, called the crystal orbitals, or Bloch states. Each hydrogen atom contributes one electron, so the band will be partially filled and the ground state a metal. If the distance between hydrogen centers is made longer, or if the size of the atomic orbitals is made smaller, thereby reducing the orbital overlap and hence the kinetic energy, at some point the repulsion will dominate and the system will localize electrons, one to a center. Higher-order interactions generally lead to an antiferromagnetic ordering of the spins. An insulating gap will develop, which is the energy it takes to move an electron from one center to another. This energy is given by the Hubbard repulsion term  $U$ .

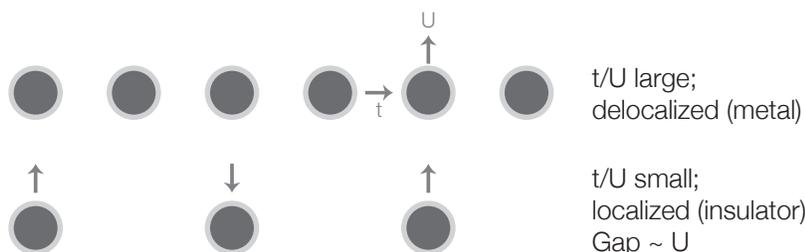


Figure 2: The electronic properties of a chain of equally spaced hydrogen atoms changes if the distance between H centers becomes longer or the size of the orbitals smaller. These changes can lead to localization and an insulating gap. This energy is given by the Hubbard repulsion term  $U$ .

While the basic physics of this situation has been understood for some time, the point at which the transition from delocalized to localized behavior occurs has been difficult for first-principles theories to predict. For example, the workhorse of electronic structure theory, density functional theory (DFT), generally overestimates the electronic delocalization, predicting metallic behavior for these insulators, as in this case: the first-generation functional, the local density approximation (LDA), predicts NiO to be metallic. NiO is in fact an antiferromagnet with a gap of some 4eV. Second- and third-generation approximations—generalized gradient (GGA) and meta-GGA functionals—do no better. A fourth generation, the hybrid functionals, departs from the conventional local and semi-local approximations by incorporating a component of the full nonlocal Hartree–Fock exchange term:

$$E_{xc} = aE_x^{HF} + (1 - a)E_x^{GGA} + E_c^{GGA} \quad (1)$$

The constant  $a$  is in principle adjustable, but a value in the vicinity of 0.25, selected from heuristic theoretical arguments, has proven to be quite successful. It is not varied from one material to another, and it is in that sense universal. This functional, with  $a=0.25$ , when combined with generalized gradient exchange and correlation functionals, is known as PBE0. This refinement largely remedies the problem. A number of studies have now shown that hybrid density functional theory with  $a=0.25$  yields the proper lattice constants, insulating behavior, band gaps, and magnetic properties of many Mott insulators, when known.

In what follows, we review the results of calculations for  $UO_2$  using PBE0<sup>1</sup> or the closely related screened hybrid functional HSE, and compare our results with experiments that probe the occupied density of states (photoemission) and the unoccupied levels (X-ray absorption). Excellent agreement with experiment is observed, and the calculations suggest that  $UO_2$  is indeed a Mott insulator, the 5f levels being quite localized with very little dispersion. We then turn our attention to plutonium oxide ( $PuO_2$ ), where hybrid density functional theory predicts a strong, counterintuitive orbital mixing between the Pu 5f and O 2p orbitals. This manifests as a large dispersion in the band structure, a prediction most easily tested with angle-resolved photoemission spectroscopy. Unfortunately, measurement of the dispersion requires an ordered, single-crystal quality sample of  $PuO_2$ , which has in the past eluded attempts at synthesis. We address that challenge here and report the preparation of a single-crystal quality thin film of  $PuO_2$  using the new technique of polymer-assisted deposition (PAD).

## Synthesis

We have prepared thin films of  $UO_2$ ,  $NpO_2$ , and  $PuO_2$  with PAD<sup>2</sup> (Fig. 3). PAD, as applied to actinides, is a water-based process in which a nonvolatile molecular precursor is bound directly to a charged water-soluble polymer. The pH and actinide concentration is adjusted to ensure high complexation of the polymer. It is then spin coated onto an appropriate

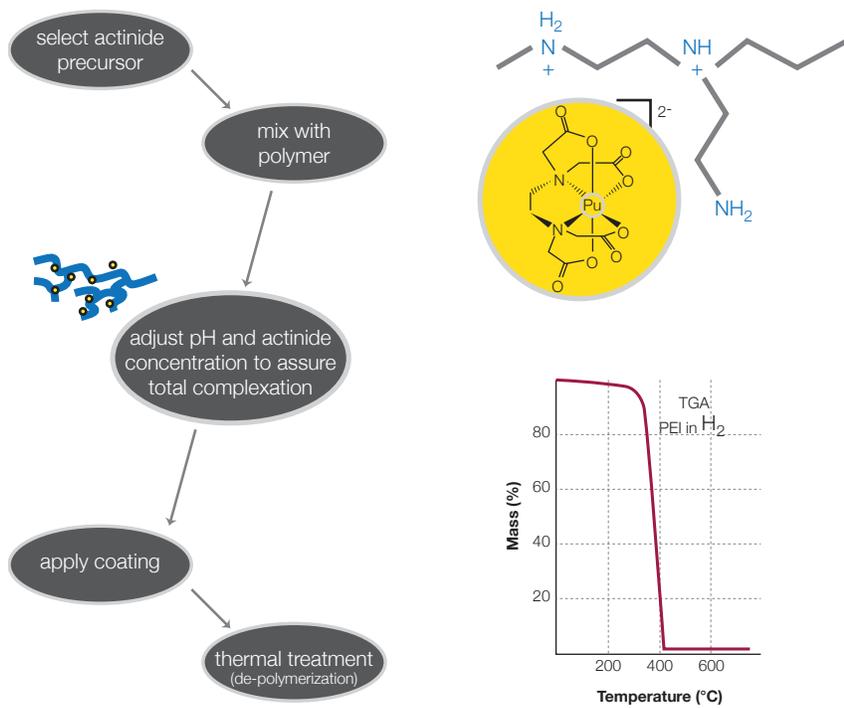


Figure 3: Creating single-crystal thin films using PAD allows for material studies.

substrate chosen to have a good lattice match with the desired film. In the case of  $\text{PuO}_2$ , yttrium-stabilized zirconia was used. The coated substrate is then heated in an oxidizing atmosphere to drive off the polymer.

Highly ordered, single-crystal quality films result. Comparison of the PAD spectrum for  $\text{UO}_2$  from these films vs the  $\text{UO}_2$  spectrum from available single-crystal samples shows that the films created by PAD are indistinguishable from available samples.

### Characterization

Before discussing  $\text{PuO}_2$ , it is instructive to review what has been learned from single-crystal studies of  $\text{UO}_2$ . It is an antiferromagnet in its ground state, with  $T_N = 31\text{K}$ . Both the LDA, local-density approximation, and GGA, generalized gradient approximations, predict  $\text{UO}_2$  to be a ferromagnetic metal. Figure 4 compares the DOS, density-of-states, in the

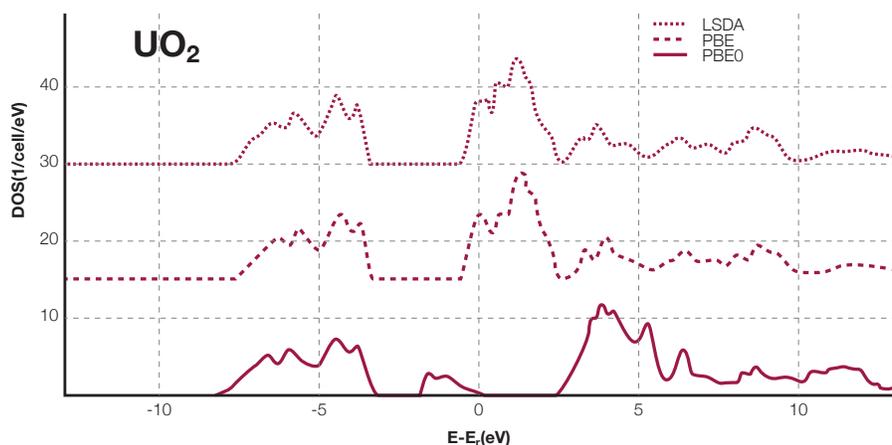
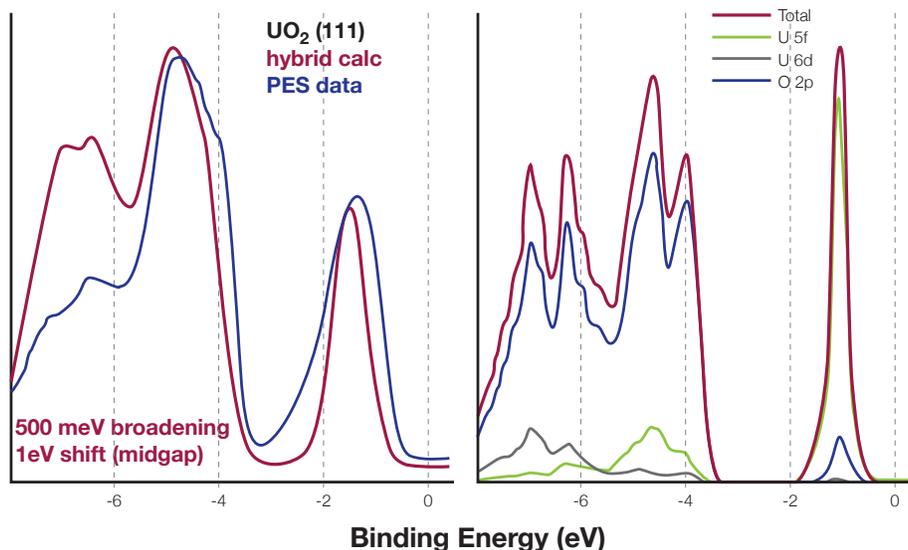


Figure 4: Comparisons of the DOS using three generations of DFT for single-crystal  $\text{UO}_2$ . The first two generations of DFT (LSDA and PBE) predict  $\text{UO}_2$  to be a metallic ferromagnet, while the fourth generation approximation, PBE0, correctly predicts  $\text{UO}_2$  to be an antiferromagnetic insulator.

various approximations. The hybrid functional opens a gap of 2.2eV, in good agreement with the experimental value of 2.1eV. In addition, PBE0 yields the correct antiferromagnetic ground state. The equilibrium lattice constant predicted with the LDA is 5.28Å, compared with 5.47Å experimentally. This is unusual because the LDA generally leads to good bond lengths. The error reflects the fact that the ground state in the LDA is metallic; that is, the bonding is stronger than appropriate, leading to the short bond distance. On the other hand, the hybrid functional tends to localize the f electrons on the U site, decreasing the bond energy and yielding a lattice constant (5.42Å) in much better agreement with experiment.

A particularly direct probe of the character of the occupied states is provided by photoemission experiments. The left panel of Fig. 5 compares the photoemission spectrum measured by Durakiewicz et al.<sup>3</sup>, with the theoretical DOS for UO<sub>2</sub>. The spectrum was measured at a photon energy where the U 5f and O 2p ionizations cross sections are comparable, thereby allowing a direct comparison with the theoretical DOS. A fairly narrow peak

**Figure 5:** The left panel compares the photoemission spectrum with the theoretical density of states for UO<sub>2</sub>. The spectrum was measured at a photon energy where the U 5f and O 2p ionizations cross sections are comparable, thereby allowing a direct comparison with the diffuse optical spectroscopy (DOS). The right panel shows the calculated partial DOS; the peak near the Fermi energy is predominantly of f character, while the higher binding energy features reflect the O 2p bands.



at the valence band maximum is separated by a few eV from a broader feature at binding energies of 3–8 eV. This is faithfully reflected in the calculation. The right panel reports the calculated partial DOS, where it can be seen that the peak near the valence band maximum Fermi energy is predominantly of f character, while the higher binding energy features reflect the O 2p bands. This assignment had been made much earlier using the technique of energy-dependent photoemission spectroscopy (PES).

The top panel in Fig. 6 shows the band structure computed for UO<sub>2</sub>. Note the very narrow f band at the Fermi energy. This flat band confirms the localized nature of the electrons. If the f electrons were perfectly localized on the uranium sites, the band would be a straight line with zero slope. The theory finds a dispersion of 190 meV from  $\Gamma$  to X; angle-resolved PES (ARPES) measurements by Durakiewicz and Joyce<sup>3</sup> find a dispersion (130 meV) in good agreement<sup>3</sup>. Thus both experiment and theory agree on a

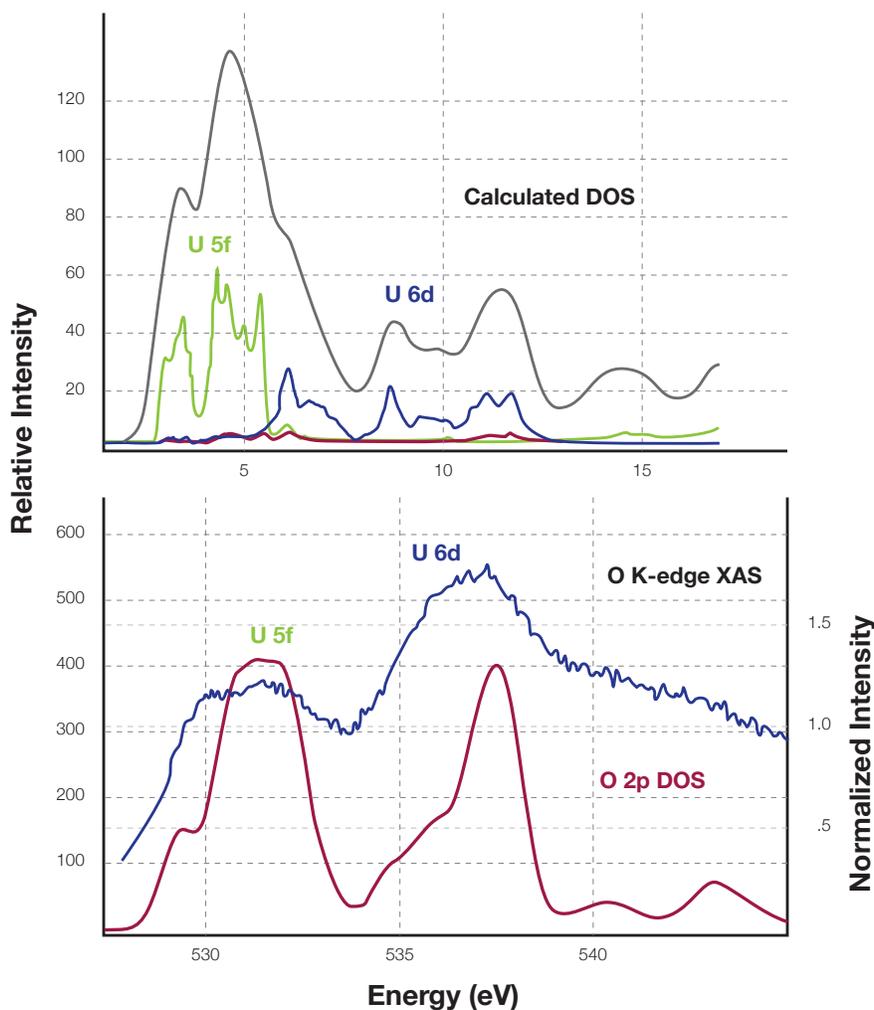
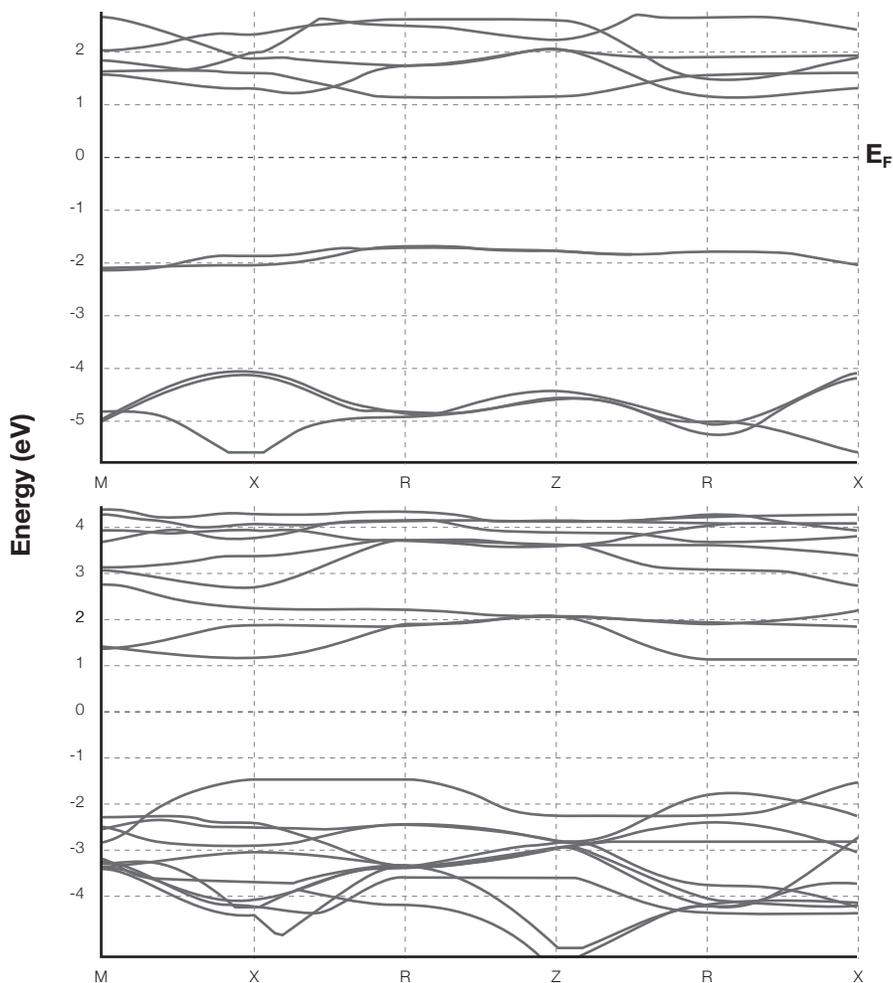


Figure 6: The  $UO_2$  (top). The U5f component is given in green, the U6d in blue, while the O2p partial DOS is in red. The lower panel shows a magnification of the O2p density of states compared with the Oxygen K-edge X-ray absorption spectrum.

very ionic picture for  $UO_2$ ; there is a measurable dispersion in the f manifold, but it is quite small.

The unoccupied states may be probed using X-ray absorption spectroscopy (XAS) experiments. In particular, we have implemented new soft X-ray capabilities for transuranic samples at the Stanford and Berkeley synchrotron laboratories. The soft X-ray regime allows us to access the O 1s edge. This capability provides a very sensitive measure of the mixing between the metal orbitals and O 2p states. Optical excitation of an electron from the O 1s level to unoccupied levels bound with respect to the O 1s ionization potential may be seen as pre-edge features in the O1s X-ray absorption. These transitions are governed by the usual dipole selection rules in which the angular momentum must change by plus or minus one unit. The power of ligand edge spectroscopy arises because the O 1s orbital is quite small, and so the oscillator strength is governed by the amount of O 2p character in the unoccupied orbital. Stated differently, the intensity of a near-edge bound state reflects the O 2p partial DOS in that state and can therefore be used to determine ligand-metal orbital mixing.

**Figure 7:** While little dispersion is seen in the 5f band of U in  $\text{UO}_2$  with hybrid DFT (top), strong orbital mixing is reflected in the large dispersion seen for  $\text{PuO}_2$  (bottom). The Fermi energy resides at a value of 0eV. While  $\text{UO}_2$  shows two distinct bands below the Fermi energy, in  $\text{PuO}_2$  they merge and are mixed together indicative of a strong hybridization.



In Fig. 7 we compare the O 1s XAS spectrum with the O 2p partial DOS from the HSE calculation (Conradson 4). The O 2p DOS in the unoccupied states is quite small, but if we magnify it, the comparison with the XAS is gratifying.

Turning now to  $\text{PuO}_2$ , it is once again predicted to be a ferromagnetic metal with standard functionals but an antiferromagnetic insulator with the hybrid functionals. In both states the local unpaired spins couple to an  $S=2$  moment on each Pu. The actual magnetic ground state of  $\text{PuO}_2$  does not exhibit magnetic order. We have recently shown that the moment is quenched by a very subtle interplay between atomic multiplet effects and covalency with the O ligand. We also note that antiferromagnetic spin fluctuations have been argued to be important for understanding the magnetic susceptibility (Brooks<sup>5</sup>), so antiferromagnetic coupling appears to be a low-energy alternative to multiplet formation. At any rate, we do not believe that this omission affects our conclusions in any qualitative way.

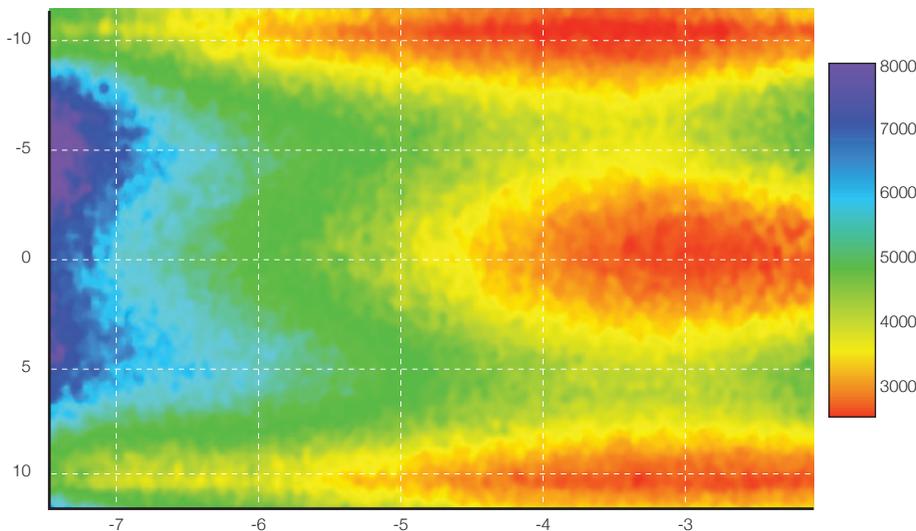
The interesting aspect of  $\text{PuO}_2$  that emerges from the hybrid calculations is that the Pu 5f states have fallen in energy and there is no longer a large separation from the O 2p states. This manifests itself in the fact that the states near  $E_f$  in  $\text{PuO}_2$  are nearly 50:50 mixtures of Pu 5f : O 2p orbitals.

Excitations across the gap now involve a significant component of O 2p character. PuO<sub>2</sub> marks the boundary between Mott (f → f) and charge-transfer (O 2p → Pu 5f) regimes, according to hybrid density functional theory. This strong orbital mixing is reflected in the band structure (Fig. 7). There is no longer a visible narrow band associated with the f orbitals. The occupied bands now show a great deal of dispersion, indicative of strong orbital hybridization or mixing.

This prediction of strong orbital mixing in PuO<sub>2</sub> seems at odds with our intuition. We know that as one progresses to the right in the actinide series toward larger atomic number, the f orbital radius decreases (the actinide contraction), and so the hopping integral connecting them with O 2p orbitals is getting smaller, implying even greater localization than in UO<sub>2</sub>. On the other hand, it is also true that as one progresses to the right, the 5f orbital energy decreases for similar reasons. Our calculations suggest that in the vicinity of Pu, the 5f and O 2p orbitals become nearly degenerate. Because the magnitude of the orbital mixing depends on the ratio of the hopping integral to the difference in orbital energies, the energy denominator becomes small as the atomic states become nearly degenerate, driving significant mixing and dispersion. This is sufficient, according to the calculations, to overcome the effect of the reduction in the hopping integral.

This prediction can now be addressed, given the high-quality films, with angle-resolved PES experiments. The results are shown in Fig. 8. The kinetic energy of the electron is plotted vs the angle of detection relative to the surface normal. The amplitude of the signal is signified by the color. If the f band showed little dispersion, the spectrum would appear to have a single narrow line at a specific binding energy (the signal would be independent of the k-vector of the electron, and hence the detection angle). Here we see amplitude (dispersion) over a range of a few eV, in stark contrast to the dispersion in the 100 meV range observed in UO<sub>2</sub>. The theory is confirmed.

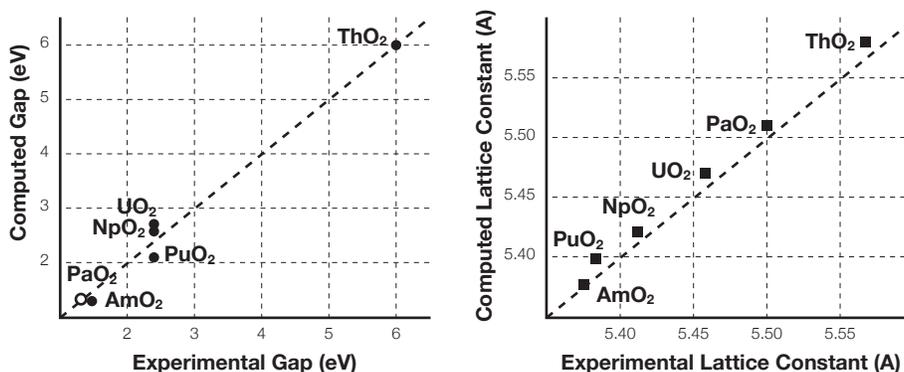
The availability of high-quality thin films also allows measurement of optical gaps for these materials. The new measurements for NpO<sub>2</sub> and



*Figure 8: Angle-resolved PES experiments on the PuO<sub>2</sub> film. The horizontal axis is energy and the vertical axis is angle (crystal momentum). The green shaded region in the ARPES data shows 3 eV of dispersion in the hybridized orbitals, an order of magnitude more than in UO<sub>2</sub>.*

**Figure 9:** The predictions of hybrid DFT for the optical gaps of the series. These theory predictions were made in 2007, and the gratifying agreement with experiment suggests the hybrid DFT may be used as a predictive tool for this class of materials.

*This work was funded by the Laboratory Directed Research and Development Program at Los Alamos National Laboratory under the auspices of the U.S. Department of Energy (DOE). In addition, portions were supported by the Division of Chemical Sciences, Geosciences, and Biosciences and the Division of Materials Science and Engineering in DOE's Office of Basic Energy Sciences. Additional support was provided by the U.S. Department of Defense through a Multidisciplinary University Research Initiative grant (Rice University).*



PuO<sub>2</sub> are quite different from those in the literature, yielding gaps of 2.80 eV (0.4eV) and 2.75 eV (1.4eV), respectively, where the older literature values are in parentheses. The reason for these large changes is that previous measurements were generally made on powders, as opposed to ordered films, and the gap was inferred from optical conductivity measurements, as opposed to direct optical absorption. The conductivity measurement is quite sensitive to the presence of defects, and a reliable measurement, as in other contexts, begins first with excellent samples. The accumulation of this data has allowed us to distinguish among several competing theories for these Mott insulators<sup>5</sup>. The predictions of hybrid DFT for the optical gaps of the series is shown in Fig. 9. It is important to realize that the theory predictions were made in 2007, and the gratifying agreement with experiment suggests the hybrid DFT may be used as a predictive tool for this important class of materials, and used in conjunction with experiment to develop controlled functionality.

## Conclusions

Recent advances in the PAD process invented and patented at LANL have allowed the first synthesis of epitaxially grown thin films of NpO<sub>2</sub> and PuO<sub>2</sub>. This important development has enabled much more detailed measurements of a very fundamental property, the optical band gap; the existing values in the literature were shown to be in significant error. The advances have also allowed the first angle-resolved photoemission measurements of their electronic structure, using an experimental capability unique to LANL. These measurements have confirmed an earlier theoretical prediction of unexpected covalency in PuO<sub>2</sub>, supporting similar surprising conclusions reached by XAS studies of the bonding in small molecules. The combination of these two is providing new guiding principles for understanding reactivity, bonding, and electronic structure in actinide materials. These experimental advances have confirmed the value of hybrid DFT as a predictive tool for these materials; it is important to emphasize that this theory, unlike other approaches such as the LDA+U and the dynamical mean field theory (DMFT) contains no material-dependent empirical parameters. This collaborative basic science effort has led to applications of these capabilities to problems involving advanced nuclear fuels and the science of signatures.

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# Stockpile Certification:

## Improving Agility through a Product-Based Approach

Certification of the stockpile has evolved dramatically over the last fifty years. In the era of nuclear testing, a performance-based certification scheme with rigorous control of processes was the route to certifiable products. Stockpile development demanded an intimate coordination of the design agency with the production agency, often including numerous engineering and nuclear tests to ensure that the components met engineering and physics performance requirements. Once a final design was issued, production parameters were specified and carefully controlled at the production agency.

Given that the understanding of weapons physics was incomplete, it wasn't feasible to simply state a set of product characteristics, measure those in the final product, and certify on that basis. Indeed, even if such characteristics could be completely described, the resultant product would often require destructive evaluation to ensure that it met such specifications. Hence, the approach taken was to confirm performance in a nuclear test and then freeze and control the production parameters to ensure all subsequent builds were as identical as feasible to the tested units.

In practice, this was exceptionally challenging. Throughout nuclear weapons production history, uncontrolled variables crept into all elements of production. Variances were frequent, and individual assessment was needed to certify most stockpile components. Variances were closely monitored and individually approved or rejected through formal assessment. These variances were documented for each warhead in its individual quality assurance documentation, known colloquially as that unit's "bomb book." The lore at Rocky Flats was that a pit didn't leave the site until its bomb book weighed more than the nuclear core itself.



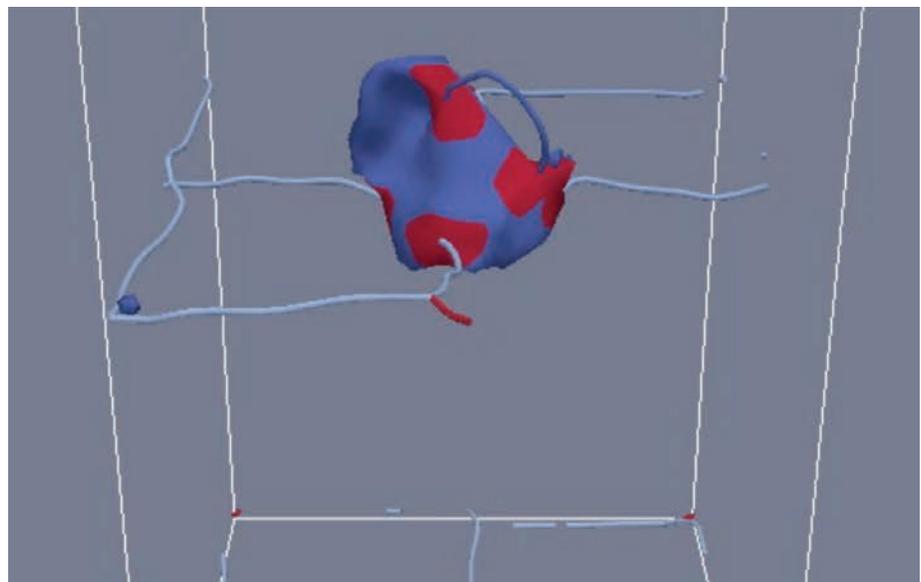
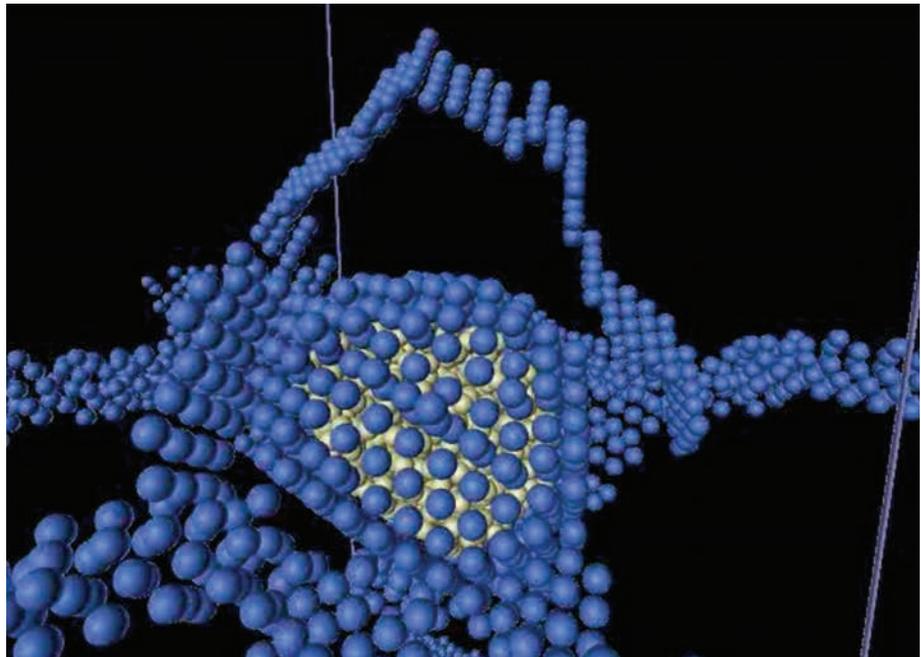
*In 2012, NNSA deployed a nondestructive process at its Y-12 facility for assessing nuclear weapon components, called nondestructive laser gas sampling (NDLGS). The NDLGS system is capable of assessing the internal gas constituents of hazardous components in a nondestructive manner. The technology is anticipated to save several million dollars per year by reaccepting weapon components back into the stockpile and avoid the cost of new manufacture. The process greatly improves the safety and minimizes workers exposure to hazardous material.*

Source: <http://nnsa.energy.gov/mediaroom/pressreleases/ndlgs6412>

*This article was adapted by Joseph Martz from a report by Joseph Martz, David Clark, Franz Freibert, Robert Hackenberg, Deniece Korzekwa, David Teter, and Stephen Sterbenz of Los Alamos National Laboratory.*

Computer simulation of materials behavior, showing He bubbles forming at a Cu <100> twist grain boundary.

Source: <http://www.lanl.gov/mst/mst8/index.shtml>



This reliance on nuclear testing and control of production processes arose for several reasons. Foremost, it was the most certain way to ensure nuclear performance. Further, given an incomplete understanding of weapon physics and material properties, it was the most practical means for ensuring that systems met performance requirements. Calculations of weapon performance were not rigorous and relied in part on assumptions regarding certain material properties. Computational codes evolved the means to address these shortcomings with parametric fits, sometimes called “knobs.” To this day, key elements of weapon performance calculations rely upon expert judgment in setting these knobs.

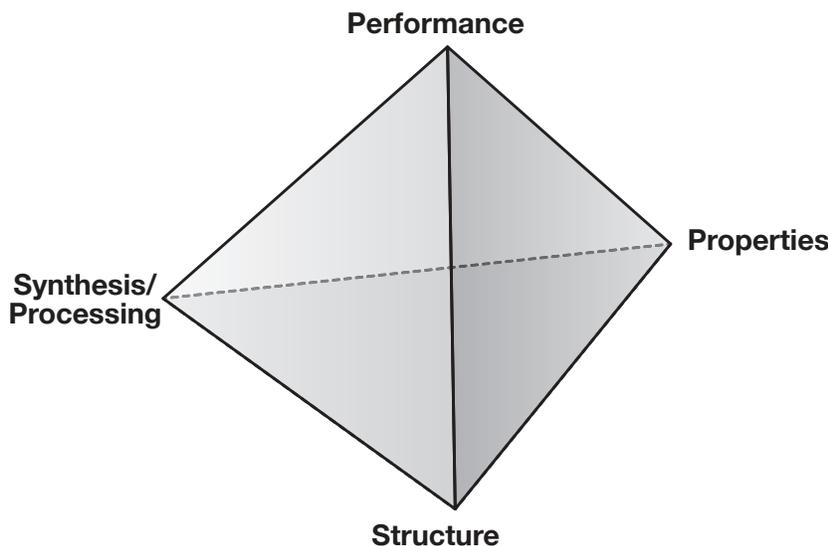
### Science-Based Certification

In 1992, the United States imposed a test moratorium on the nuclear weapons complex, dramatically altering the means for certification of the stockpile. This resulted in the adoption of science-based stockpile stewardship, a bottom-up approach where measurement of relevant material properties and understanding of weapon physics (and engineering) were used to assess weapon performance computationally.

By 1995, a formal “annual stockpile assessment” program was begun. As part of this program the laboratory directors at Los Alamos and Livermore assign Red Teams to independently review the assessment process and other issues associated with the health of the stockpile. Each director submits an annual assessment report that addresses the safety and functionality of each weapon system in their purview, modifying the certification if necessary. This strategy has been successful in certifying enduring weapons systems as safe and reliable and in identifying future issues to be addressed as a component of life extension programs.

In addition, the need to relocate critical manufacturing processes has led to a number of manufacturing campaigns, most notably in pits. In 1996, Los Alamos National Laboratory was assigned the job of rebuilding the W88 pit. The objective of this program was multifold, including a desire to reestablish the critical manufacturing capability that had been lost with the closure of the Rocky Flats pit production plant. Also important was a demonstration that, in the absence of additional nuclear testing, the tools of stewardship were sufficient to respond to stockpile aging issues.

There was also a need to supplement the very limited supply of W88 pits, especially because some pits had been removed.. This program produced the first certified pit in 2006, ten years after program inception. The certification of the W88 pit was a success, but the set of challenges that it presented to the design, engineering, and manufacturing communities was considerable, and the technical solutions that it developed are not without lingering issues.



*This model shows the intersections of the many aspects of materials, all of which are related and used to evaluate options so the best choices can be made in a product-based approach to weapons manufacturing.*

Source: LANL Materials Design Institute, <http://institutes.lanl.gov/mdi/>

The need for process-based strategies is clear when the properties of interest to the design agency cannot be measured directly in the final product. The strategy used to ensure that the product met specifications and that key—and difficult-to-measure—properties were within specifications, was to tightly control production processes. This has the advantage of ensuring consistency in at least the manufacturing process. It has the disadvantage of restricting production, often leading to multiple pieces of the same equipment, each certified for a different product. In contrast, bringing agility to manufacturing and production operations can take maximum advantage of a product-based certification strategy. For example, an agile casting furnace could be set to produce multiple products. Product-based certification relies on relevant material and component properties for certification, rather than on a rigidly controlled production process. Properties measured directly on individual components are recorded and form part of the certification record.

Materials and components that can be completely described by such specifications are ideal candidates for product-based certification because measurement of component variations can verify function and are amenable to statistical methods for certification. Product-based certification becomes much more challenging when critical components have key properties which cannot be directly measured.

### The Materials Science Model

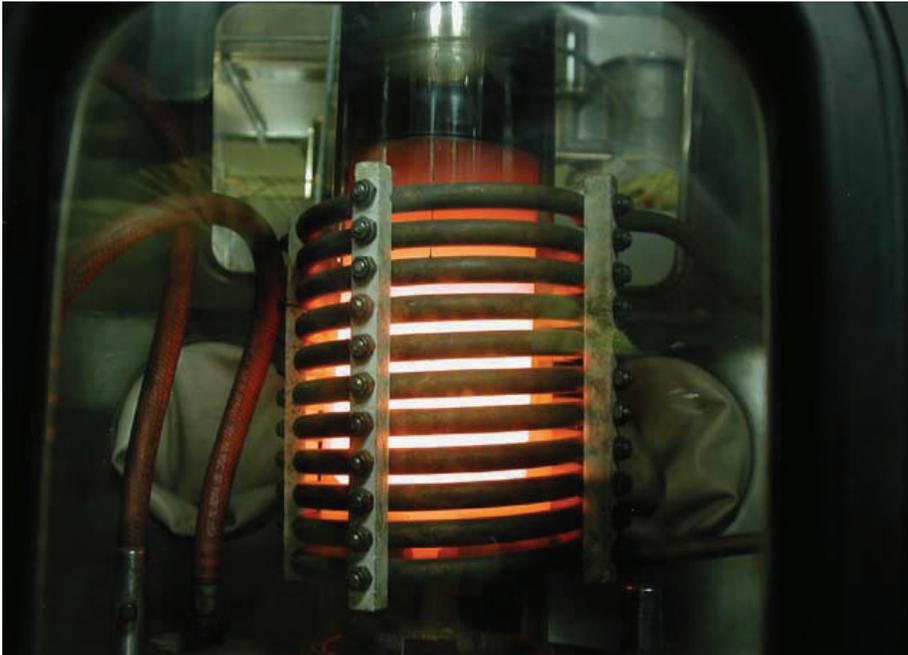
A product-based certification approach requires a thorough understanding of the relationships between processing, structure, properties, and performance. These relationships are often called the “materials science pyramid” because they may be depicted as the edges of a tetrahedron with “processing,” “structure,” “properties/chemistry,” and “performance” as vertices. This model is at the heart of a new approach to certification. The strategy proposed is predicated on the idea that relevant properties can be evaluated with sufficient accuracy to have confidence in important properties that cannot be measured. That there are relationships among processing, structure, and properties/chemistry is the foundation for such an extrapolation.

Modern advances in the instrumentation for process monitoring and inspection would be key in collecting diagnostic information on the measurable properties of components throughout the fabrication process. Determination of a set of such measurements would support the building of a statistically based set of properties as a function of component fabrication to create a quantifiable justification for component rejection. A statistically determined set of production samples would still be destructively evaluated to gain confidence in the assessments made on the basis of nondestructive evaluations alone and to ascertain and to validate justification for component rejection.

Take, for example, plutonium strength, or more properly, flow stress under dynamic load, which is a known important property in the evaluation of primary performance. In the W88 program, Los Alamos plutonium was subjected to considerable testing to show that dynamic strength fell within acceptable bounds. Process steps such as casting and thermal homogenization were placed under strict war-reserve quality-control procedures to ensure that subsequent material continued to meet these specifications.

In a product-based approach, initial certification efforts would not only measure plutonium strength, but would also establish the importance of controlling variables such as density, composition, grain size, and grain orientation. These latter properties are directly measurable on each finished component. Relationships between these observables and strength would be evaluated using state-of-the-art materials science.

With the chosen set of measured properties within scientifically justified limits, the product would be certified with confidence that performance characteristics such as strength will have been met. A statistical basis would be used to determine the number of components to be destructively sampled to validate this strategy. As can be seen, implementation of a product-based strategy requires an understanding of the materials science model. If a process change is needed, and the process is agile, the certification of that change is driven by the product and its properties. If it can be shown that proposed changes do not change the properties identified as relevant, then the change can be accepted rapidly.



*PU casting at TA-55 is among the most challenging manufacturing operation to transfer to a product-based certification regime.*

To cite another example, the cutting lathe that produced the plutonium hemishells for the W88 program is under strict process-based war-reserve control. That lathe is unavailable for use in other pit manufacturing programs because changes of fixturing would violate the war-reserve quality-control regime.

In a product-based approach, the pit geometry, density, and overall mass would provide the basis for certification. With direct measurement of these specifications, components could be certified on a part-by-part basis. The production agency would have the flexibility to change the potting chuck and use this same lathe for other hemishell manufacture, with concurrent demonstration that those hemishells meet similar specs. Such agility has compelling benefits.

## The Grand Challenge

The essential grand challenge is a quantitative understanding of plutonium metallurgy and corrosion science, which would enable a product-based approach. The challenge applies to processing, structural properties, analytical chemistry, and the performance model for in-service nuclear weapons. Plutonium experiments, measurements, theoretical understanding, modeling, and weapons physics and engineering calculations must also be integrated to reach this goal.

Many of the people whose expertise is needed in these areas are nearing (or are beyond) retirement age. Initiatives at both the Los Alamos and among sponsor agencies will be critical within the next decade to capture and transfer knowledge of plutonium to the next generation of plutonium scientists and engineers as part of this grand challenge.

Another element of the grand challenge relates to the availability of both experimental facilities and appropriate test specimens. Critically limited availability of experimental facilities and the exceptional efforts needed to work with plutonium will present a great challenge to providing the information needed for this product-based certification. Finally, there is a challenge to develop new experimental techniques for plutonium. The better our ability to measure the properties of plutonium, the less we need to extrapolate, and the more accurate the certification.

A range of information sources will be required for this product-based certification strategy. For it to succeed, existing information needs to be better organized for effective use. Some new data can be obtained from existing equipment and approved experimental capabilities. Other necessary data will require new and perhaps novel capabilities involving substantial development work and possible modification of a facility or safety basis.

Given the complex interactions at the corners of the model, statistics-based design of measurements will be essential to support product-based certification. Foundational theoretical studies (for example, electronic structure calculations) will guide development of an understanding of relevant variables and so perhaps reduce the required scope or depth of experimental campaigns.

A move toward product-based certification requires agility and will improve the effectiveness of the nuclear weapons production complex. Modern U.S. nuclear weapon systems contain dozens of components with hundreds of materials manufactured by thousands of production operations. Some operations and activities are more easily adapted to this strategy than others. Product-based certification is not an all-or-nothing strategy; instead, a product-based strategy centered on an understanding of key properties of components and materials has built into it the ability to evolve with technology and mission changes.

# A Legendary Los Alamos Actinide Chemist and Technical Leader Passes Away

**Bob Penneman**  
1919-2012

## Introduction

Robert A. Penneman, an important chemist in the Manhattan Project and leader of a major actinide chemistry group at Los Alamos for nearly four decades, died peacefully in his sleep on July 28, 2012, at the age of 93.

Bob was born into an Illinois family of modest means, worked his way through college to earn B.S. and M.S. degrees in chemistry, and joined the Manhattan Project in 1942 at the Metallurgical Laboratory at the University of Chicago. His first job was to help prepare uranium metal for the world's first nuclear reactor, which was being built under the direction of Enrico Fermi. He then worked directly under future Nobel Laureate Eugene Wigner, making critical measurements of radiation damage on materials ranging widely from ion exchange resins for plutonium separation to carbon moderator blocks in the Hanford production reactors. After World War II, Bob obtained his Ph.D. and joined Los Alamos National Laboratory in 1947. There he spent the remainder of his career, developing and managing what some considered one of the world's premier transuranium chemistry groups (as attested to in the following remembrances submitted by his colleagues). Bob published well over a hundred peer-reviewed open literature papers and countless technical reports. His last peer-reviewed paper, on the solid state structure of  $\text{PuO}_{2+x}$ , was published in 2005 in the *Journal of Solid State Chemistry* when he was 87. He could entertain for hours with wonderful stories about his career, especially from the 1940s and 1950s.

The accomplishment that Bob considered to be his greatest, however, was hiring an amazing number of outstanding scientists at Los Alamos. With these new hires, his group branched out from actinide chemistry and established highly successful and wide-ranging programs, including transition metal chemistry, spectroscopy, isotope separation, and biochemistry. Today, staff hired into his group (originally



*This article was contributed by these friends and colleagues of Bob Penneman: Gary Eller, Robert Ryan, Alfred Sattelberger, David Moody, Nan Sauer, Kenneth Salazar, Suki Coonley, Lester Morss, Ray Wymer, Boris Myasoedov, Stepan Kalmykov, and Darleane Hoffman.*

**Introduction by P. Gary Eller,**  
*Actinide chemist, Ph.D.,  
Chemistry Division, Los Alamos  
National Laboratory, retired*

“After World War II, Bob obtained his Ph.D. and joined Los Alamos National Laboratory in 1947. There he spent the remainder of his career, developing and managing what some considered one of the world's premier transuranium chemistry groups.”

CMF-4, then CNC-4, then finally INC-4) can be found in positions of significant responsibility all across the Laboratory and at other national laboratories and universities. To celebrate these accomplishments, in 2009 a symposium was held at Los Alamos. The 2nd/3rd quarter 2010 issue of the *Actinide Research Quarterly* was devoted in its entirety to this symposium. There the reader can find much more information on Bob's life.

The University of Chicago Met Lab team gathered for this photo. Bob is on the left end of the top seated row.



“Bob felt, perhaps modestly, that the development of his group was his most important contribution.”

Aside from his technical and management expertise, Bob was an outstanding human being. Those of us who worked closely with him recall that he rarely raised his voice in anger or disparaged others. He was a close colleague and friend even when he was the boss. Bob also was a devoted family man to his beloved wife Mary, two daughters, and son.

Bob had a great sense of humor (including a fondness for terrible puns), which he often used to make a point. As an example, I remember grumbling to him about writing yet another proposal to secure funding for a project I was interested in. He responded, “You have to throw a lot of bread out on the ocean and hope a hamburger floats back once in a while.” I got the message.

Bob's friends and colleagues, and the broader actinide science community, will miss him dearly.

## Remembrances

### Robert R. Ryan,

*Group Leader, Inorganic, Isotope, and Nuclear Chemistry, Los Alamos National Laboratory, retired*

It is widely recognized that Bob developed and led a highly successful research group at Los Alamos and was, in his own right, a celebrated researcher in actinide chemistry. Bob felt, perhaps modestly, that the development of his group was his most important contribution. His extraordinary success as a group leader had many facets but perhaps the most important was his clear vision of what the group should become. He envisioned a group that was recognized for excellence in the area of actinide chemistry and that could respond to Los Alamos' programmatic needs but he also recognized that the group's potential should transcend these fundamental requirements. He felt that the group should establish programs that would bring recognition to LANL from

throughout the chemical community and would serve to draw the best young talent from that base. His approach can best be illustrated by an example.

Greg Kubas came to Bob's group as a post-doc in vibrational spectroscopy but he also had an interest in preparative inorganic chemistry that he demonstrated by producing some interesting iron sulfur transition metal complexes. This was at a time when acid rain was an issue of national concern. Bob recognized the potential application of Greg's expertise to this important issue, identified a funding source within DOE's Department of Basic Energy Sciences and encouraged Greg to write a proposal. When the work was funded, Greg was hired, and Bob encouraged the participation of other group members who could contribute to this new direction.

In order to develop new chemistry to reduce sulfur dioxide to harmless components, the work focused on the interaction of sulfur dioxide, the cause of acid rain, with transition metal complexes. It caught the imagination of the group, whose multidisciplinary talents were focused on the issue for several years, resulting in nearly 100 publications in the peer-reviewed chemical literature. The work spanned the range from preparation of new compounds through structural characterization and to the development of bonding models, and finally to the development of new complexes capable of promoting the reaction of sulfur dioxide with hydrogen to produce sulfur and water. During the pursuit of this last goal, Greg isolated a complex that bound molecular hydrogen as a ligand, an observation that provided a fundamentally new insight into the mechanism of hydrogenation catalysis. Even more important, it established a new type of chemical bonding: nonclassical coordination of a bonding electron pair to a metal center. This accomplishment was heralded as the most important discovery in inorganic chemistry in the previous three decades, and it catapulted Greg to instant fame. It has been stated by several that this body of work "put Los Alamos on the map in inorganic chemistry" in general and, as Bob had envisioned, brought the group a flood of new talent, among which were some who were recognized as the best young investigators available in the country.

I was hired into INC-4 in the summer of 1984. It was a group that already had a national and international reputation for excellence and innovation in inorganic chemistry, a legacy that Bob Penneman and the staff he hired during his tenure as group leader had created. By the time I arrived, Bob had retired and Basil Swanson (one of Bob's strategic hires) had succeeded him as the group leader of INC-4. My initial assignment was to do actinide organometallic chemistry, building on the early transition metal chemistry I had done as a faculty member at the University of Michigan and on the discoveries of group members Bob Ryan, Dave Moody, Ken Salazar, and others. Needless to say, it was a nirvana assignment and one that I attacked with great enthusiasm. Group members Larry Asprey and Gary Eller took me under their respective wings and taught me what I needed to know about working safely with radionuclides and hazardous chemicals in a national laboratory environment. In fact, it was Gary who instilled in me the merits of a well-written standard operating procedure, or SOP. Bob Penneman would visit the group frequently and often stopped by my office to hear what was new with our section's chemistry. Even though he wasn't trained in organometallic chemistry, he knew the field quite well, had an ency-

**Alfred P. Sattelberger,**

*Associate Laboratory Director, Energy Engineering and Systems Analysis, Argonne National Laboratory*

“He was a visionary, one of those rare individuals who understood the 'big picture,' the challenges and rewards of doing world class science, and what it took to achieve shared goals.”

clopedic memory, and always had good suggestions for us to pursue in the lab. He enjoyed telling me stories about the group, the challenges it had faced over time, and the successes his staff members had achieved. He was always modest about the role he had played in those advances, but over time I came to appreciate the significant contributions he had made either directly or indirectly to the scientific breakthroughs made by the group. He was a visionary, one of those rare individuals who understood the “big picture,” the challenges and rewards of doing world class science, and what it took to achieve shared goals. As others have noted, he was also a great recruiter. Those of us who followed him in group and division leadership positions had a great role model to emulate.

**David C. Moody III,**

*Manager, Department of Energy, Savannah River Site*

“He was always supportive of new initiatives and gave young researchers the freedom to excel.”

Bob Penneman was a boss, a mentor, and a friend. Bob hired me twice at Los Alamos National Laboratory: once as a postdoctoral research associate and finally as a staff member in INC-4. Bob grew and led one of the most diverse chemistry groups within the national laboratory complex. He was always supportive of new initiatives and gave young researchers the freedom to excel. As we were establishing our research programs, Bob ensured that we were also connected into ongoing Laboratory mission elements to provide additional growth opportunities. I will never forget Bob’s encouragement and support as we discovered novel trivalent uranium chemistry. The established community was skeptical at first, but Bob never wavered in his commitment and provided invaluable advice on how to gain acceptance. I will forever be thankful for Bob supporting and mentoring me early in my career, a support that has continued as my professional career has changed directions many times. Bob will be missed by those of us whom he influenced so deeply.

**Nan Sauer,**

*Associate Director in Chemistry, Life, and Earth Sciences, Los Alamos National Laboratory*

“Bob Penneman had a passion for people, for science, and for the Laboratory.”

Bob Penneman had a passion for people, for science, and for the Laboratory. I met him as a young staff member, and I was struck by his extensive knowledge and experience and by his willingness to pass on what he knew. When he came back to the Lab for visits, he would always spend the time to meet with various members of the group (INC-4 at the time), especially the younger staff. He was engaged and thoughtful and it was fun to talk about science with him. I enjoyed the time I spent with him and learned a great deal as well. He was a very special person.

**Kenneth V. Salazar,**

*Chemist, Materials Science and Technology Division, Los Alamos National Laboratory, retired*

“Bob was my scientific Dad!”

In the early ‘70s it was very difficult for a nondegreed “valley boy” to get a technical job on the Hill. I applied for several weeks for technician-level openings. Bob gave me my first break! He offered me a job as a chem tech and told me, “If you want to advance, you need to take some chemistry courses.” So, I started taking chemistry, math, and physics courses at the UNM branch campus and eventually worked my way into the Technical Staff Member ranks. He always had faith in me and encouraged me daily. I will always be grateful to Bob for having given me a chance at science! Bob was my scientific Dad!

**Meredith (Suki) Coonley,**

*Editor, Actinide Research Quarterly, Los Alamos National Laboratory, retired*

I first met Bob when he coauthored an article for a 2004 issue of *ARQ* titled “Proposing a hydroxide ion, rather than a central oxide ion, in the structure of  $\text{PuO}_{2+x}$ .” It was a very technical subject that I had trouble getting my head around, but I remember his patience in explaining the science to me. His first question to me was, “How did you get that nickname?”

He contributed to several other articles in *ARQ*, including reminiscences of his fellow actinide pioneer Larry Asprey (2005), “Al Ghiorso recalls a moment in time” (2007) a retrospective of the early days of INC-4 (2010) and “helpful comments” to author Lester Morss for “Tracing the Evolution of Actinide Science Research in the United States” (2011).

I came to rely on Bob as a source of historical information, and any time I had a question about the early days of actinide science, he could provide the answer. Over the years we became email pen pals, and I always looked forward to receiving one of his jokes. He read *ARQ* cover to cover, and if there was an error in science, he’d let me know, but in the most gracious manner. He was generous with his praise and frugal with his criticism; I will remember him as one of my favorite “coneheads.”

I first “met” Bob Penneman during my graduate student years (1966–69) at UC Berkeley, in Burris Cunningham’s laboratory at the Lawrence Radiation Laboratory, probably when I read the americium chapter of *The Chemistry of the Actinide Elements* by Katz and Seaborg (1957). My first research challenge was to search for and synthesize stable complex compounds of the transuranium elements. Using cerium as a possible model for the actinides americium through californium, I was puzzled by the stability of tetravalent cerium in acidic aqueous solution and the absence of solid Ce(IV) compounds such as  $\text{CeCl}_4$ . I attempted without success to prepare  $\text{CeCl}_4$  by traditional (high-pressure  $\text{Cl}_2$  oxidation of  $\text{CeCl}_3$ ) and “soft chemistry” approaches, but I succeeded in preparing  $\text{Cs}_2\text{CeCl}_6$  (and was disappointed that its synthesis and structure were published by others just after I had deduced the structure). I immediately turned my attention to the parallel americium system, reading the many papers by Bob Penneman, especially his comprehensive review of Am and Cm chemistry with Larry Asprey, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 7, 355 (1956).

My interests focused on actinide thermodynamics, a specialty of Los Alamos scientists such as C. E. Holley, Jr., L. B. Asprey, and R. A. Penneman. The first time I met Bob in person was probably at the spring 1968 ACS national meeting in San Francisco, and the second time was probably at a Gordon Research Conference on actinide science in 1970 or 1971.

During my years at Argonne National Laboratory, I met Bob several times. Most clear in my memory is the Actinides 1981 conference at Asilomar, when Bob introduced me to Gary Eller. Bob’s insights into the mysteries of actinide science continued through his distinguished career, culminating in his 2005 paper (*Journal of Solid State Chemistry* 178, 563) on the probable hydroxyl component of the unique hydrogen evolution from  $\text{PuO}_{2+x}$  discovered by John Haschke and colleagues at LANL in the 1990s and published in 2000. He insightfully drew on the wisdom of W. H. Zachariasen in this paper.

Bob and I remained in active contact, most recently when I phoned him in 2011 while I was writing my article “Tracing the Evolution of Actinide Science Research in the United States” (*Actinide Research Quarterly*, May 2011, pp. 10-29). He explained to me that during the late 1940s he and colleagues were accumulating significant amounts of americium as a byproduct of plutonium purification. Bob recalled that he went to LASL director Norris Bradbury,

“I came to rely on Bob as a source of historical information, and any time I had a question about the early days of actinide science he could provide the answer.”

#### Lester Morss,

*Actinide chemist, Argonne National Laboratory; Program Manager, Heavy Element Chemistry, Office of Basic Energy Sciences, Department of Energy, retired*

“By 1957, when *The Chemistry of the Actinide Elements* was published, Bob’s published references are cited on 32 pages, a tribute to his leadership in carrying out fundamental science during the Cold War’s most secretive years.”

asking for and obtaining informal permission to carry out the first systematic studies of the fascinating chemistry of americium—studies that lasted several decades. By 1957, when *The Chemistry of the Actinide Elements* was published, Bob's published references are cited on 32 pages, a tribute to his leadership in carrying out fundamental science during the Cold War's most secretive years.

For me, Bob Penneman's most lasting tribute was his coauthorship of the americium and curium chapters in *The Chemistry of the Actinide Elements*, 1986, which I had the privilege of coediting with J. J. Katz and G. T. Seaborg. Bob was also a coauthor of these chapters in *The Chemistry of the Actinide and Transactinide Elements*, 3rd edition. It has been a privilege for me to consider Robert A Penneman as one of my mentors in actinide science.

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**Ray Wymer,**

*Director, Chemical Technology Division,  
Oak Ridge National Laboratory, retired*

“Bob Penneman's unrivaled ability to unravel this tangled skein of chemical yarn contributed hugely to weaving the fabric of the present-day nuclear fuel cycle industry and distinguished Bob, setting him apart from other workers in his field.”

There are rare periods in the history of science when wholly new fields of discovery and endeavor emerge. The chemistry of the transuranium actinide elements is such a field. The challenges of unraveling the interwoven chemistries of the lanthanide and actinide elements and of understanding and employing the subtle chemical differences among the actinides themselves are some of the greatest challenges in the history of chemistry. Bob Penneman's unrivaled ability to unravel this tangled skein of chemical yarn contributed hugely to weaving the fabric of the present-day nuclear fuel cycle industry and distinguished Bob, setting him apart from other workers in his field.

Bob Penneman's long and highly productive career at Los Alamos National Laboratory helped to establish the Laboratory's world class preeminence in the field of transuranium element chemistry that persists to this day. Many of Bob's coworkers whom he trained and directed went on to become leaders in the transuranium element chemistry field in their own right. In this way he lives on and continues to make valuable contributions.

We in the United States are indeed fortunate to have such gifted and productive scientists as Bob Penneman among us. I am sure he would have blushed to read such a tribute and would have made a characteristic and humorous self-effacing comment belittling his many important contributions.

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**Academician Boris F. Myasoedov,**

*Chairman of the Chemical Branch of  
the Division of Chemistry and Material  
Sciences of the Russian Academy of Sciences,  
Head of the Interdisciplinary Council on  
Radiochemistry of the Presidium of the  
Russian Academy of Sciences and the State  
Corporation "Rosatom."*

Bob Penneman was one of those who made the first “wet” chemical experiments with weighable quantities of americium and curium, which were earlier discovered at the University of California, Berkeley, by Glenn T. Seaborg, Leon O. Morgan, Ralph A. James, and Albert Ghiorso. In 1960 Bob and Thomas Keenan published a book, *The Radiochemistry of Americium and Curium*, that has been translated into many languages, including Russian. This book became a handbook for many radiochemists in Russia, including research institutes and universities. I remember this time well. In 1969–1972 I was working on my doctoral dissertation at the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the USSR. My work dealt with the development of novel effective separation and extraction methods for actinides using their redox transformations. This task was quite challenging and required methods to stabilize americium in oxidation state +4 and +6. The successful solution came only after study of the properties of Am, as described in the book by Penneman and Keenan. By using new substances that form stable Am complexes in acidic solutions, we developed simple and effective sorption



Attendees at the September 1972 symposium on the Chemistry of Transplutonium Elements in Moscow included G.T. Seaborg (sitting in the first row, fourth from left), and Bob Penneman (standing fourth right from Seaborg with glasses and wearing a white jacket).

and solvent extraction separation methods that are still used today for separation of weighable quantities of Am and Cm, which otherwise have very similar chemical properties. Even today their book is recommended for undergraduate and Ph.D. students of radiochemistry at Moscow State University as one of the best books on transplutonium elements chemistry.

Bob Penneman had friendly relations with many Soviet radiochemists whom he met at various international scientific conferences, even during the years of the Cold War. Among the first Soviet radiochemists Bob met at one of Geneva Conferences on the Peaceful Use of Nuclear Energy was Dr. Georgy N. Yakovlev. At this time Georgy was the director of actinide laboratory of Kurchatov Institute of Nuclear Energy, participated in the Soviet Atomic Project, and was one of the first who studied transplutonium elements in USSR (we called him the “Soviet Penneman”). Later, Bob and Georgy met many times at various international conferences and had productive scientific discussions. We have kept the letter that Bob sent to G.N. Yakovlev and his hand-signed chapter “Structural Systematics in Actinide Fluoride Complexes” by Penneman, Ryan, and Rosenzweig in the series *Structure and Bonding*. In September 1972 Penneman visited Moscow for the first time and participated in the symposium on the Chemistry of Transplutonium Elements. This symposium was held in the Institute of Physical Chemistry of the Academy of Sciences, where the possibility of Np, Pu, and Am in the heptavalent state was discovered. Much of the discussion of the symposium participants was centered on redox reactions and various properties of simple and complex compounds of transuranium elements. This symposium attracted about 100 Soviet radiochemists and 23 radiochemists from the United States, France, and Germany. Nobel Prize winner and former AEC Chairman Glenn T. Seaborg and Bob were among the U.S. delegation. During this symposium, I met with Bob for the first time. Our next meeting was in 1981 during Actinides-81 conference in Asilomar. I was amazed by Bob’s very broad scientific knowledge, his interest in many aspects of the nuclear fuel cycle and his very sincere wish to discuss them.

Since then I met with Bob several times and exchanged letters in which we discussed new ideas and research results. His last message was a Happy New Year 2012 to me and my family.

“Bob Penneman had friendly relations with many Soviet radiochemists whom he met at various international scientific conferences even during the years of the Cold War.”

**Stepan N. Kalmykov,**

*Ph.D., Professor, Head of Radiochemistry  
Division, Department of Chemistry,  
Lomonosov Moscow State University*

Because of my age, I had no chance to meet Bob Penneman during his active scientific career, but while visiting various U.S. national laboratories and universities and discussing different aspects of actinide chemistry, I was referred to his publications many times. When I am lecturing the basic course in radiochemistry at Moscow State University, I always cite classical books by Bob Penneman in my lectures on transplutonium elements chemistry.

**Darleane Hoffman,**

*Professor Emerita of Chemistry,  
University of California, Berkeley, and  
former Division Leader,  
Isotope & Nuclear Chemistry Division,  
Los Alamos National Laboratory.*

I think I first met Bob Penneman in 1953 after I finally got my clearance transferred from Oak Ridge to Los Alamos and was able to begin work as a radiochemist in Rod Spence's Radiochemistry Group, part of the Test Division at that time. I had just missed being a codiscoverer of einsteinium (99) and fermium (100), which were discovered in debris from "Mike," the first thermonuclear device ever tested in the South Pacific. The group was still working on new isotopes of plutonium, but we had to go to another site to use alpha-pulse analyzers. As I recall, they were available in Bob's group, and we were graciously allowed to use them.

“Early in his career Bob was chosen as the only Los Alamos chemist to be a delegate to the first Atoms for Peace Conference in Geneva in 1954.”

From this time on I became aware of Bob Penneman's broad spectrum of scientific interests, which included nuclear waste treatment and storage, the chemistry of hydrazine, infrared spectroscopy of inorganic solutions, complex fluorides, structural inorganic chemistry, and, of course, his frontier research on the chemistry of plutonium, americium, and curium.

Bob has a prolific publication record and was a sought-after lecturer on both scientific and applied topics. Early in his career Bob was chosen as the only Los Alamos chemist to be a delegate to the first Atoms for Peace Conference in Geneva in 1954. This was the first international conference in which U. S. scientists were allowed to participate, and it was where he made a host of valuable international contacts. He was a Round Table discussion leader at the 1969 Welch Conference on The Transuranium Elements—the Mendeleev Centennial. He coauthored chapters in both the 2nd and 3rd editions of *The Chemistry of the Actinide Elements*. Concurrent with his important scientific accomplishments, Bob held numerous management positions at Los Alamos, beginning with section leader in 1947 and culminating as group leader and associate division leader. His influence both as scientist and manager will long be fondly remembered.

In 1983, Bob and I both attended a Workshop on Opportunities and Challenges in Research with Transplutonium Elements that we helped organize. One of the results of this workshop was that we became coauthors of a March 1984

*At age 89, Bob gave a special lecture at Kirtland AFB recounting his work on the Manhattan Project and the development of the first nuclear weapons in the early 1940s.*



*Physics Today* article entitled, “Accomplishments and promise of transplutonium research” by Keller, Hoffman, Penneman, and Choppin.

During this 1983 workshop in Washington, D.C., Bob “smuggled” Dr. Trish Baisden and me into the Cosmos Club (Bob was a member, but at that time the policy was “no women allowed”). Then he handed me a martini, which I didn’t dare drink as I didn’t drink much of anything in those days, let alone martinis! He then asked if I would kindly hold his martini for him, proceeded to take out his camera, and quickly took a photo of me as a “two-fisted drinker” with a martini in each hand!! I was greatly embarrassed and don’t know whatever became of that photo, but he teased me about it for years and threatened to show it. I never saw the photo, and I suspect Bob had no intent to ever show the photo, but he continued to enjoy my reaction to it.



*Cosmos Club (NO WOMEN ALLOWED), Washington, D.C., dinner for organizers of the Transplutonium Workshop, February 27, 1983. Pictured here (l. to r.) are Gregory Choppin, Penneman, Darleane Hoffman, Trish Baisden, and Walter Herrmann.*

In addition to conducting early frontier fundamental chemical research to elucidate the chemistry of Pu, Am, and Cm chemistry, Penneman’s group also spawned many practical applications—one example being the ICONS (isotopes of carbon, oxygen, and nitrogen) program that used distillation to separate the stable isotopes of these elements for use in a broad array of R&D efforts in the United States.

Not one to rest on past laurels, Bob became an adjunct professor and teacher after his formal retirement. He received the prestigious Glenn T. Seaborg Actinide Separations Award in 1995 when he was 76. His last scientific paper (relevant to safe storage of plutonium) was published in the *Journal of Solid State Chemistry* in 2005 when he was 86!

Even more impressive is that at age 89 Bob gave a special lecture at Kirtland AFB recounting his work on the Manhattan Project and the development of the first nuclear weapons in the early 1940’s! He is one of those wonderful people whom I expected to be “always with us,” and it was a great shock to learn of his passing.

It is, indeed, my honor to be able to pay tribute to Robert A. Penneman (Bob) as a friend, colleague, eminent scientist, and communicator whose legendary sense of humor brightened so many of our days and helped us all keep life in perspective.

***“Let’s offer a toast to Robert A. Penneman—and, Bob,  
don’t ask me to hold your drink!”***

**“The Age of Space is perhaps the most exciting time in human history since the Age of Discovery that followed Columbus' voyage. What intuitive inspiration was Queen Isabella's when she offered to pawn the crown jewels to finance the poor mariner's voyage! We have no visions of gold and the riches of the Indies before us; but we have learned long since that there are things more valuable than gold.”**

- Glenn Seaborg, 1961

