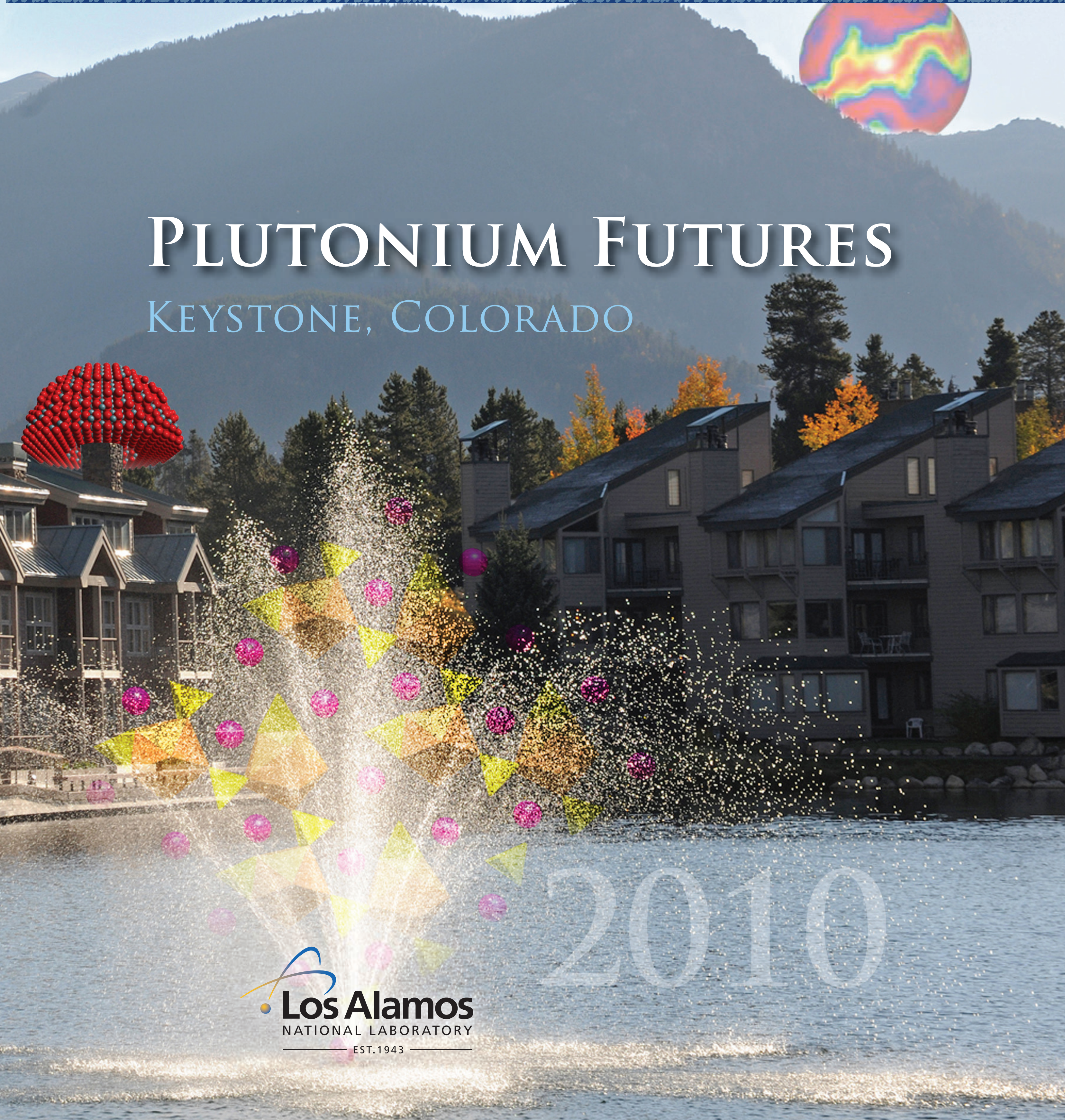
ACTINIDE RESEARCH QUARTERLY

LOS ALAMOS NATIONAL LABORATORY
NUMBER 2 · OCTOBER 2011



PLUTONIUM FUTURES

KEYSTONE, COLORADO

2010

Los Alamos
NATIONAL LABORATORY
EST. 1943

Actinide Research Quarterly

Plutonium Futures 2010

Introduction

This issue of *Actinide Research Quarterly* is devoted to coverage of the sixth Plutonium Futures—The Science conference, which was held in Keystone, Colorado, September 19–23, 2010. Plutonium Futures is a series of international conferences that provide a forum for presenting and discussing current research on the physical and chemical properties of plutonium and other actinide elements.

Los Alamos National Laboratory initiated the conference series in 1997 to enhance the international dialogue among scientists on plutonium's fundamental properties and their technological consequences. The conferences are intended to recapture the spirit of cooperation that was originally established in the "Plutonium" conferences that started in 1960 following President Dwight Eisenhower's "Atoms for Peace" speech to the United Nations.

Plutonium Futures—The Science 2010 provided attendees the opportunity to examine present knowledge of the chemical and physical properties of plutonium and other actinides in complex media and materials, to discuss the current and emerging science of plutonium and other actinides relevant to enhancing nuclear security in an era of global expansion of nuclear power, and to exchange new ideas and techniques.

The scope of the conference ranged from the complexities of condensed-matter physics in plutonium to important practical issues such as trace detection of plutonium particles in the environment. "In bringing together people from this diverse range of disciplines, the conference aims to address the current and emerging challenges of plutonium and actinide materials science," Carl Beard of Los Alamos told the audience in his opening remarks.

"The study of plutonium is a 21st century grand challenge for chemists, materials scientists, and solid-state physicists. We hope that this conference series will stimulate the next generation of scientists and students to study the fundamental properties of plutonium," Beard concluded.

The 2010 conference was co-sponsored by the Los Alamos and Lawrence Livermore national laboratories and the American Nuclear Society. It attracted 235 registrants from thirteen countries and included ninety-nine talks (ninety of them about plutonium) and two evenings of poster sessions. Previous conferences were held in Santa Fe, New Mexico, in 1997 and 2000; Albuquerque, New Mexico, in 2003; Pacific Grove, California, in 2006; and Dijon, France, in 2008. Plutonium Futures 2012 will be held July 15–20 in Cambridge, United Kingdom. (See page 52 for more information.)

Carl Beard of Los Alamos welcomed participants to Plutonium Futures 2010. At the time of the conference Beard was associate director for Plutonium Science and Manufacturing; he is now principal associate director for Operations.

David Hobart (left), Gordon Jarvinen (center), and David Clark of Los Alamos go over last-minute business before Monday morning's opening session. Hobart was program co-chair; Jarvinen and Clark were general co-chairs.

Keystone, Colorado, provided attendees with a beautiful venue.

TUTORIAL

PLUTONIUM—THE SCIENCE AND THE POLITICS

Editor's note: In keeping with tradition, the 2010 Plutonium Futures conference kicked off with a Sunday afternoon tutorial designed for students and scientists interested in looking a bit outside their particular field of expertise. This section of *Actinide Research Quarterly* highlights A. David Rossin's talk on the politics and socioeconomics of plutonium and provides brief overviews of the other three talks: Nik Kaltsoyannis's on heavy-element electronic structure, Brian Boyer's on international safeguards efforts, and Gordon Jarvinen's on nuclear fuel cycles.

A. David Rossin's career spans more than five decades, beginning at Argonne National Laboratory in 1955. His résumé includes service as Department of Energy assistant secretary for nuclear energy, president of the American Nuclear Society, director of the Nuclear Safety Analysis Center at the Electric Power Research Institute, director of research and chair of the Nuclear Waste Task Force for the Commonwealth Edison Company, visiting scientist at the University of California Berkeley, and Center Affiliated Scholar at Stanford University's Center for International Security and Cooperation. Rossin currently is writing a book about the policy decisions that led the United States to abandon the reprocessing of spent nuclear fuel.

INTENDED CONSEQUENCES OF PRESIDENT CARTER'S COMPREHENSIVE POLICY TO STOP PROLIFERATION

In 1977 Jimmy Carter made a decision that changed the history of nuclear power and undermined the fuel cycle plans for civil nuclear power. These plans had been authorized over and over by Congress and supported by all presidents since Eisenhower. That decision has a lot to do with some of the things that people attending the Plutonium Futures conference are working on today.

On April 7 of that year, Carter announced that the United States would "defer indefinitely the reprocessing of spent nuclear fuel" and the separation of plutonium for recycling it into new fuel. Doing so ourselves, he said, would "set an example for other nations to do the same." As history shows us, the United States did stop, but its actions didn't influence other nations to abandon their programs and plans. U.S. activists who promoted the Carter policy seized on it as a triumph.

Carter, along with nuclear experts all around the world, was right that nuclear proliferation was a problem. Carter said that he wanted to find a comprehensive policy that would stop proliferation and earn him a place in history for his search for peace.

Some of Carter's advisors had told him that reprocessing was not economical and that the benefits were too small. Carter decided that nuclear power could go ahead without reprocessing and that there would not be an economic penalty.

He was dead wrong about both of these key points. His policy did not deter proliferation, and no more nuclear power plants were ordered in the United States. Many plants planned and under construction were cancelled at great cost. The lost generating capacity was replaced largely by using natural gas and by keeping older coal plants running. Of longer-term impact, the plans for nuclear waste disposal were derailed, and three decades later, politics has killed the program that did emerge (Yucca Mountain) and the waste issue still worries most Americans.

These critical decisions were reached without extensive investigation. There were people who had a lot to say in the public domain who influenced the president's decision, but few of these people had ever seen plutonium close up, certainly had never held a sample of shielded plutonium in their hands, and had never worked on a hot salt. So Carter's policy was shaped more by his political intentions than by people with hands-on knowledge of the technical realities and possibilities.

To put some of this into perspective, look at where we were in 1977. That's three decades after the end of World War II and two decades after President Eisenhower's "Atoms for Peace" speech to the United Nations. The Nuclear Nonproliferation Treaty had been in effect for a decade and had been ratified by more than 100 nations. The USSR, United Kingdom, France, and China were the four nuclear weapons powers at the time of the treaty signing. In May 18, 1974, India had exploded a nuclear device.

I was struck by the rapidity with which Carter's nuclear policy emerged. The announcement was made within his first 100 days in office. It had been held close even through the final editing. One of the reasons the administration was emboldened to take action was that the nuclear industry was politically weak and under fire at that time, and that was well known by the people who came in at the beginning of the Carter administration. The administration felt that it could take a major step that affected the nuclear and the energy industries—blocking reprocessing—without a lot of public understanding or political backlash.

A former Carter pollster told me that when people were polled and prompted specifically about proliferation—as in, are you concerned about proliferation?—they said yes. But if people were asked to list ten or twenty issues that really concerned them, proliferation of nuclear weapons never came up. It was off the screen unless people were prompted on it.

Carter's announcement caught the nuclear industry by surprise, and we wondered why. Didn't we see what was coming? Didn't we have any politically aware people? Didn't Carter tip his hand during his campaign speeches? Actually, he did, but only a bit. In May 1976 he gave a speech in New York and said he was worried about proliferation and reprocessing. He gave another speech in San Diego in September 1976 in which he tipped his hand a little more, but never on the campaign trail did he ever actually call for stopping reprocessing.

I find it amazing how much the written word and published material impact political activities. (As you can see, it's much worse today than it was back then because now you've got all the blogs in the world getting into the act.)

In early 1977 Carter was given a copy of a report titled "Nuclear Policy: Issues and Choices," also known as the Ford–MITRE Report. The study discussed in the report was conducted over two years by a team of scientists, academics, and statesmen, four of whom had won Nobel Prizes. It was funded by a grant from the Ford Foundation and managed by Spurgeon Keeny of the MITRE Corporation (a contracting organization that grew out of the Massachusetts Institute of Technology). The work seemed scholarly; however, it was never subjected to outside review or debate. But Carter was aware of it, found that it fit his ideas, and used it to support his nuclear policy.

The original purpose of the Ford–Mitre study was to compare nuclear power with coal for producing electricity. That original purpose got lost. The study began to focus on whether the United States should proceed with reprocessing spent nuclear fuel and recycling plutonium. Keeny said in the summary, "We believe the

Faces & Places

Lester Morss (left), retired from the Department of Energy, John Gibson (center), Lawrence Berkeley National Laboratory, and Dick Haire, retired from Oak Ridge National Laboratory

Sig Hecker (left), Stanford University, and John Cardinal, Federal Bureau of Investigation

Vladimir Dremov, Russian Federal Nuclear Center–All-Russian Institute of Technical Physics consequences of proliferation are so serious compared to the limited economic benefits of nuclear energy that we would be prepared to recommend stopping nuclear power in the U.S. if we thought this would prevent further proliferation."

Carter was handed the first copy a couple of weeks before he announced his policy statement. Several of the people who worked on the report ended up in influential positions within the Carter administration.

Carter's policy statement includes these operative words: "The U.S. is deeply concerned about . . . a further spread of nuclear weapons capabilities. We believe that these risks would be vastly increased by the further spread of sensitive technologies, which entail direct access to plutonium. The question I have had under review since my first day in office [is] how to reduce these risks without foregoing the tangible benefits of nuclear power. We are now completing an extremely thorough review of all the issues that bear on nuclear power."

There was, in fact, one interagency review, but it's not clear that the results of that review ever reached Carter. The Energy Research and Development Administration (the predecessor to the Department of Energy) and the State Department had different views. But what Carter saw was mostly jelled from the Department of Defense, the Arms Control and Disarmament Agency, and his National Security Council, which sifted through everything and then prepared a one-page Decision Memo for the President.

In truth, Carter had made up his mind several months before the election that he wanted the United States to stop reprocessing and that he would make it his policy if he got elected. He was looking for a way to justify it—one that was politically feasible—and the Ford–MITRE Report gave him a very good published basis to hang his hat on. It came out just in time! Keeny's intention was to get the report to Carter before he made a final decision on the subject.

Carter's policy was an Executive Order, and Executive Orders have the force of law. It was a policy statement that had never been voted on in Congress. Nor did it have an Environmental Impact Statement, as all major government actions must have.

The Reagan administration, which followed Carter's, had a different view on the subject of reprocessing. Reagan's deputy secretary of energy, Ken Davis, who had worked for the Atomic Energy Commission and Bechtel, got enough backing to convince Reagan to enact his own Executive Order that rescinded Carter's policy statement.

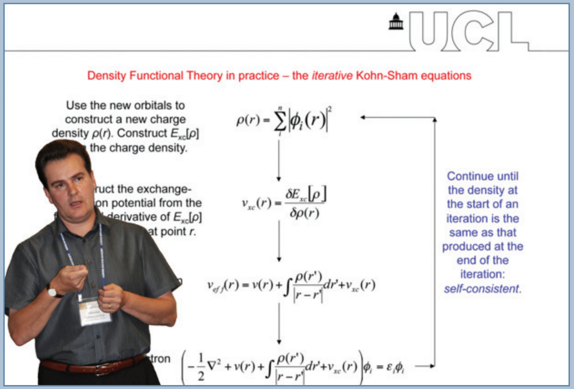
The problem is that by then all the industrial momentum was gone. The trust that was necessary for industry and government to work together on long, complex projects was gone. The confidence of the financial community to provide long-term capital investment in anything nuclear was gone, too, because it had seen that nuclear enterprises could be abruptly overturned politically. One of our problems as an industry was that we were politically naïve about a new president. We were out in our own states negotiating with public utilities commissions about rates. Our top executives were very astute about that, but we didn't know enough about politics at the national level. And we did not know Jimmy Carter. His policy radically derailed a vital and once-promising energy industry.

FACES & PLACES

Victor Pushkov (left) and Boris Nadykto, both Russian Federal Nuclear Center–All-Russian Scientific Research Institute of Experimental Physics

Vijay Manchanda, Bhabha Atomic Research Center, India, and Punam Thakur, New Mexico State University

ELECTRONIC STRUCTURE THEORY FOR HEAVY ELEMENTS: PRINCIPLES AND APPLICATIONS OF DENSITY FUNCTIONAL THEORY



Density Functional Theory in practice – the *iterative* Kohn-Sham equations

Use the new orbitals to construct a new charge density $\rho(r)$. Construct $E_{xc}[\rho]$ … the charge density.

…ruct the exchange-…on potential from the …derivative of $E_{xc}[\rho]$ …at point r.

…tron

$$\rho(r) = \sum_{i}^{n} |\phi_i(r)|^2$$

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$

$$v_{eff}(r) = v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}(r)$$

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}(r)\right)\phi_i = \varepsilon_i \phi_i$$

Continue until the density at the start of an iteration is the same as that produced at the end of the iteration: *self-consistent.*

Nik Kaltsoyannis is a molecular computational chemist in the Department of Chemistry at University College London. His research areas include electronic and geometric structure, transition metals and f-elements, density functional and ab initio theory, and relativistic effects. He received his Ph.D. in 1992 from the University of Oxford and joined University College London in 1994. His research group collaborates with several experimental groups, including Los Alamos National Laboratory and the universities of Oxford, Edinburgh, and Glamorgan.

Nik Kaltsoyannis treated the audience to something a bit different from the other tutorial speakers. Instead of an overview, he drilled down to one particular area of heavy element science with a particular focus on plutonium: the electronic structure theory for heavy elements. In the majority of cases, according to Kaltsoyannis, that means density functional theory (DFT) because in practice that is the tool that is most widely used by computational scientists to study the electronic structure of actinide solids and also molecules.

He began by trying to answer the question, what is density functional theory? While DFT traces its origins back to the 1930s and the work of Enrico Fermi and Paul Dirac, it was born out of solid-state physics in the mid-1960s from the work of Walter Kohn and his collaborators, Lu Sham and Pierre Hohenberg, explained Kaltsoyannis. Hohenberg and Kohn told us that the ground-state charge density rho (ρ) of a system is sufficient to describe all of the ground-state properties. And with that in hand, you can write the total energy of a system:

$$E[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] + V_{\mathrm{ne}}[\rho]. \qquad (1)$$

E of rho is the sum of three terms: T of rho, the electronic kinetic energy; V_{ee} of rho, the electron interaction energy; and V_{ne} of rho, the nucleus electron interaction energy.

And shortly afterwards, Kohn and Sham suggested that this equation could be rewritten, where the total energy E of rho is now broken down not into three terms but into four:

$$E[\rho] = T_{\mathrm{non\text{-}int}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] + V_{\mathrm{ne}}[\rho]. \qquad (2)$$

The fourth term, V_{ne} of rho, is the same as it was before the nucleus electron term. Three new terms are now used: $T_{non\text{-}int}$ of rho, the electronic kinetic energy of a fictitious system in which the electrons don't interact with one another; J of rho, the classical Coulomb electron–electron repulsion energy; and E_{xc} of rho, the electronic exchange correlation energy. This contains the difference between the kinetic energy of the real system of interacting electrons and the fictitious system of non-interacting electrons and also the non-Coulombic part of the electron–electron interaction of energy.

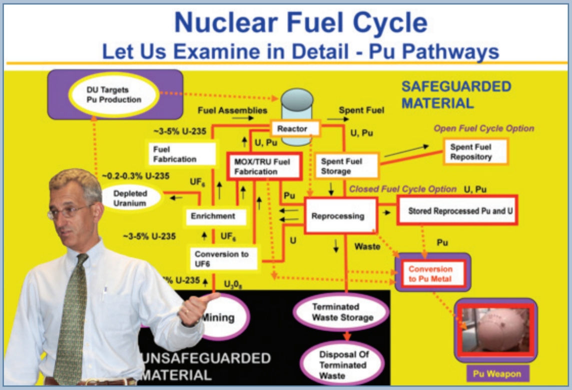
What is the point of rewriting Equation (1) as Equation (2)? The answer, according to Kaltsoyannis, is that three of those four terms—the kinetic energy of the fictitious system, the Coulomb term, and the nucleus-electron interaction energy—can be calculated exactly. So in principle, if we knew the exact form of the exchange correlation energy for a given charge density, we could calculate an exact energy.

"But there is a catch; there's always a catch," said Kaltsoyannis. "Although in principle the Kohn-Sham equations are exact, they are exact only if we know the exact form of the exchange correlation energy, but nobody knows the exact form of the exchange correlation energy." However, there are many approximate forms, and there are lots of people around the world developing ever more complicated and clever forms of the exchange correlation energy.

"And, in fact," said Kaltsoyannis, "when you read in the literature about different flavors of density functional theory, all the acronyms that surround it, both in the physics literature and the chemistry literature, that's really where they differ. They differ in the mathematical form of the exchange correlation energy."

Kaltsoyannis continued his tutorial with a discussion of the consequences of relativity for electronic structure and how to deal with those consequences using density functional methods. He concluded with examples of the applications of DFT to problems in plutonium science.

THE CHALLENGES OF INTERNATIONAL SAFEGUARD EFFORTS TO VERIFY THE PEACEFUL USES OF PLUTONIUM



Brian Boyer of Los Alamos National Laboratory received his Ph.D. in nuclear engineering from Penn State University. He worked at Brookhaven National Laboratory on reactor safety from 1992 to 1996, was an inspector for the International Atomic Energy Agency (IAEA) for five years, and then returned to Brookhaven to work on international safeguards. Boyer joined Los Alamos in 2006 and is currently project leader for international safeguards in the Safeguards and Security Systems Group (N-4) of the Nuclear Nonproliferation Division. His talk focused on international safeguard aspects of plutonium.

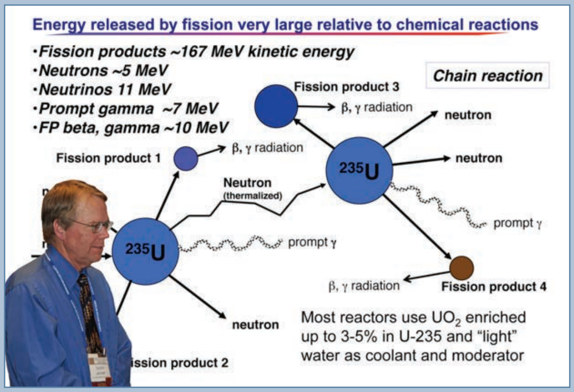
Brian Boyer began his portion of the tutorial by defining safeguards as interpreted by the IAEA: "The objective of safeguards is the *timely* detection of *diversion of significant quantities of nuclear material* from peaceful nuclear activities to the manufacture of nuclear weapons or of other nuclear explosive devices or for purposes unknown, and *deterrence of such diversion by the risk of early detection*."

He explained that the basis of traditional safeguards systems was the state declaration, in which the state made a declaration of the amounts of and usage of nuclear materials in its borders and the IAEA verified it. This came out of a principle of independent verification and was a marriage of principles and practices borrowed from property accounting, statistical quality control, and financial accounts auditing. Strengthened safeguards systems make use of additional protocol and complementary access to sites in a state, emphasis on information-based safeguards, and increased transparency in a state's nuclear activities. The inspector became more of an investigator and less of an accountant, which made the job more interesting, but harder, according to Boyer.

Boyer described four broad safeguards concerns in the fuel cycle for plutonium: the fuel-to-reactor path, the transport-from-reactor path, the reprocessing path, and use of mixed oxide (MOX) fuel. "In looking at reactors," he said, "you must make sure there is no unreported plutonium production and verify the integrity of spent fuel and its final disposal. In reprocessing, you have to be able to follow that plutonium through the process. And in MOX fuel fabrication, you have to monitor the integrity of that final MOX assembly."

Boyer concluded that controlling the source material is of key importance in safeguarding plutonium in the fuel cycle: "The biggest part of an IAEA inspector's job in relation to safeguards and reactors is to make sure that the integrity of the material doesn't get tampered with, because if it gets tampered with, then you worry that they could be going to clandestine reprocessing."

NUCLEAR FUEL CYCLES



Energy released by fission very large relative to chemical reactions

- Fission products ~167 MeV kinetic energy
- Neutrons ~5 MeV
- Neutrinos 11 MeV
- Prompt gamma ~7 MeV
- FP beta, gamma ~10 MeV

Most reactors use UO_2 enriched up to 3-5% in U-235 and "light" water as coolant and moderator

Gordon Jarvinen served as general co-chair of the Plutonium Futures conference. He received his Ph.D. in inorganic chemistry from the University of California, Los Angeles and came to Los Alamos National Laboratory as a postdoctoral fellow in 1979. He has been a member of the technical staff at Los Alamos since 1981 and currently is associate director of the Seaborg Institute. In that position he serves as scientific advisor to Actinide Research Quarterly. *He specializes in separation science for the the actinides and lanthanides and also is involved in the study of nuclear fuel cycles, the topic of his tutorial.*

Gordon Jarvinen opened with an overview of the fission process and the composition of used or "spent" fuel from light-water reactors, which are the primary nuclear power sources around the world today. He discussed the reasons for reprocessing and the pros and cons of a once-through, or "open" cycle, versus a "closed" cycle, with recycle of the actinides. He then turned to PUREX, the extraction process that is the predominant technology used to recover uranium and plutonium from used fuel. He discussed how most of the current work worldwide focuses on improvements to PUREX and other liquid–liquid extraction processes to further partition the used fuel or allow more-efficient disposition of the fission products.

Jarvinen gave what he called a "whirlwind overview" of separation schemes for advanced nuclear fuel cycles under consideration. In reviewing such schemes, for example, fluoride volatility, pyrochemical methods, ionic liquids, supercritical fluids, and alkaline aqueous solutions, he stressed that very few have gone beyond the exploratory scale. He also discussed the six Generation IV International Forum nuclear energy systems identified for further development, along with concepts like dispersion fuel structures, which could simplify separations for recycling the actinides, and the TerraPower concept for a traveling-wave reactor. TerraPower's innovative concept is a pool-type, sodium-cooled fast reactor that uses a large core of depleted uranium and a "sparkplug" of enriched uranium or plutonium to start a fission/breeding "wave" in the fuel that could be deployed in a once-through or recycle system.

Jarvinen concluded by stressing that these advanced fuel cycles will require a large *integrated* effort to develop efficient alternatives for fuels, energy generation, separations, safeguards, waste forms, and repository performance. "This has often not been the case in the past; we've often studied those somewhat independently," said Jarvinen. "Fundamental data in many areas are needed, and I hope many of you in the audience will be working on these in the future and will bring them to fruition."

FACES & PLACES

Suguru Ohta, Tohoku University, Japan

Robert Lascola, Savannah River National Laboratory

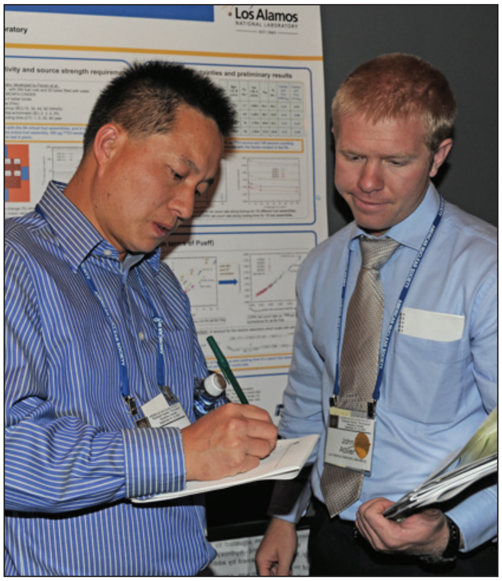
Stepan Kalmykov, Lomonosov Moscow State University, Russia

A STUDENT'S PERSPECTIVE ON PLUTONIUM FUTURES

Editor's note: John D. Auxier II attended Plutonium Futures 2010 as a student volunteer. Auxier received his bachelor of science in chemistry and mathematics from Adams State College in Alamosa, Colorado. During his undergraduate years, beginning in 2007, Auxier interned at Los Alamos National Laboratory in the Actinide Analytical Chemistry Group (C-AAC). At the suggestion of his mentor, Donivan Porterfield, Auxier attended the ACS/DOE Nuclear and Radiochemistry summer school, which solidified his interest in plutonium chemistry and related fields. Auxier currently is a graduate research assistant in C-AAC and is in his second year of studies at the University of Tennessee, Knoxville, working toward his doctorate in inorganic chemistry under Dr. George K. Schweitzer. Auxier provided *ARQ* with his impressions of the conference.

When I was invited to participate in the 2010 Plutonium Futures—The Science conference as a student volunteer, I anticipated setting up poster boards, helping with registration, or doing other tasks to ensure that the conference went smoothly. My anticipation was eclipsed by my actual experience.

I was able to attend many of the invited talks, whose topics spanned a wide range of scientific and engineering disciplines, yet focused almost solely on one subject: plutonium. I interacted and conversed as part of a group and, in some cases, individually, with renowned experts and veterans in the field of plutonium science. During the poster sessions, I met emerging experts in the plutonium field who came from a wide span of scientific disciplines and backgrounds.



John Auxier (right) and Jianwei Hu, a research assistant at Los Alamos National Laboratory, discuss Hu's poster on "Quantifying fissile content in spent fuel assemblies using the ^{252}Cf interrogation prompt neutron (CIPN) technique." Hu co-authored the poster along with Stephen Tobin and Stephen Croft of the Nuclear Nonproliferation Division.

Plutonium Futures 2010 opened with a tutorial that set the stage for the rest of the conference. This session blended theoretical science, typified by Nik Kaltsoyannis's discussion of electronic structures in heavy elements, with applied science, as discussed by Gordon Jarvinen in his talk on the nuclear fuel cycle. The tutorial also included a discussion by

Brian Boyer on the nonproliferation of nuclear material and efforts to safeguard plutonium and touched on politics with David Rossin's talk on how the policies set by the Carter administration have affected the nuclear energy industry. (See article beginning on page 2.)

While it is common for conference speakers to address the theoretical and applied areas of a scientific field, from my perspective this conference was unique in that the politics surrounding plutonium were discussed in almost as much detail as the science itself. This focus brought me new insight into how the world political environment impacts science. Examples include Rossin's tutorial and the roundtable discussion with representatives of France, India, Russia, and the United States. The global roundtable allowed speakers with varied backgrounds to present their countries' respective approaches to meeting the growing energy need with the use of nuclear energy.

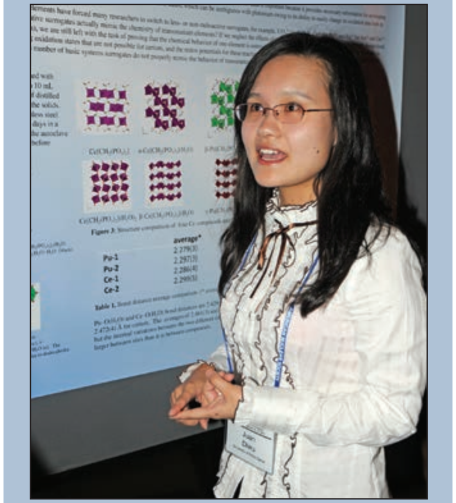
Particularly interesting to me was the overwhelming international participation in the conference. Students had the opportunity to learn about different career choices and about the high standards to which international scientists are expected to work. It was a great opportunity for me to meet distinguished scientists from around the world, including Dr. Vijay Manchanda of India, who was especially interested in expanding his knowledge of fuel cycles, and Dr. Lester Morss of the United States and Dr. Jean Fuger of Belgium, who announced the publication of the sixth volume of *The Chemistry of Actinide and Transactinide Elements*.

Drs. Morss and Fuger took time to discuss with me their interest in the field of plutonium science, their academic paths, and the unique series of events that led them to their current stations—and they were not alone. Many participants shared their backgrounds, which lent a sense of community to the conference, as senior scientists encouraged and delighted in the success of their eventual successors. These conversations created pathways for students to make contacts with experienced individuals who could assist them in future research—and identify potential job opportunities!

On the final evening of the conference, author Richard Rhodes delivered an excellent banquet speech that encouraged attendees to continue developing new technologies and expanding international cooperation to provide a unified, but diverse, approach to delivering safe, clean energy to the world's growing population. His talk became a rallying cry—not just to those currently in the field but also to future scientists—to develop a source of reliable energy while eliminating the threat of proliferation. In short, it presented a vision and an unspoken challenge for today's students to become tomorrow's leaders.

FACES & PLACES

Ken Czerwinski, University of Nevada–Las Vegas



Juan Diwu, University of Notre Dame

Ruth Tinnacher, Lawrence Livermore National Laboratory, and Doug Farr, Los Alamos National Laboratory

David Pugmire

NEW INSIGHTS INTO THE OXIDATION OF PLUTONIUM AT ROOM TEMPERATURE

This article was contributed by David Pugmire and Harry Garcia Flores, Los Alamos National Laboratory and Department of Chemistry, University of Nebraska–Lincoln, United States; David Moore and Amanda Broach, Los Alamos National Laboratory, United States; and Paul Roussel, Atomic Weapons Establishment, Aldermaston, United Kingdom.

An understanding of the oxidation and corrosion processes of plutonium metal at room temperature is important for the safe, effective use and storage of this reactive metal. It was observed in early studies that plutonium oxidizes at a nearly imperceptible rate in dry air at room temperature and that this rate is greatly increased by the presence of moisture. For these reasons, much of the historical work on plutonium (Pu) oxidation/corrosion has been performed at elevated temperatures (above 75 degrees Celsius [°C]) with some amount of water present in the oxidizing atmosphere, thereby increasing the reaction rates to allow for observable changes in oxide-film thickness.

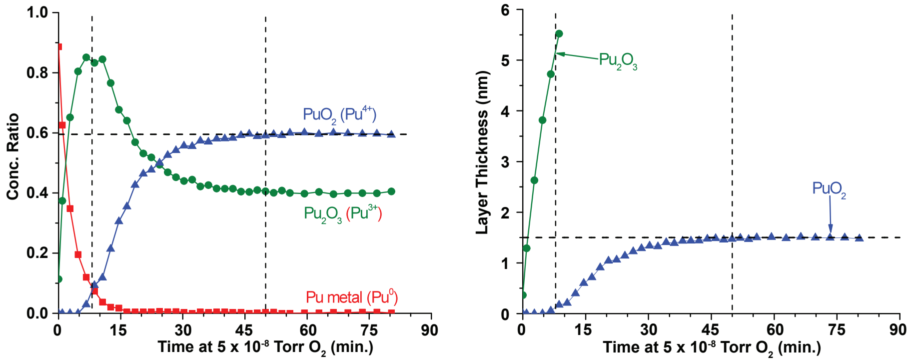
The majority of this early work on the oxidation/corrosion of plutonium was performed with mass gain measurements, generally limiting the relevance of available oxidation data to thick oxide films (greater than 50 nanometers [nm], based on the weight-change limits of detection). It was generally accepted that the relatively thick oxide film formed during these early studies consisted entirely of the dioxide species, PuO_2. Later, based on thermodynamic considerations, it was argued that a very thin film of the sesquioxide species, Pu_2O_3, must be present at the oxide/metal interface, despite the fact that it was not observed at room temperature.

An oxide film 10–20 nm thick typically develops on the surface of a piece of plutonium metal for which care has been taken to limit corrosion (i.e., stored at room temperature in a dry environment). Such conditions are used for surplus plutonium and weapons stored in the U.S. nuclear stockpile, thus understanding the oxide film characteristics and the oxidation process for these thin films is very important. The 10–20 nm thickness is significantly less than the 50 nm limit of detection for the early mass-gain measurements on oxidation, so those measurements are not entirely relevant to an understanding of the thin-film regime.

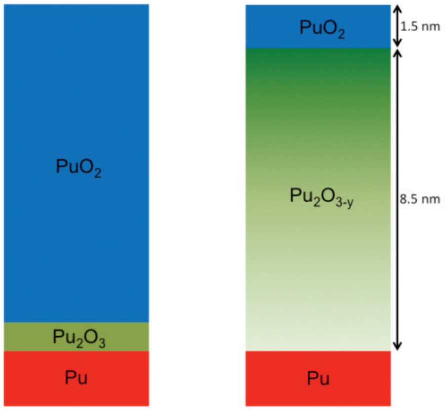
The vast majority of the work in the literature was performed at elevated temperatures, often with the presence of trace amounts of water, even for “dry air” experiments. There is clearly a change in the mechanism and/or kinetics of oxidation between room temperature and elevated temperatures as well as with the presence or absence of water, making the historical data even less relevant to an understanding of plutonium oxide thin films. Additionally, it is not entirely clear how the presence of water alters the mechanism and kinetics of plutonium oxidation at room temperature, particularly in the thin-film regime. The clearest conclusion to be drawn from a survey of the historical literature is that, while much is known about the latter stages of plutonium oxidation/corrosion at elevated temperatures, very little is known about the initial, thin-film stages of oxidation/corrosion at room temperature.

To better understand the initial stages of the oxidation/corrosion process of plutonium at room temperature, we have studied the reaction of clean plutonium metal with pure oxygen (O_2) under the controlled conditions of an ultra-high-vacuum system. Surface-sensitive techniques were employed to monitor the elemental/chemical constituents of the plutonium's near-surface region during and after exposure to oxygen. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used to determine relative concentrations of plutonium and oxygen species.

With AES, it is possible to measure the relative atomic concentration ratios of oxygen and plutonium in the top 3 nm of the exposed plutonium oxide surface. Argon ion (Ar^+) sputter etching was used in conjunction with AES to perform depth profiles (concentrations vs depth) through oxide films by repeated cycles of AES analysis and sputter etching. XPS has a deeper probe depth of 5–6 nm, and in addition to elemental concentration ratios, it can give relative concentrations of different species of plutonium (Pu^0 as metal, Pu^{3+} as sesquioxide [Pu_2O_3], and Pu^{4+} as dioxide [PuO_2]).

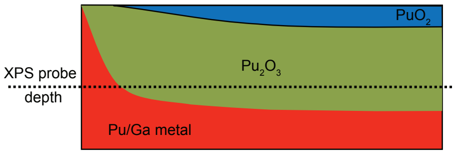


Analysis of XPS data collected during the exposure of a plutonium metal sample to very low oxygen pressures shows an initial rapid increase in the Pu^{3+} signal and concomitant decrease in the Pu^0 signal as a sesquioxide layer grows. Eventually, the Pu^0 concentration reaches zero, implying that the oxide film has reached a thickness greater than the 6 nm probe depth of XPS. As the oxygen exposure is continued, the signal due to Pu^{3+} begins to decrease with the appearance of the Pu^{4+} species, indicating that the relative concentration of the sesquioxide species is decreasing within the XPS analysis depth. This is due to the conversion of the Pu_2O_3 at the surface to a PuO_2 overlayer, which eventually reaches a maximum thickness of approximately 1.5 nm. While the oxygen overpressure affects the time required for the dioxide layer to the reach this thickness, no growth beyond this

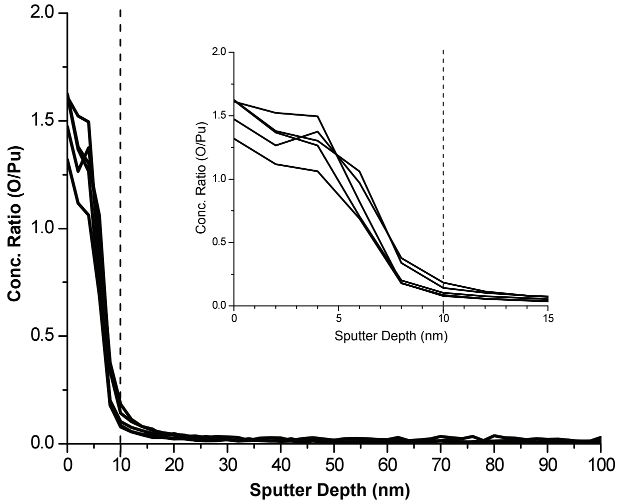


Comparison of schematic representations of thin plutonium oxide film surmised from historical data (left) with thin film as determined from data collected in our laboratory (right). The representation derived from historical data shows an oxide film consisting of mostly PuO_2 with, perhaps, a very thin Pu_2O_3 layer at the oxide/metal interface. The representation derived from the present studies shows a film consisting of a very thin PuO_2 overlayer with a thicker Pu_2O_{3-y} layer.

Far left: Relative concentrations of plutonium species as determined from Pu 4f XPS data during the oxidation of plutonium metal at 5×10^{-8} Torr oxygen: Pu^0 (red squares), Pu^{3+} (green circles), and Pu^{4+} (blue triangles). Left: Estimated layer thicknesses from concentration ratios determined from XPS data: Pu_2O_3 (green circles) and PuO_2 (blue triangles).



Schematic representation of the oxide film growth during plutonium oxidation as observed with XPS. The data indicate that Pu_2O_3 is the initial product of the reaction of oxygen with a plutonium metal substrate. This layer grows thicker, with eventual growth of a PuO_2 overlayer, as oxygen exposure is continued. The PuO_2 overlayer appears to reach a maximum thickness of 1.5 nm.



AES depth profiles (oxygen/plutonium concentrations vs sputter depth into sample surface) of a number of oxide films grown by exposing a plutonium metal substrate to a range of oxygen pressures for various times (1 × 10^{-8} to 1 × 10^{-6} Torr for 5 to 90 minutes). The inset consists of the same data sets expanded to show the first 15 nm of the depth profiles. The data show similar oxide film thicknesses (approximately 10 nm) regardless of oxygen exposure pressures and times. This indicates that plutonium rapidly forms a protective oxide layer upon exposure to oxygen at low pressures, halting the oxidation process.

thickness is observed, regardless of exposure time or pressure. This is a possible indication that the sample has stopped oxidizing, as an increase in the total oxide thickness would be expected to result in an increase in the PuO_2 overlayer thickness. However, because the thickness of the total oxide film is already greater than what can be probed with XPS, this cannot be conclusively determined from these data.

While the probe depth of AES is even less than that of XPS, when it is used for depth profiling, it is ideal for determining the approximate total oxide-film thickness on plutonium samples by monitoring the oxygen-to-plutonium relative concentration ratio while sputter etching through the film. A variety of oxide films grown by exposing a clean plutonium-metal substrate to a range of oxygen pressures for different times shows very similar thicknesses. Regardless of the oxygen exposure, the total oxide-film thickness is observed with AES depth profiling to be approximately 10 nm. These results indicate that after reaching this thickness, no further oxidation occurs, which is very similar to what was concluded from the studies of the thin PuO_2 overlayer with XPS.

Preliminary studies of plutonium-metal exposure to atmospheric conditions at room temperature show similar results. Oxidation of plutonium by dry air for 10 minutes yields a thin oxide film (total thickness approximately 10 nm) with a 1.5 nm thick dioxide overlayer. Only exposing plutonium metal to wet laboratory air results in observably thicker oxide films with thicker dioxide overlayers. These results highlight the importance of understanding the role of water during the atmospheric corrosion of plutonium.

The results obtained in our laboratory and discussed here indicate that low-pressure oxygen exposure of plutonium results in rapid growth of a thin oxide film that protects against further oxidation. This conclusion is in agreement with even the earliest observations that plutonium metal is relatively inert to dry air. The oxide films grown under these conditions are approximately 10 nm thick, consisting of an outermost PuO_2 layer 1.5 nm thick, with the remaining thickness of the film being composed of a plutonium sesquioxide-like (Pu_2O_{3-y}) layer. We first discussed a substoichiometric sesquioxide layer in a paper titled "Characterization and stability of thin oxide films on plutonium surfaces," published in *Surface Science* in February 2011. This plutonium/oxygen thin-film description is significantly different from what can be surmised from historical data and will lead to new thinking about the surface chemistry of the oxide/plutonium system.

Further reading:

"Corrosion and Oxidation," J. T. Waber. *Plutonium Handbook,* Chapter 6; O. J. Wick, editor; American Nuclear Society; La Grange Park, Illinois; 1980.

"Surface and Corrosion Chemistry of Plutonium," J. M. Haschke et al. *Los Alamos Science 20,* 2000.

ONE-STOP PREVENTION: THE FBI WEAPONS OF MASS DESTRUCTION DIRECTORATE


John Cardinal

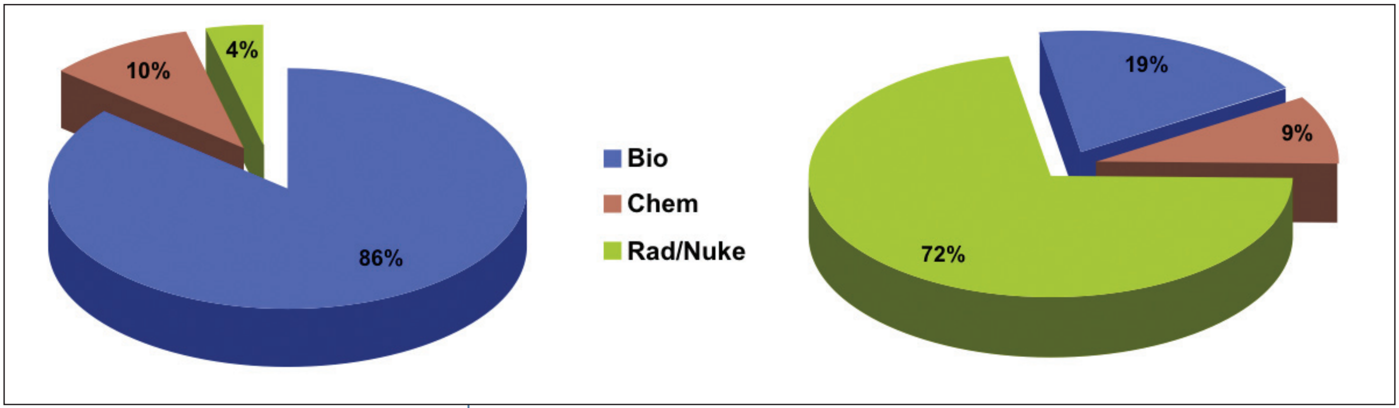
This article was contributed by John K. Cardinal, unit chief for Counterproliferation Operations, Weapons of Mass Destruction Directorate, Federal Bureau of Investigation (FBI), United States. Any opinions expressed in this article are those of the author and not the FBI.

Following the terrorist attacks of September 11, 2001, it was clear that the Intelligence Community and its member agencies needed to reorganize and retool to deal with the post–Cold War threats. The 9/11 Commission report of 2004 found that the FBI needed to reorganize its counterterrorism and counterintelligence functions to meet the next threat, rather than prepare to fight the last war. The Weapons of Mass Destruction (WMD) Commission reiterated these points in 2005 and stated bluntly that the FBI needed to be brought all the way into the Intelligence Community.

As a response to these calls, the FBI created the Weapons of Mass Destruction Directorate within its National Security Branch. Simply put, the WMD Directorate is the hub for all WMD investigations, analysis, prevention, and intelligence production conducted by the FBI. The WMD Directorate was created out of a nucleus of existing units from the Counterterrorism and Counterintelligence Divisions. Over the past five years, the WMD Directorate has grown from its humble origins to an operational FBI division with a well-trained cadre of agents and analysts assigned full-time at FBI headquarters and across the United States. All these personnel work toward a common goal: the elimination of the illicit use of WMD.

The FBI headquarters component of the WMD Directorate is further broken down into the Intelligence and Analysis Section, the Countermeasures and Preparedness Section, and the Investigations and Operations Section. Experienced FBI analysts and program managers as well as detailees from other Intelligence Community entities staff the Intelligence and Analysis Section. The goal of the Intelligence and Analysis Section is to review cases and threat-stream information and produce intelligence products that are timely and relevant to FBI management, the law enforcement community in general, the Intelligence Community, and senior decision-makers in the U.S. government.

The Countermeasures and Preparedness Section works to both educate the FBI workforce on the basics of WMD and to develop and implement countermeasures and tripwires that will either prevent WMD events from taking place or provide warning of them in the pre-execution phase. WMD awareness training starts with new agents and analysts training and culminates in a WMD career path specialty with a certification process. Additionally, the Countermeasures and Preparedness Section expends significant amounts of resources on WMD Directorate countermeasures and prevention.



WMD modality by percentage of criminal and terrorist WMD threats (fiscal year 2010) is shown on the left. WMD modality by percentage of FBI WMD proliferation cases (fiscal year 2010) is shown on the right.

It is worth noting that the cost of mitigating and investigating a single major WMD incident would be enormous, thus justifying the significant resource allocation toward prevention measures. For example, the cost of cleaning the anthrax-contaminated buildings from the 2001 attack was estimated to exceed $1 billion. Aggressive and proactive countermeasures can be conducted with a minute fraction of this budget and will ultimately save money and lives. As a consequence of the FBI's outreach program, there have been many instances in which various corporations contacted law enforcement (including the FBI) to report sales inquiries that didn't seem quite right, including cases of individuals likely attempting to obtain exotic toxins to commit murder.

The WMD Directorate has the capability to draw upon the expertise of other components and capabilities within the FBI. For instance, a response to a threat situation may be tailored to include specialized tactical capability such as Special Weapons and Tactics operators, behavioral analysts/profilers, and hazardous-devices response specialists and bomb technicians. The WMD Directorate also calls upon the expertise of the FBI Laboratory, including the Hazardous Materials Response Teams; the Hazardous Materials Sciences Response Unit; the Hazardous Materials Operations Unit; and the Chemical, Biological, Radiological, and Nuclear Sciences Unit.

The forensic exploitation of WMD evidence presents some specialized challenges to law enforcement agencies. The FBI Laboratory in Quantico, Virginia, is a modern, state-of-the-art forensic-examination facility. It was, however, not designed to process WMD-contaminated evidence. The FBI has, therefore, developed forensic capabilities at partner laboratories that can safely handle these materials. Evidence that has been contaminated with radiological materials can be examined by FBI forensic scientists at the Radiological Evidence Examination Facility at Savannah River National Laboratory in Aiken, South Carolina. At this facility, FBI examiners can safely examine contaminated materials for traditional forensic evidence, such as fingerprints, trace evidence such as hairs and fibers, tool marks, and DNA.

Additionally, the leading-edge capabilities resident in the Department of Energy (DOE) national laboratory complex are also available to the FBI to garner specialized information and evidence from the radioisotopes contaminating the evidence. Similar facilities exist at the Sample Receipt Facility at the Edgewood Chemical and Biological Center in Aberdeen, Maryland, for chemically contaminated evidence, as well as at the National Bioforensics Analysis Center in Frederick, Maryland, for biologically contaminated evidence (this facility is operated by the Department of Homeland Security).

The final portion of the WMD Directorate to be described here is the Investigations and Operations Section. While local field divisions investigate FBI cases, national programs are managed from FBI headquarters. The Investigations and Operations Section is responsible for the national management of hundreds of WMD investigations across the United States. FBI WMD cases break down into two distinct categories: usage or attempted usage of WMD materials by criminals/terrorists and WMD proliferation.

The WMD Operations units annually deal with hundreds of threats in which criminals/terrorists claim to possess WMD materials and threaten to use them as a means to an end. Many of these threats come in the form of white powder included in threatening letters sent to a variety of victims (bank personnel, judges, elected officials, media workers, jilted lovers, etc). The sheer number of these threats encountered per year has resulted in the development of a standardized, scalable response that draws on the expertise of first responders, FBI field and laboratory personnel, and relevant partner agencies across the U.S. government. Criminal and terrorist use or threatened use of WMD tends to center on the biological modality. In fiscal year 2010, 86 percent of these threats were biological in nature.

WMD proliferation is the spread of technology, expertise, or manufacturing capability from a nation that has created this technology to one that does not have this capability. Counterproliferation can be described as being somewhat the opposite of counterterrorism: While much of counterterrorism is devoted to keeping bad actors or materials out of the United States, counterproliferation is devoted to keeping U.S. WMD expertise and materials from being spread or proliferated to other nations.

Given the importance of protecting these technologies, the National Security Branch of the FBI recently created the Counterproliferation Center. This entity brings together resources from the WMD Directorate, the Counterintelligence Division, and the Directorate of Intelligence. This center is also capable of leveraging other resources and capabilities as appropriate, including the FBI Laboratory and the Cyber Division.

Not surprisingly, the distribution of WMD modality for counterproliferation cases differs from criminal/terrorism WMD cases. Seventy-two percent of all WMD proliferation cases involve nuclear technologies. This is probably due to the fact that the manufacture of most chemical and biological threat agents is dependent on widely known industrial processes; virtually any nation can manufacture sarin or anthrax with indigenous technology. Sources for nuclear technology are rarer, being more specialized and more expensive.

In our attempts to prevent acts of terrorism, it is often said that law enforcement is at a disadvantage in that “we” need to be good investigators every

John Cardinal's talk on the work of the FBI's Weapons of Mass Destruction Directorate was a conference favorite.

day, while persistent terrorists simply need to get lucky once. By employing multiple layers of defense using tripwires, countermeasures, and industry and academic outreach and partnerships, in addition to investigations, we are attempting to level the playing field by establishing a stratified defense against WMD terrorism. To be successful, terrorists, criminals, and proliferators need to defeat multiple levels of security to achieve their goals. This increases the chances that we will detect their activities and catch them before their plans can fully unfold.

It is worth reiterating the importance of partnerships in the prevention and investigation of the illicit use of WMD materials. The FBI does not work these matters in a vacuum; virtually all cases are worked in conjunction with local, state, federal, and international partner agencies. This partnering always begins with person-to-person contact and rapport. While the FBI does employ numerous scientifically trained agents and analysts, we do not profess to be subject matter experts regarding all aspects of WMD. Don't be surprised if we knock on your door and ask for help someday.

Plutonium Isotopic Analysis without Radiochemical Separation

This article was contributed by Christopher Poile and Pam Thompson, Atomic Weapons Establishment, Aldermaston, United Kingdom.


Pam Thompson

Early thermal ionization mass spectrometry (TIMS) work carried out in the 1950s and 60s on atmospheric and underground test samples demonstrated that isobaric (same mass) interferences existed between americium-241 and plutonium-241 and between uranium-238 and plutonium-238. In addition, ionization was most efficient for actinides in the nitrate form. Therefore, traditionally it has been considered necessary to perform radiochemistry on plutonium samples before the determination of isotopic ratios by TIMS.

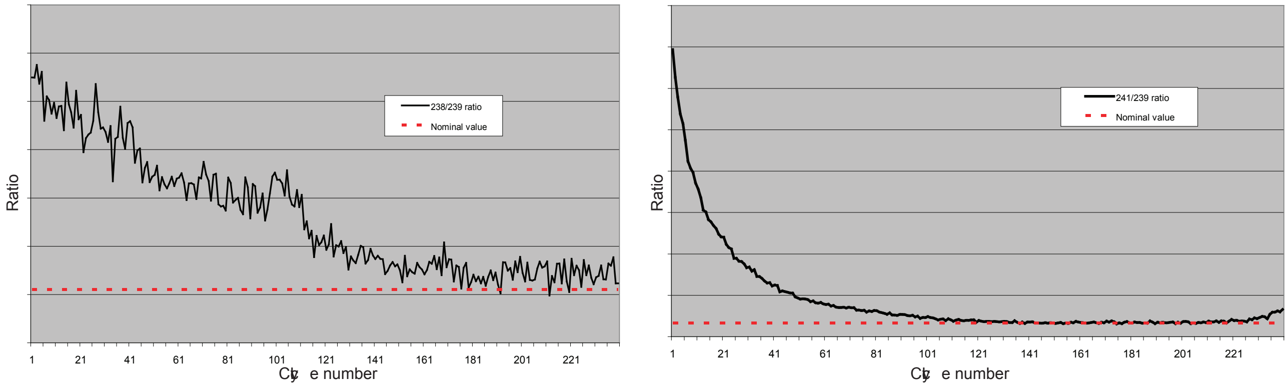
Commonly used radiochemical methods separate americium (Am), plutonium (Pu), and uranium (U) on a chromatographic column by manipulating oxidation states and ionic strength; evaporation steps then produce samples in nitrate form. However, TIMS instrumentation and techniques have developed greatly since the initial work was undertaken. This study details the investigations that have been carried out to determine if it is possible to measure the isotopic composition of plutonium by TIMS without time-consuming preparative radiochemistry.

Many of the nuclear laboratories in the United Kingdom that utilize TIMS for isotopic analysis use the triple- or double-filament technique; triple filaments are common on VG Micromass instruments and double filaments on Thermo Electron Corporation instruments. Both techniques work in the same manner: a sample is evaporated from one filament, the vapor impinges on another filament that is held at high temperature, and ions are produced.

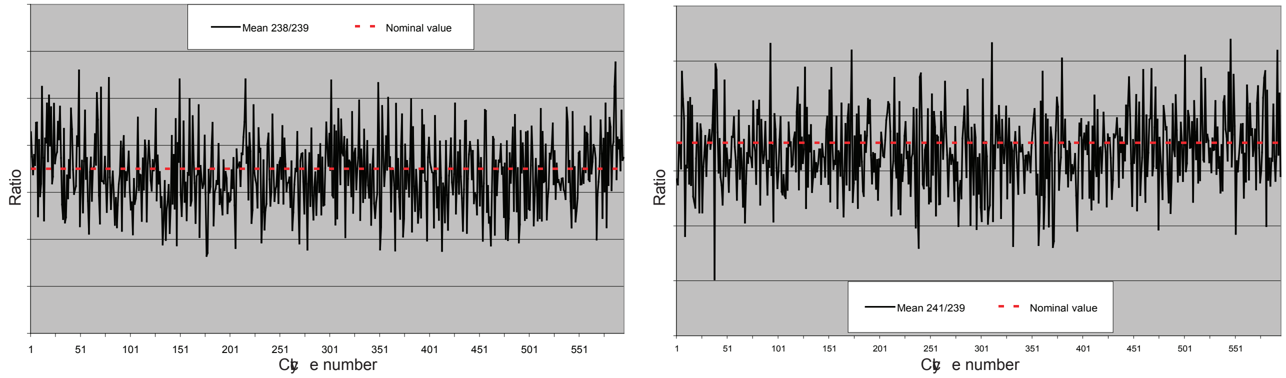
Both elemental and compound ions (for example, U^+, UO^+, UO_2^+, Pu^+, PuO^+) are commonly seen from double and triple filaments. If the temperature of the ionizing filament is high enough, then mainly elemental ions are produced. As this is basically an evaporative process, it is common to observe more than a single peak in the evaporation profile of an element from the filament. This may be caused by different compounds evaporating, material evaporating from different parts of the filament, or a combination of both effects.

Sample preparation on the filament involves loading with a sample in a nitrate form, drying, and heating to red heat in air. This stage converts the analyte to an oxide, but care is needed because overheating in air causes the filament to burn out or the sample to evaporate. In addition, work undertaken by the Atomic Weapons Establishment (AWE) has shown there can be a variation of up to 50 degrees Celsius (°C) in temperature along the filament.

It is not surprising, therefore, that when using double and triple filaments, evaporation profiles of elements can be complex, and if multiple species are



The effect of isobaric interference on isotope ratios 238/239 and 241/239 during the course of analysis using double filaments.



The apparent absence of isobaric interference on isotope ratios 238/239 and 241/239 during the course of analysis from single carburized filaments.

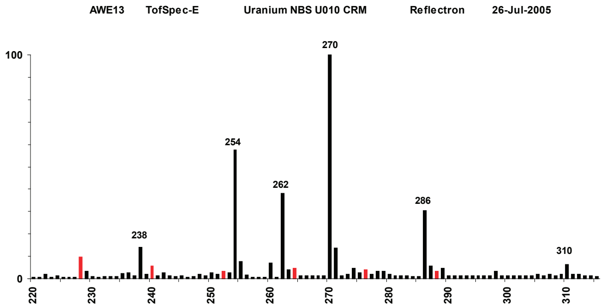
Double and single filaments were loaded with 1 μL of a solution of metal dissolved in hydrochloric acid and diluted to approximately 0.1 ppm. Data were collected on an array of miniature secondary electron multiplier detectors, and a stable ion beam was maintained using a standard filament-heating method until the sample was exhausted. More than twice as many data points were collected using single carburized filaments as double filaments.

present, isobaric interferences can be observed.

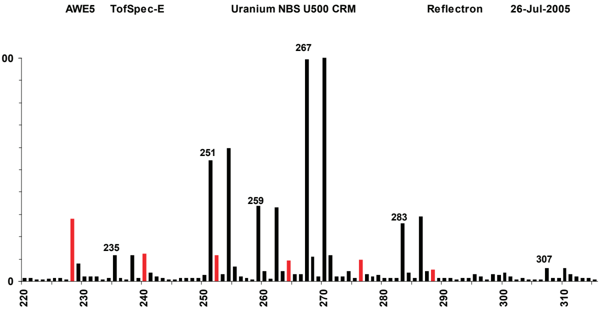
However, AWE has for many years used single carburized rhenium filaments and ion counting detectors (Daly and electron multiplier) to reduce the amount of material actually analyzed and so keep the instruments effectively "cold." Although the technique uses preparative radiochemistry, there is little evidence to demonstrate it is necessary in order to eliminate the interference problems observed with multiple-filament techniques.

The single rhenium filaments are heated in an organic vapor, usually benzene to produce carburized filaments. The organic material "cracks" and deposits carbon on the surface of the filaments. Depending on temperature, this carbon may stay on the surface or dissolve in the rhenium metal and form a solution of carbon. This carbon is available for reaction with the sample to form carbides. For actinides, these carbides require high temperatures to decompose them. When this happens they are emitted from the filament as elemental ions.

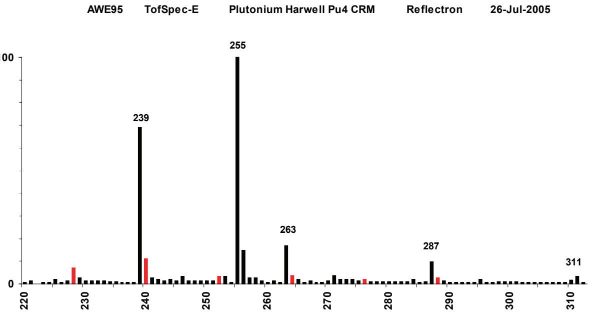
Evidence of carbide formation has been supported during a parallel investigation at AWE using matrix-assisted laser desorption/ionization (MALDI) from a graphite matrix. In this very soft ionization technique, ions for uranium (U^+, UO^+, UO_2^+,UC_2^+,UC_4^+) and plutonium (Pu^+, PuO^+, PuC_2^+, PuC_4^+) have been observed. It is reasonable to assume that these are representative of species/reaction products produced when uranium and/or plutonium are heated to extremes in a carbon-rich environment.



MALDI spectra of U010-certified reference material (99 percent uranium-238) from a graphite surface. Note the carbon cluster ions (in red) at 228, 240, 252, 264, 276, and 288 mass-to-charge ratio. Uranium-238 appears as a series of ions at 238 U^+, 254 UO^+, 262 UC_2^+, 270 UO_2^+, 286 UC_4^+, and 310 UC_6^+.



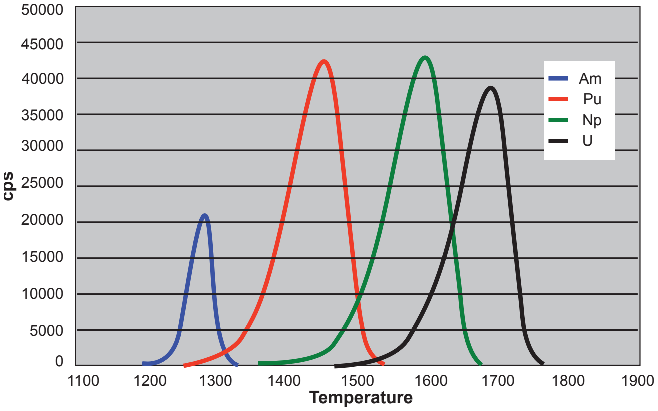
MALDI spectra of U500-certified reference material (50 percent uranium-238, 50 percent uranium-235) from a graphite surface. Support of 235 and 238 uranium species assignment is given by the additional ions at 235 U^+, 251 UO^+, 259 UC_2^+, 267 UO_2^+, 283 UC_4^+, and 307 $UC6^+$ at intensities similar to the 238 analogs.



MALDI spectra of plutonium reference material (>90 percent plutonium-239) from a graphite surface. As in the second spectra, support of species assignment is given by the ions at 239 Pu^+, 255 PuO^+, 263 PuC_2^+, 287 PuC_4^+, and 311 PuC_6^+.

This investigation examined whether the radiochemical preparation process was still necessary when single carburized filaments were used. A plutonium solution of metal dissolved in hydrochloric acid was taken before normal separation for isotopic analysis. Following dilution to approximately 0.1 parts per million (ppm), 1-microliter (μL) aliquots were loaded on both double and single filaments. The results for the double filament show obvious isobaric interference, as demonstrated by the changing 241/239 and 238/239 ratios. However, for the single carburized filament, isobaric interference does not initially appear to be significant. In addition, ionization efficiency appears to have increased; the single filament gave rise to twice as many ions as the double filaments.

Because there was no apparent interference when single carburized filaments were used, the obvious question that needed to be answered was "Why?" Using a number of isotopic standards in dilute nitric acid, it was shown that the actinides evaporated from the single carburized filaments in a very predictable manner and always in the same order: americium < plutonium < neptunium < uranium,



Evaporation profiles from a single carburized filament loaded with approximately 30 picograms of each actinide. The filament was heated at a steady rate of 25 milliamperes per minute while each mass from 233 to 244 was measured. The plot shows selected isotopes to demonstrate on a single graph the order of evaporation.

starting at about 1100 °C and going to 1800 °C. In addition, from previous experience it is known that thorium evaporates after uranium at approximately 1800 °C.

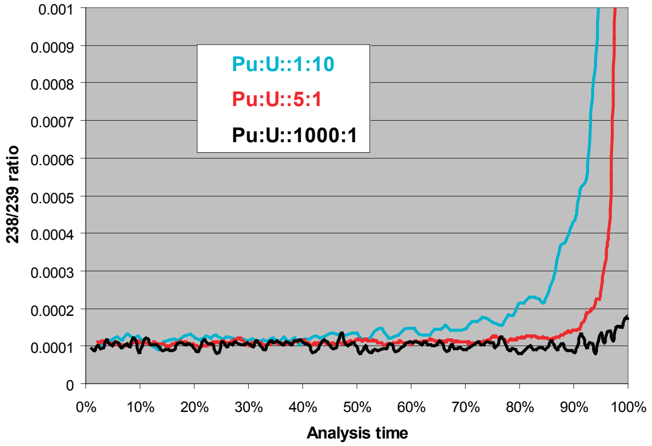
The order of evaporation is very reproducible; however, under conditions of excess carbon, additional species appear at higher temperatures. These may tentatively be assigned as derived from the dicarbide and tetracarbide; both are seen in the MALDI spectra.

While there is very little overlap of the evaporation profiles of americium and plutonium in typical plutonium materials, further work was performed to assess the tolerance of this technique to high levels of americium. Using a non-isobaric isotope of americium, americium-243, interference was found to be very slight, even at relatively high atom ratios.

Filament Loading (pg)		^{243}Am/^{239}Pu	
^{239}Pu	^{243}Am	Actual Ratio	Measured Ratio
30	0	na	0.000002
30	0	na	0.000002
30	0.45	0.015	0.000002
30	4.5	0.15	0.000004
30	45.0	1.5	0.000074

In typical plutonium material, the 241/239 ratio is approximately 0.0015, with americium that "grows in" to plutonium over time due to the beta decay of the plutonium-241 isotope, currently at the 0.15 percent level.

Uranium interference manifests itself as a rise in the 238/239 ratio in the later stages of plutonium isotopic measurement. The point at which the interference becomes significant depends on the relative amounts of plutonium and uranium present. In normal acquisitions only about 25–30 percent of the filament loading is used for measurement, and even at plutonium-to-uranium ratios of 1:10, the effect of uranium-238 is not apparent.



Plot of the 238/239 ratio for a number of plutonium/uranium mixtures. In each case a plutonium-239 beam was maintained at an output of approximately 120,000 counts per second until the plutonium had been exhausted.

It has been shown that, for the routine isotopic analysis of plutonium of known provenance (for example, routine material certification analysis), the use of carburized single rhenium filaments negates the requirement for a radiochemical separation. However, a separation will still be required for analyses of plutonium materials of unknown origin or when the isotopic ratios of the uranium present in the plutonium must be determined.

MEASURING AND PREDICTING SWELLING IN PLUTONIUM ALLOYS

This article was contributed by Benoit Oudot, Brice Ravat, and Francois Delaunay of CEA Valduc, F-21120 Is-sur-Tille, France.

The radioactive nature of plutonium presents an interesting interplay between nuclear and electronic processes. Pure plutonium metal has six different phases between room temperature and the metal's low melting point, 640 degrees Celsius (°C), at ambient pressure. High-temperature delta-phase plutonium (a face-centered-cubic structure), stable from 315 to 451 °C, can be held at room temperature by alloying it with a few atomic percent of a so-called "delta-phase stabilizer" element such as gallium, aluminum, cerium, or americium.

However, the plutonium–gallium alloy stabilized in the delta phase at room temperature is metastable and undergoes an extremely slow eutectoid decomposition to a mixture of alpha plutonium and the plutonium–gallium alloy Pu_3Ga. The stabilizing mechanisms induced by adding delta-phase stabilizer elements are still not well elucidated, making understanding and predicting the impact of plutonium-alloy aging on the safety of the nuclear stockpile one of the most challenging aspects of plutonium metallurgy.

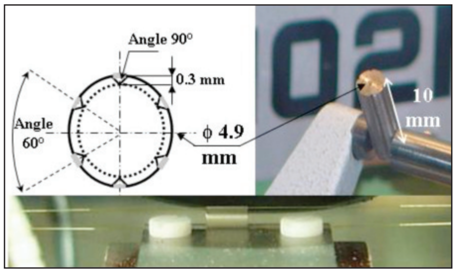
Radiation defects, helium, and other decay products accumulating in the bulk of the material cause actinide aging (for example, the change in their properties with time due to self-irradiation). Alpha-plutonium decay leads to the creation and recoil of an energetic helium nucleus (5 megaelectronvolts) and a uranium nucleus (86 kiloelectronvolts), both of which produce defects such as vacancies and interstitials (Frenkel pairs) and clusters of these.

The range of the alpha particle (helium nucleus) in the plutonium crystal is about 10 micrometers (μm), which induces a displacement cascade with a diameter of 0.8 μm. The range of the uranium nucleus is much shorter, about 12 nanometers (nm), and the diameter of the cascade is about 7.5 nm. Helium atoms and vacancies may also combine, stabilizing vacancies or vacancy clusters as well as forming helium bubbles. Finally, the radioactive decay of plutonium over time will change the composition of the material.

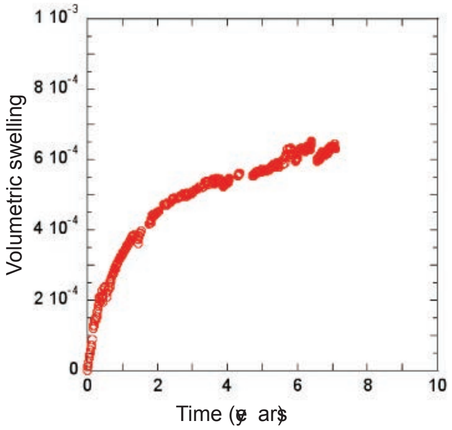
All these phenomena (change in composition, defects and vacancies, helium bubble formation) are possible contributors to the dimensional changes (called swelling) observed in plutonium–gallium alloys at the macro- and microscopic scales. However, if swelling is the most obvious consequence of radiation damage in plutonium alloys, very little data have been published regarding ongoing research on micro- and macroscopic swelling of delta-plutonium alloys.

To address the lack of data, researchers at CEA, France's Atomic Energy and Alternative Energies Commission, developed a powerful dilatometry device to evaluate material dilatation and volume swelling in relation to time. The specially designed dilatometer, which is based on optical-fiber Bragg grating sensors, is set

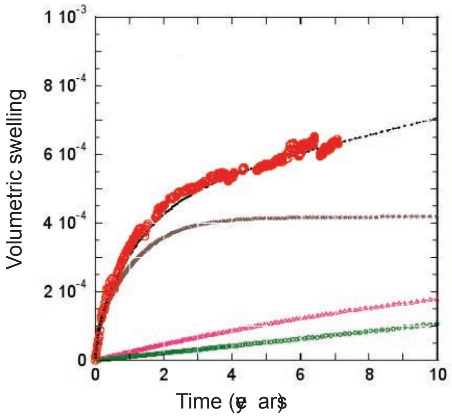
Benoit Oudot



Schematic and photographs of the special machined grooves of the sample where two Bragg gratings sensors were glued.



Macroscopic swelling evolution obtained by Bragg grating optical fiber dilatometry during more than seven years for a studied alloy stored at close to 40 °C.



Data on the three swelling contributions (defects=brown, chemical changes=pink, and helium bubbles=green) were gathered and compared with the macroscopic swelling evolution obtained by Bragg grating optical fiber dilatometry.

up inside a glovebox. Some Bragg grating sensors are inserted into grooves specially machined parallel to the cylinder axis in the plutonium alloy sample to measure the dilatation, and others are uncovered to measure temperature and pressure variations. After defects annealing by a heat treatment at 360 °C for 30 minutes, the sample is then placed into a furnace at a constant temperature, and the length and the temperature of the sample are continuously measured.

Over the course of more than seven years, we used Bragg grating optical fiber dilatometry to study an alloy stored at near 40 °C. The macroscopic swelling measurements indicate that the swelling started immediately after defects annealing without any saturation process, as was observed by X-ray diffraction at the microscopic scale by B. Ravat and others (*Journal of Nuclear Materials,* 2007). However, the sample does not grow linearly, and the experimental length variation presents two phases: a transient phase and a linear swelling phase. To carry out and quantify the different contributions of the swelling mainly on the transient phase, we used several previously published theoretical studies, which are discussed below.

By considering only three daughter products—namely uranium, americium, and neptunium, which need to be considered as solute elements affecting the alloy chemistry—it is possible to calculate their content over time by resolving the classic decay-law system obtained for each plutonium isotope and daughter products present in the alloy at the beginning of the seven-year study. Indeed, a plutonium atom that undergoes a radioactive decay changes to a different actinide daughter product with a different atomic volume, inducing what it is called chemical swelling.

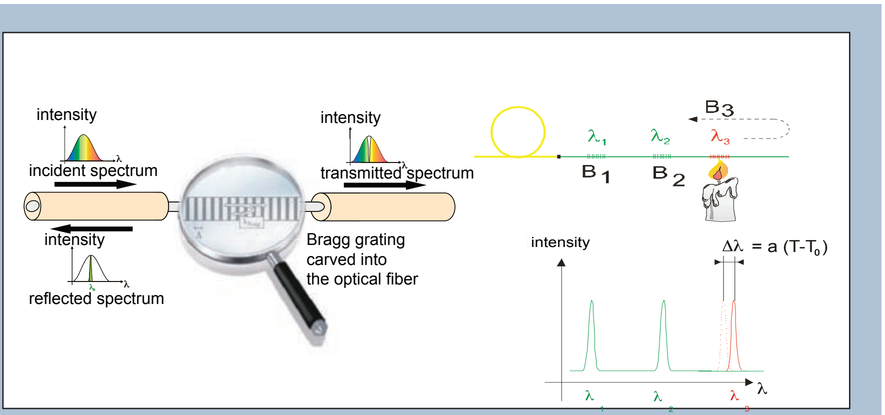
W. G. Wolfer and others (*Journal of Nuclear Materials*, 2006) calculated the daughter products per plutonium isotope using two different computational techniques. They estimated the dilatations for americium, uranium, and neptunium in delta plutonium at infinite dilution. So, considering only the result of this dilatation induced by decay product content, the chemical swelling was estimated.

Helium, the other major decay product, must be treated differently and separately. The helium concentration is equal to the concentration of uranium and neptunium daughter products. The helium generated by alpha decay either resides in bubbles or is still in solution. A rate-equation model developed by A. J. Schwartz and others (*Philosophical Magazine,* 2005*)* has been used to predict the change in concentration of helium in solution and in bubble form, the size and the number density of the bubbles as a function of time, and the swelling induced by the bubbles.

The final point of this theoretical approach considers a model of radiation structural defects accumulation, developed by V. V. Dremov and others (*Journal of Nuclear Materials,* 2009), that accounts for different types of defects and grain size. The current version of the model considers defects of four types: self-interstitial, vacancy, divacancy, and trivacancy, the last two of which may dissociate.

Data on the three swelling contributions (defects, chemical changes, and helium bubbles) were gathered and compared with the obtained experimental data. The best fit between measurements and modeling was obtained by considering a vacancy radius equal to 95 percent of the plutonium atomic radius. The data show that defects such as vacancies play an important role during the first two years of aging. Subsequently, the volume changes in delta-phase plutonium caused by americium, uranium, and neptunium are significant and add to the swelling from helium bubble formation and growth.

Comparison with experimental results so far suggests that the decay products dominate the rate of volumetric change in the long run. Nevertheless, this theoretical approach needs to be studied further, and consideration should be given to helium reinjection by cascades and helium bubble coalescence for the approach to be completely predictive.



How does Bragg grating optical fiber dilatometry work?

Bragg grating optical fiber dilatometry ensures a continuous length measurement versus time at a given temperature. A Bragg grating is carved into a specific area of an optical fiber and acts like a mirror at a specific wavelength called the Bragg-wavelength. For instance, if a Bragg grating is heated, it will expand and the Bragg-wavelength will be shifted in the reflected spectrum. Thus, the grating step evolution versus time is then a function of deformation, temperature, and pressure. By using different Bragg gratings we can follow a sample dilatation by correcting the temperature and pressure effect on the raw signal.

Further reading:

"Supporting evidence for the double-C curve kinetics in the isothermal $\delta \rightarrow \alpha'$ phase transformation in a Pu-Ga alloy using differential scanning calorimetry"; B. Oudot, K. J. M. Blobaum, M. A. Wall, and A. J. Schwartz; *Journal of Alloys and Compounds,* 2007.

"Self-irradiation effects in plutonium alloys"; N. Baclet, B. Oudot, R. Grynszpan, L. Jolly, B. Ravat, P. Faure, L. Berlu, and G. Jomard; *Journal of Alloys and Compounds,* 2007.

"Density changes in plutonium observed from accelerated aging using Pu-238 enrichment"; B. W. Chung, S. R. Thompson, C. H. Woods, D. J. Hopkins, W. H. Gourdin, and B.B. Ebbinghaus; *Journal of Nuclear Materials*, 2006.

"Study by XRD of the lattice swelling of PuGa alloys induced by self-irradiation"; B. Ravat, B. Oudot, and N. Baclet; *Journal of Nuclear Materials*, 2007.

"Volume changes in δ-plutonium from helium and other decay products," W. G. Wolfer, Per Soderlind, and A. Landa; *Journal of Nuclear Materials,* 2006.

"Characterization and modeling of helium bubbles in self-irradiated plutonium alloys"; A. J. Schwartz, M. A. Wall, T. G. Zocco, and W. G. Wolfer; *Philosophical Magazine*, 2005.

"Molecular dynamics characterization of thermodynamic and mechanical properties of Pu as dependent upon alloying additions and defects concentration. Part I"; V. V. Dremov, A. V. Karavaev, S. I. Samarin, F. A. Sapozhnikov, M. A. Zocher, and D. L. Preston; *Journal of Nuclear Materials*, 2009.

Thomas Albrecht-Schmitt

NEW INSIGHTS INTO ACTINIDE BORATE MATERIALS RELEVANT TO NUCLEAR WASTE STORAGE

This article was contributed by Shuao Wang, Evgeny V. Alekseev, and Thomas Albrecht-Schmitt of the University of Notre Dame, United States.

The terrestrial abundance of boron, and therefore borates, is quite low at 10 parts per million (ppm). However, where borate deposits do occur, they are highly concentrated because of the evaporation of ancient oceans and seas. One such deposit is the Salado formation near Carlsbad, New Mexico, where the concentration of borate, predominately in the form of H_3BO_3, $B(OH)_4^-$, and $B_4O_7^{2-}$, reaches concentrations as high as 166 ppm in intergranular brines. Located within this deposit is the United States' only repository for nuclear defense waste: the Waste Isolation Pilot Plant (WIPP).

Much like boron, uranium has a relatively low terrestrial abundance at 2.7 ppm. However, a variety of processes concentrate uranium in Earth's crust, and large deposits of uranium are found throughout the world. Despite the fact that vast quantities of uranium are dissolved in oceans and seas, there are no known naturally occurring uranium borate minerals that formed as the result of evaporation of ancient bodies of water.

WIPP presents a unique environment whereby large quantities of not only uranium but also lesser amounts of the transuranium elements neptunium (Np), plutonium (Pu), americium (Am), and curium (Cm), will potentially be able to react with the brines, possibly leading to the formation of actinide borate compounds. The presence of the decaying nuclear waste will lead to heating beyond the ambient conditions in the deposit; therefore, the reaction of actinides with borates at moderate temperatures, approximately 150 degrees Celsius (°C), are important reactions to study to predict the fate of actinides in the repository.

Despite the importance of understanding actinide behavior—especially the behavior of transuranic elements—in the borate matrix, very little is known about crystalline transuranium borates. In fact, until we started this work, there was not a single example present in crystallographic databases. In an effort to gain an understanding of the structure–property relationships in uranium, neptunium, and plutonium borates, we prepared a large family of U(VI) borates, several highly unusual intermediate- or mixed-valent and monovalent (V or VI) neptunium borates, and a Pu(VI) borate that is different from most of its U(VI) counterparts.

Actinide (An) borates are difficult to prepare in general because water competes very successfully with borate for inner-sphere coordination sites for these metals under most conditions. In fact, many borates that occur naturally are found in arid regions in evaporite deposits. This synthetic challenge can be overcome by either removing water entirely from the system in high-temperature solid-state reactions or slow evaporations or by reducing the dielectric constant of water by heating it to create hydrothermal conditions.

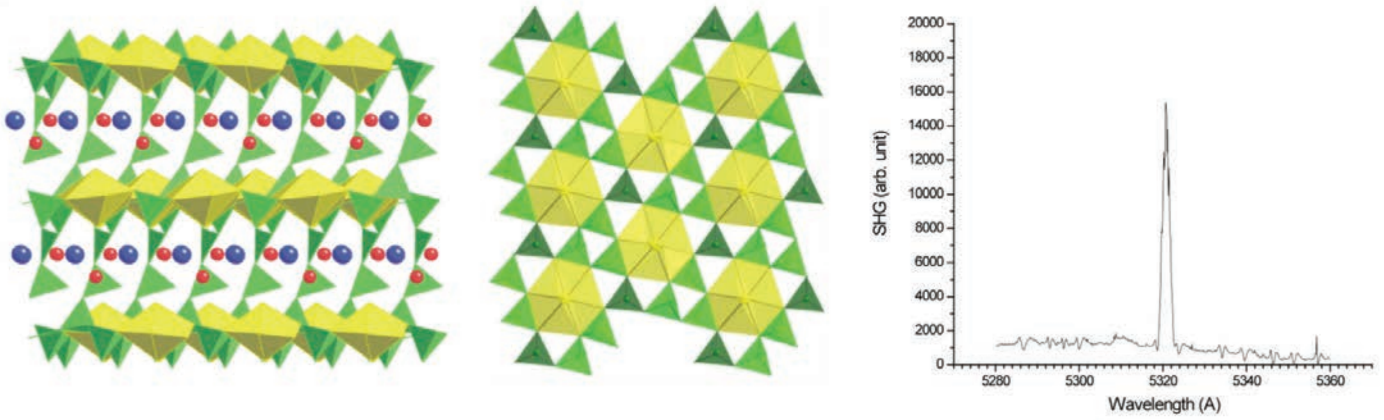
We were interested in studying high-valence actinides, either An(VI) or An(V) (An = U, Np, or Pu) initially; therefore, we avoided the potentially thermally reducing conditions of high-temperature solid-state reactions and also diminished the potential for radiolytic reduction of the neptunium or plutonium in slow evaporation crystallizations that can take months to occur. Instead, we used a boric-acid flux as the reaction medium by adding excess boric acid and various alkali metal or alkaline-earth nitrates to small droplets (approximately 5–20 microliters) of 1.8 molar Np(VI) or Pu(VI) nitrate. Much larger-scale (approximately 1 gram) reactions were performed with uranium, using a similar methodology.

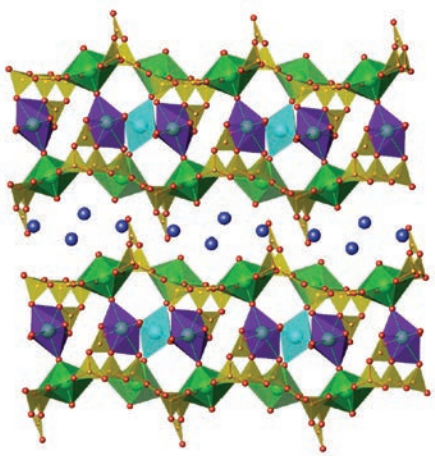
After three days of heating at approximately 220 °C in an autoclave, followed by cooling, a single translucent crystalline mass was isolated. Within this mass, crystals were observed for all actinides studied. These crystals were freed from the matrix when hot water was added, dissolving the excess boric-acid flux. Single-crystal X-ray diffraction experiments were performed to determine the crystal structure.

We have prepared more than thirty uranyl borates thus far and have selected one of these, the sodium (Na) compound Na[(UO$_2$)B$_6$O$_{10}$(OH)]·2H$_2$O, for this discussion. Despite the complexity of this large family, a single fundamental building unit exists for all of these compounds: a linear uranyl, UO$_2^{2+}$, cation surrounded by nine borate anions. This topology is substantially different from the topology observed when other triangular anions (for example, carbonate) are combined with uranyl cations.

The borate anions, which occur as both BO$_3$ and BO$_4$ polymerized units, bridge between uranyl cations to create layers. Additional BO$_3$ units extend perpendicular to these layers and link the layers into a polar three-dimensional framework with relatively large channels to house the Na$^+$ cations and the water molecules. What is most interesting is that most of the uranyl borates we have prepared adopt noncentrosymmetric space groups. Some of them, the lithium (Li) compound Li[(UO$_2$)B$_5$O$_9$]·H$_2$O, Na[(UO$_2$)B$_6$O$_{10}$(OH)]·2H$_2$O, the

Below left: The framework structure of Na[(UO$_2$) B$_6$O$_{10}$(OH)]·2H$_2$O showing Na (blue), H$_2$O (red), UO$_8$ hexagonal bipyramids (yellow), BO$_3$ triangles (dark green), and BO$_4$ tetrahedra (light green). Below center: the local structure of uranyl borate sheets. Below right: second-harmonic generation of 532 nm light from 1064 nm laser light from a polycrystalline sample of Li[UO$_2$)B5O$_9$]·H$_2$O.





The structure of $K_4[(NpO_2)_{6.73}B_{20}O_{36}(OH)_2]$ or $Ba_2[(NpO_2)_{6.59}B_{20}O_{36}(OH)_2]\cdot 0._6H_2O$ showing units of $Np^{VI}O_8$ (green), $Np^{V}O_7$ (purple), and $Np^{IV}O_6$ (turquoise) linked by BO_3 triangles, BO_4 tetrahedra, and bridging oxo atoms to form 1.6 nm-thick slabs that are separated by K^+ or $Ba_2{}^+$ cations.

potassium (K) compound $K_2[(UO_2)_2B_{12}O_{19}(OH)_4]\cdot 0.3H_2O$, and the thalium (Tl) compound β-$Tl_2[(UO_2)_2B_{11}O_{18}(OH)_3]$), which can be obtained as pure phases, display second-harmonic generation of 532 nanometer (nm) light from 1064 nm light.

The behavior of neptunium contrasts substantially with that of uranium. Two neptunium borates have been prepared that differ essentially only in their interlayer cations. The structures of $K_4[(NpO_2)_{6.73}B_{20}O_{36}(OH)_2]$ and the barium (Ba) compound $Ba_2[(NpO_2)_{6.59}B_{20}O_{36}(OH)_2]\cdot H_2O$ are extraordinary in all regards. The overall structure is layered with slabs of neptunyl borate separated by K^+ or Ba^{2+} cations. The layers diverge sharply from what is typically observed in high-valence actinyl oxoanion materials and are approximately 1.6 nm thick. Most actinyl sheets have their thickness determined by a single polyhedron and are on the order of 0.4–0.5 nm. Here, however, there are four distinct neptunium sites. In all cases the neptunium is found in the form of an approximately linear dioxo cation, $NpO_2{}^{n+}$.

An evaluation of both the neptunyl Np=O bond distances and the bond-valence sums indicates that all four sites do not contain simply Np(V). In two of the sites, $NpO_2{}^{n+}$ cations are coordinated by six oxygen atoms in the equatorial plane to form NpO_8 hexagonal bipyramidal geometries. One $NpO_2{}^{n+}$ cation is bound by five oxygen atoms to form a NpO_7 pentagonal bipyramid. Bond-valence sum calculations suggest that the NpO_8 units are primarily +6 and that the NpO_7 units are primarily +5. The final $NpO_2{}^{n+}$ cation is bonded to four oxygen atoms to yield a tetragonal bipyramid.

The core neptunyl unit has Np=O bond distances that average 1.938(14) Å, which is considerably longer than the distances found in Np(V) compounds, which average 1.83(2) Å. The neptunyl bond distances and the bond-valence sum calculations indicate the presence of Np(IV). The barium compound shows bond-valence sums more consistent with single oxidation states for each site, whereas there is slightly more intermediate valency in the potassium compound.

However, it should be noted that a dioxo Np(IV) unit has never been observed before. Thus, in a single compound, all possible coordination environments for neptunyl are realized, and there is evidence for three oxidation states existing in the same compound for neptunium.

The neptunyl polyhedra are interconnected by both BO_3 and BO_4 units in the cases of the NpO_7 and NpO_8 units. However, the NpO_6 site is held in place solely by so-called cation–cation interactions. These interactions form via the coordination of the "yl" oxo atoms from one neptunyl cation into the equatorial plane of a neighboring neptunium polyhedron. This neptunyl site is flanked on two sides by NpO_7 units and on two sides by NpO_8 units that provide the cation–cation interaction oxo atoms. The NpO_6 unit also uses its oxo atoms to form cation–cation interactions with the NpO_7 pentagonal bipyramids.

While cation–cation interactions are known in approximately half of Np(V) oxoanion compounds, this is the first example where neptunium is held in place *solely* by cation–cation interactions. The bond-valence sum for this site of 4.0

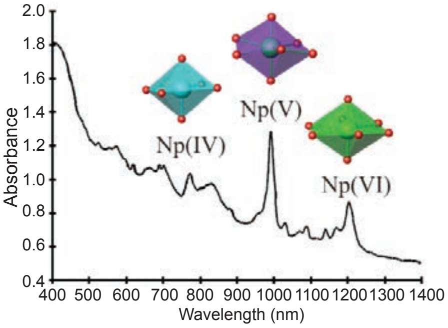
valence units again suggests Np(IV) in the barium compound. Some of the oxygen atoms in these sheets are protonated to maintain charge balance for the structure. The joining of the NpO_6, NpO_7, NpO_8, BO_3, and BO_4 units creates the remarkable layers with nanoscale features.

Bond-valence sum calculations, while effective in most cases, can only *suggest* possible oxidation states. Much stronger evidence for Np(IV) comes from ultraviolet–visible–near-infrared (UV–Vis–NIR) spectroscopy measurements taken from crystals of $K_4[(NpO_2)_{6.73}B_{20}O_{36}(OH)_2]$ and $Ba_2[(NpO_2)_{6.59}B_{20}O_{36}(OH)_2]{\cdot}H_2O$. Absorption features are present that clearly identify Np(IV), (V), and (VI). The most important f-f transitions for Np(IV) are the transitions near 700 nm and 800 nm, whereas the Np(V) and (VI) transitions are observed near 990 and 1200 nm, respectively.

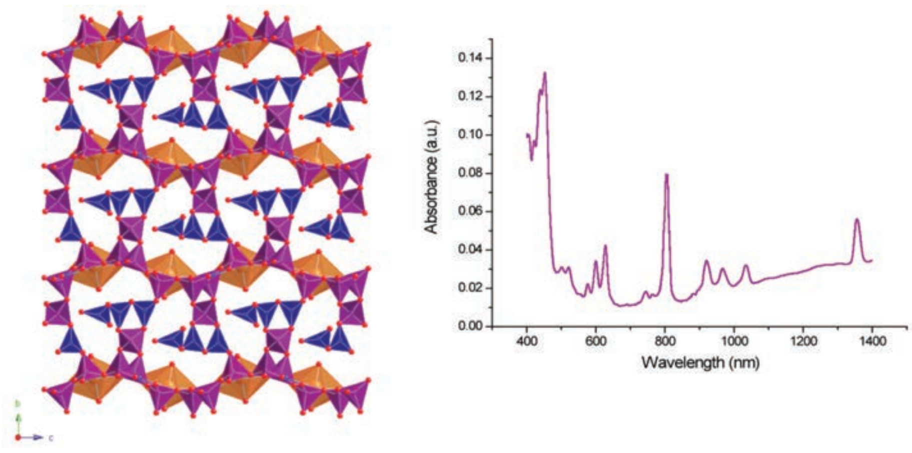
Based on the comparison of the electronic spectroscopy and the crystal structure, the following formula based on formal oxidation states could be proposed: $K_4[(Np^{IV}O_2)_{0.73}(Np^{V}O_2)_2(Np^{VI}O_2)_4B_{20}O_{36}(OH)_2]$ and $Ba_2[(Np^{IV}O_2)_{0.59}(Np^{V}O_2)_2(Np^{VI}O_2)_4B_{20}O_{36}(OH)_2]{\cdot}H_2O$.

Calculations based on the known extinction coefficients and the measured intensities of the primary peaks in the UV–Vis–NIR spectrum are consistent with this formulation. In short, the bond-valence sum calculations derived from the X-ray data are consistent with the spectroscopic measurements. Magnetic susceptibility measurements on $K_4(NpO_2)_{6.73}B_{20}O_{36}(OH)_2$ indicate paramagnetic behavior down to 2.4 kelvin (K). This behavior is similar to the mixed-valent Np(IV)/Np(V) selenite, $Np(NpO_2)_2(SeO_3)_3$, and contrasts sharply with most pure Np(V) compounds that either ferromagnetically order below 10 K or antiferromagnetically order near 20 K.

The first Pu(VI) borate prepared formed in the presence of additional cations, such as Ba^{2+}, although the additional cations diminished the size of the crystallites. Dichroic peach/pink crystals of $PuO_2[B_8O_{11}(OH)_4]$ were isolated as the sole product of the boric-acid flux reactions. UV–Vis–NIR studies clearly show only Pu(VI) in the compounds (which means no reduction has taken place).



UV/Vis/NIR spectrum of $K_4[(NpO_2)_{6.73}B_{20}O_{36}(OH)_2]$ showing regions of f–f transitions that indicate the presence of Np^{IV}, Np^{V}, and Np^{VI}. Corresponding $Np^{VI}O_8$, $Np^{V}O_7$, and $Np^{IV}O_6$ polyhedra are placed above each region of the spectrum.

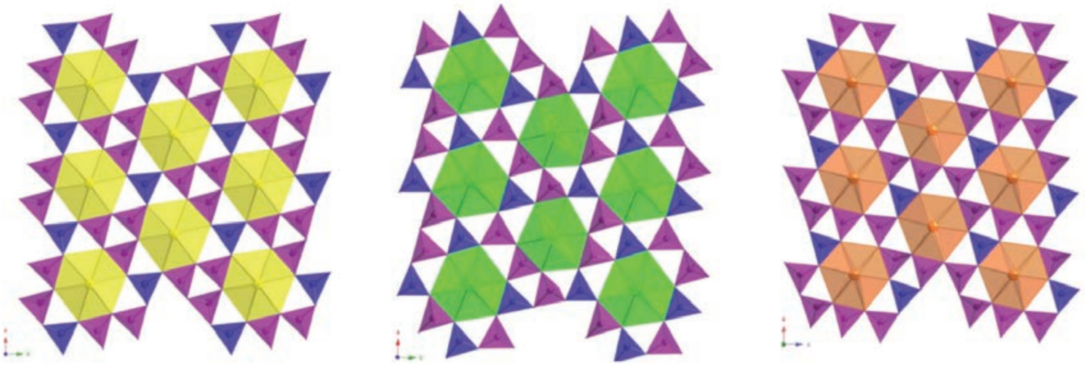


Far left: The noncentrosymmetric, three-dimensional network found for $PuO_2[B_8O_{11}(OH)_4]$. PuO_8 hexagonal bipyramids are orange, BO_3 triangles are dark blue, and BO_4 tetrahedra are red violet. Left: UV–Vis–NIR spectrum of $PuO_2[B_8O_{11}(OH)_4]$.

At first glance the structure of $PuO_2[B_8O_{11}(OH)_4]$ appears similar to that of many of the uranyl borates because it also contains a hexagonal bipyramidal environment around the Pu(VI) centers. However, while there are still nine borate groups around the equatorial plane of the plutonium, the number of BO_3 and BO_4 groups differs between U(VI) and Pu(VI).

In $PuO_2[B_8O_{11}(OH)_4]$ there are seven BO_4 units and two BO_3 units, whereas in $Na[(UO_2)B_6O_{10}(OH)]\cdot 2H_2O$, there are six BO_4 units and three BO_3 units. In the neptunium compounds the layers are also subtly different. One way of viewing these layers is to consider them as being composed of chains of BO_4 tetrahedra that are linked into sheets by BO_3 triangles.

There are other differences in the interlayer borate units: in most uranyl compounds there are only BO_3 triangles connecting the layers, while in $PuO_2[B_8O_{11}(OH)_4]$ there are BO_4 tetrahedra between the layers. The three-dimensional network found for this material is also noncentrosymmetric as indicated by the monoclinic space group configuration designation "Cc."



From left to right: the uranyl, neptunyl, and plutonyl layers found in $Na[(UO_2)\ B_6O_{10}(OH)]\cdot 2H_2O$, $K_4(NpO_2)_{6.73}[B_{20}O_{36}(OH)_2]$, and $PuO_2[B_8O_{11}(OH)_4]$ showing the hexagonal bipyramidal environments around the An^{VI} [An=U (yellow), Np (green), and Pu (orange)] as well as the BO_3 triangles (dark blue) and BO_4 tetrahedra (red violet).

These data point to the mounting body of evidence that indicates the need to conduct research on the actual actinide in question and not on a less radioactive surrogate such as uranium. However, this is not the primary message of this work. What we have observed in $K_4(NpO_2)_{6.73}[B_{20}O_{36}(OH)_2]$ and $Ba_2(NpO_2)_{6.59}$- $[B_{20}O_{36}(OH)_2]\cdot H_2O$ are materials that can successfully sequester all stable oxidation states of neptunium, not just one. Therefore, we have the ability to design advanced materials that can sequester not just one oxidation state of a radionuclide, but also all possible oxidation states for potential nuclear waste isolation applications. The low-symmetry polymeric nature of the borate anions is the key to achieving this goal, and therefore, other polyanions (for example, silicates and borophosphates) may also be appropriate for materials design.

The neptunium borates strongly underscore the need for more-versatile storage materials because, unlike other actinides, neptunium's most stable oxidation state under normal environmental conditions is +5, in the form of NpO_2^+. This cation is notorious for being only weakly bound by anions and mineral surfaces and easily migrating in the environment. Neptunium is of particular importance because neptunium-237 has a long half-life of 2.14 million years and in the long term, will be the primary contributor to the calculated dose from spent nuclear fuel stored in repositories.

Plutonium and Actinide Chemistry in Saline Solutions

This article was contributed by Marcus Altmaier and Horst Geckeis of the Karlsruhe Institute of Technology–Institute for Nuclear Waste Disposal (KIT–INE), Germany. It is dedicated to the memory of the late Dr. Volker Neck for his outstanding contribution to actinide brine chemistry. The authors wish to thank their colleagues at INE who work on high-ionic-strength systems for input and support, and acknowledge the Joint Research Center–Institute for Transuranium Elements (JRC–ITU), Karlsruhe, for scientific cooperation and for supplying the plutonium-242.

Marcus Altmaier

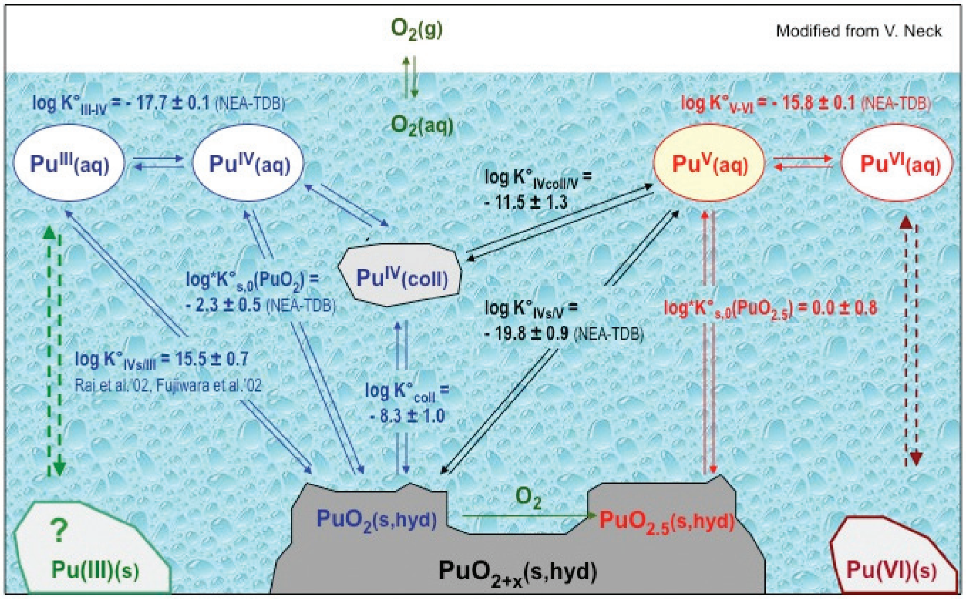
Rock salt is a safe option for the disposal of nuclear waste. Photo courtesy of Asse Einblicke

Radioactive waste is an extremely hazardous material and must be isolated from the environment over geological time scales. Deep underground facilities are considered to be the best option for the safe long-term disposal of nuclear waste. Several types of host rock formations are currently being discussed, and granite, clay, and rock-salt deposits are the most favored. Nuclear waste repositories in rock salt are presently realized in the United States (the Waste Isolation Pilot Plant, near Carlsbad, New Mexico) or under planning in Germany (Asse, Gorleben).

To assess the safety of a repository, we must understand how the repository system will perform and respond to disturbances. A crucial scenario is intrusion of water into the repository, leading to nuclear waste coming in contact with aqueous solutions. Although this scenario is rather unlikely due to the intrinsic characteristics and self-sealing properties of rock salt, it is essential to understand the effect of water intrusion and analyze the resulting highly saline systems.

Detailed investigations of actinide geochemistry in concentrated salt brines are therefore required and are directly relevant for predictions of actinide mobilization and the assessment of potential risks to the environment and biosphere. Actinide solubility phenomena play an important role because the maximum amount of radionuclides mobilized from a repository into the aqueous phase is linked to the amount of dissolved radionuclides in solution. Radionuclide solubility limits constitute an intrinsic and inherent retention mechanism for actinide release.

Actinide solubility and speciation are strongly dependent on the geochemical boundary conditions controlling basic chemical parameters of the aqueous phase, such as pH, redox potential, and ionic strength. Research into brine chemistry and composition, redox control by iron phases, and the mechanism controlling the free carbonate concentration therefore provides vital input for studies of actinide



Main redox equilibria and oxidation states of plutonium in aqueous solution.

geochemistry. Brines dominated by sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) are frequently studied because they are the most likely compositions to be found in candidate salt-formation waste repositories.

Chemical processes in brine systems cannot be extrapolated from low-ionic-strength systems because concentrated salt brines are significantly different from dilute solutions and typical groundwaters. Dissolved actinide species in brines face a unique environment in which various ions are competing for water. Strong interaction processes between the charged ions, leading to either stabilization or destabilization of actinide species, strongly influence their chemical behavior. As a consequence, dedicated research efforts focusing on high-ionic-strength conditions are necessary.

Plutonium is a focus of attention because it dominates radiotoxicity and has a large impact on the potential radiation exposure to the biosphere. A simplified scheme shows the important plutonium oxidation states (III, IV, V, VI) in aqueous solutions. As different oxidation states exhibit markedly different chemical behaviors, the importance of redox reactions and the high complexity of plutonium chemistry becomes apparent.

Because deep underground repositories will operate under electrochemically reducing conditions, the plutonium oxidation states relevant to long-term safety analysis are limited to trivalent Pu(III) and tetravalent Pu(IV). Solid plutonium dioxide (PuO_2) is known to be very stable and to control plutonium solubility over a broad range of geochemical conditions. However, it is not sufficiently known how Pu(III) solid-phase formation may be triggered and stabilized by complexing ligands such as carbonate under high-ionic-strength conditions or how this affects the total solubility. Complex formation likewise strongly affects the aqueous actinide speciation and enhances the amount of actinides dissolved in solution. A comprehensive understanding of actinide redox chemistry and complex formation is therefore necessary for robust solubility models and safety predictions.

Over the last several decades, research at KIT–INE on actinide geochemistry has often focused on saline systems relevant to nuclear waste disposal in rock salt. As a typical example, we discuss our recent work on plutonium solubility and phase stability in reducing $MgCl_2$ brines.

The solubility, solid-phase stability, and redox speciation of plutonium in 3.5 molar (M) $MgCl_2$ is investigated in strongly reducing solutions with and without carbonate. Magnesium (Mg^{2+}) is known to scavenge carbonate by formation of solid magnesium-carbonate phases, but the formation of the thermodynamically stable and sparingly soluble magnesite $Mg(CO_3)(s)$ (s = solid) is kinetically hindered. Instead, the formation of magnesium-hydroxo-carbonate phases both controlling pH and fixing rather high carbonate concentrations is observed. Under these conditions, the carbonate concentration in solution cannot be neglected, and actinide-carbonate interactions need to be considered.

Solubility experiments and sample preparation for X-ray-absorption near-edge structure (XANES) investigations were preformed in a glovebox under inert argon (Ar) atmosphere conditions. In a first step, 3.5 M $MgCl_2$ solutions were spiked with sodium carbonate (Na_2CO_3) solution, leading to precipitation of Mg-OH-CO_3 phases. After a pre-equilibration with iron (Fe) powder to fix strongly reducing redox conditions, plutonium-242 was added to the systems. Experiments were performed from both undersaturation by addition of $PuO_{2+x}(s)$ and oversaturation by addition of an electrochemically prepared Pu(III) stock solution.

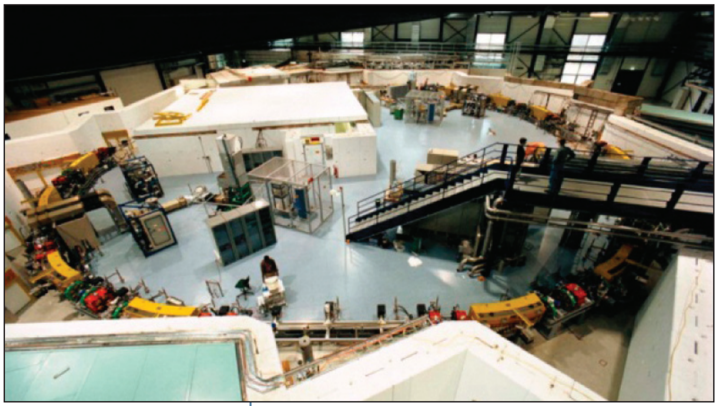
The samples were analyzed over a period of 582 days, and pH, redox potential, and plutonium concentration were monitored. After the experiments, solid phases were prepared for XANES analysis. Plutonium L3 XANES spectra were measured at the INE–Beamline at the Ångströmquelle Karlsruhe (ANKA), the synchrotron light source at KIT.

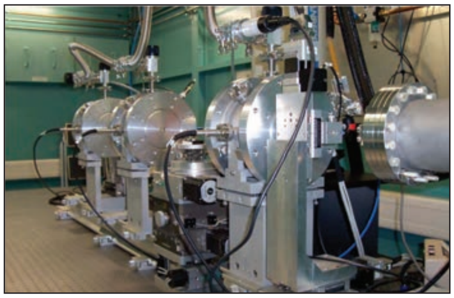
Data on the solubility of the three investigated samples showed the following:

Series 1: The sample in 3.5 M $MgCl_2$ under carbonate-free conditions, with initial $PuO_{2+x}(s)$, shows constant plutonium solubility and concentrations scattering around $10^{-8.0}$ M. This is expected for Pu(III) solution species in equilibrium with a Pu(IV)-oxyhydroxide solid phase.

Series 2: The carbonate-free system with initial Pu(III) solution added exhibits a pronounced decrease of the plutonium concentration with time (from [Pu] = $10^{-5.7}$ M to $10^{-7.3}$ M). The high concentrations measured after short equilibration times can be explained by a trivalent $Pu(OH)_3(am)$ (am = amorphous) solid phase in equilibrium with Pu(III) solution species. The decrease of the plutonium concentration to $10^{-7.3}$ M is correlated with a solid-phase transformation into Pu(IV)-oxyhydroxide as evidenced by XANES analysis. The experimentally observed instability of the $Pu(OH)_3(am)$ phase relative to $Pu(OH)_4(am)$ is in agreement with thermodynamic calculations for carbonate-free systems.

Series 3: The sample in contact with the magnesium-hydroxo-carbonate phase with initial Pu(III) solution added from oversaturation shows a remarkably different behavior. Even after 582 days equilibration, the plutonium concentration in solution is still at a rather high $10^{-5.4}$ M. Contrary to the observation in Series 1 and 2, XANES analysis of Series 3 clearly proves that plutonium in the solid

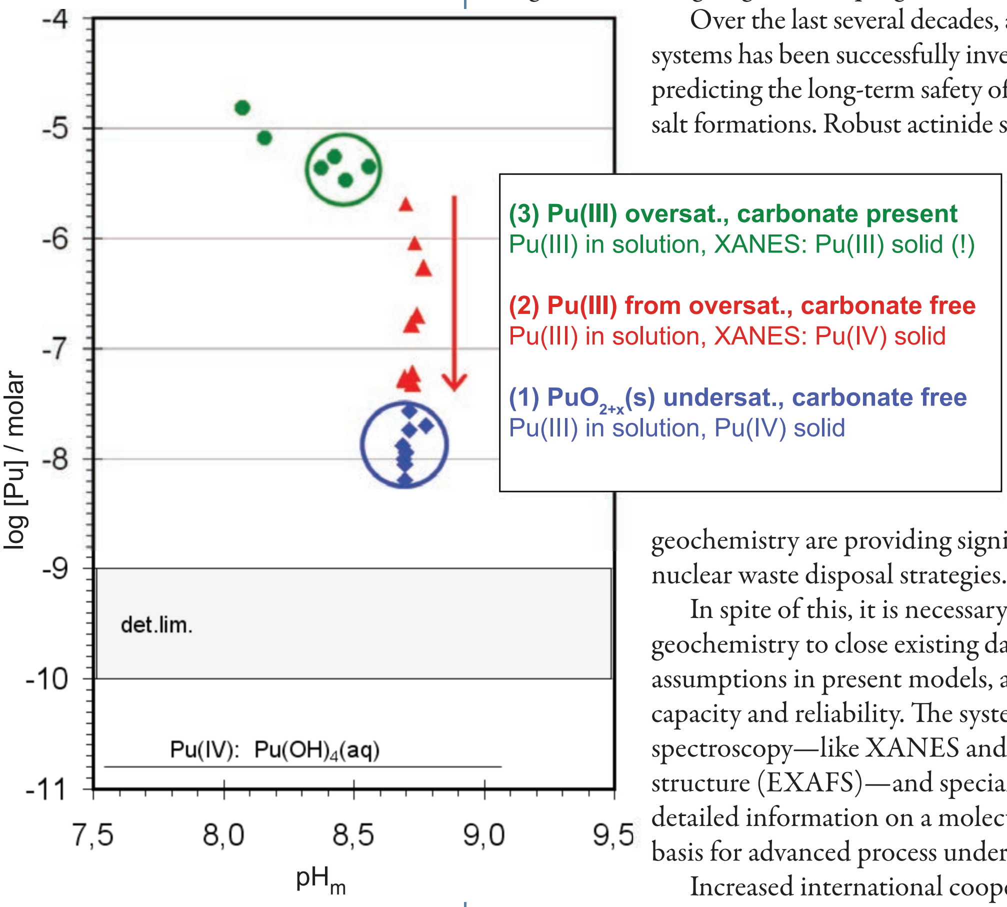




The INE–Beamline at ANKA, Karlsruhe Institute of Technology, a dedicated facility for actinide research. Top: The ANKA 2.5-gigaelectronvolt storage ring. The white-roofed construction contains the electron source, microtron, booster, and injector. Center: Ionization chambers and solid-state germanium detectors in the INE–Beamline experimental hutch. Bottom: The optics hutch contains a collimating mirror, in the foreground, and a double crystal monochromator and second focusing (toroid) mirror, in the background.

phase is present in the unexpected trivalent oxidation state. The formation of a Pu(III) solid phase can be explained by a stabilization of Pu(III) by coordinated carbonate ligands in the solid but this needs further investigation.

The present study confirms that tetravalent plutonium-hydroxide/oxyhydroxide solid phases are limiting plutonium solubility in $MgCl_2$ brines under carbonate-free conditions, as expected for typical anoxic groundwaters. However, it also raises an important question: To what extent do Pu(III) solid phases control plutonium solubility in reducing brine systems containing carbonate or other strongly complexing ligands? Plutonium redox chemistry and solubility in brine systems are being studied in ongoing research programs at KIT–INE.



Solubility of plutonium in 3.5 M $MgCl_2$ under the presence and absence of carbonate.

Over the last several decades, actinide geochemistry in brine systems has been successfully investigated as a key parameter for predicting the long-term safety of a nuclear waste repository in rock-salt formations. Robust actinide solubility limits can be derived for a variety of boundary conditions based on experimental data and geochemical modeling. Depending entirely on the laws of nature (chemical reactions and thermodynamics) not changing over time, geochemistry offers a robust and reliable tool for ensuring long-term repository safety. Expertise and concepts from actinide chemistry and geochemistry are providing significant contributions for optimized nuclear waste disposal strategies.

In spite of this, it is necessary to extend studies on actinide geochemistry to close existing data gaps, reduce overconservative assumptions in present models, and improve the overall predictive capacity and reliability. The systematic application of modern spectroscopy—like XANES and extended X-ray absorption fine structure (EXAFS)—and specialized analytical techniques gives detailed information on a molecular level that can be used as the basis for advanced process understanding and chemical models.

Increased international cooperation and scientific exchange on actinide brine chemistry topics are likewise required. The international workshops on Actinide Brine Chemistry (ABC–Salt) are promising steps in that direction. The workshops were initiated and co-organized by KIT–INE and Los Alamos National Laboratory's Carlsbad Office, with support from DOE. ABC–Salt (I) was held in September 2010 in Carlsbad, New Mexico; ABC–Salt (II) is scheduled for November 2011in Karlsruhe.

UNLOCKING THE MYSTERIES OF PHASE TRANSFORMATIONS IN PLUTONIUM–GALLIUM ALLOYS

This article was contributed by Kerri Blobaum, Jason Jeffries, Adam Schwartz, Mark Wall, Hyunchae Cynn, and William Evans, Lawrence Livermore National Laboratory, United States, and Wenge Yang, Geophysical Laboratory, Carnegie Institution of Washington, United States.

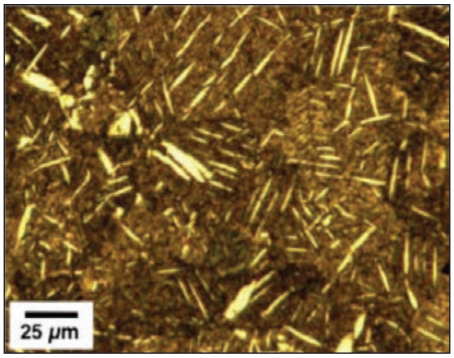
Kerri Blobaum

The metallurgical properties of plutonium and its alloys have been studied since Glenn T. Seaborg and his co-workers first synthesized the element in 1940. Seemingly small perturbations in temperature, pressure, or alloying elements can have dramatic changes on the material's physical properties. For example, pure plutonium (Pu) can undergo a series of phase transformations from the delta (δ) phase to the alpha (α) phase, resulting in a 25-percent volume contraction when the temperature is decreased from 325 degrees Celsius (°C) to 125 °C. The addition of approximately 2 atomic percent (at.%) of gallium (Ga) suppresses formation of the intermediate phases, and a partial transformation to an α-like phase (α') does not occur until the temperature is decreased to approximately -125 °C; increasing the gallium content to 3 at.% quashes the δ-to-α' transformation altogether.

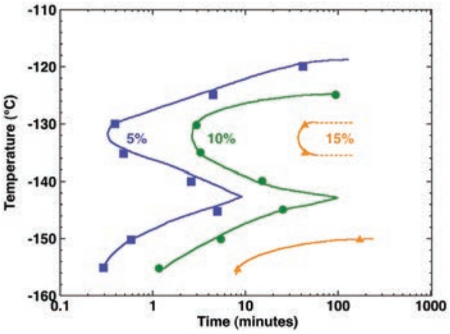
Adding to this complexity is the fact that plutonium is never truly thermodynamically stable. The element constantly undergoes radioactive decay, resulting in compositional variations as plutonium initially fissions to uranium and helium. Furthermore, the crystal lattice suffers internal damage as the decay products smash through it, traveling in opposite directions. The long-term effects of this self-irradiation on phase transformations are not well understood and are the subject of much study.

Scientists at Lawrence Livermore and Los Alamos national laboratories are engaged in investigations of the fundamental properties of phase transformations in plutonium alloys, with the goal of predicting the effects of composition, microstructure, and aging on these transformations. With plutonium aging naturally in our nation's stockpile, it is important to understand how this material might change during long-term storage.

As a pure metal, plutonium exists in the α phase at ambient conditions. Alpha plutonium is a brittle material with a complicated monoclinic crystal structure and a density of 19.8 grams per cubic centimeter (g/cm^3). With the addition of 2–10 at.% of gallium, the ductile face-centered-cubic (fcc) δ phase is typically observed at ambient conditions; the density of this phase is 15.9 g/cm^3. The fcc structure is considered "close packed," and it is unusual for a material to be denser in a monoclinic lattice than in an fcc arrangement. Plutonium is the only metallic element that crystallizes in a low-symmetry monoclinic ground state.



An optical micrograph of a plutonium-gallium alloy containing both the α′ and δ phases. The α′ particles have light contrast and are needle shaped; the δ grains have darker contrast and are distinguished by dark outlines marking approximately hexagonal equiaxed shapes.



The time–temperature–transformation diagram for a Pu-1.9 at.% Ga alloy showing the double-C curve kinetics, based on the published work of M. Faiers and colleagues. The "noses" at approximately -130 °C and -155 °C indicate the temperatures where the maximum transformation rate from δ to α′ occurs.

When plutonium is alloyed with 1.9 at.% of gallium (Pu-1.9 at.% Ga), the δ phase is retained in a metastable state at room temperature. This means that the material is not in thermodynamic equilibrium, but on human time scales, it is reasonably safe to assume that the δ phase will not transform to its equilibrium phase, α + Pu_3Ga, without significant perturbation. (Carbon exhibits a similar behavior at ambient conditions: while graphite is the thermodynamically stable phase at ambient conditions, the metastable diamond phase is "effectively stable" for most practical purposes.)

Cooling a Pu-1.9 at.% Ga alloy to approximately -125 °C initiates a partial transformation to another metastable phase, α′. The α′ phase is monoclinic, like the α phase, but it contains gallium trapped in the crystal lattice. In an optical micrograph of a plutonium-gallium alloy containing both the α′ and δ phases, the α′ particles look like small needles, and the δ grains are larger and equiaxed.

The transformation from δ to α′ is martensitic, meaning that atoms make small coordinated shifts, rather than long-range diffusional movements. Because the α′ phase is 25 percent denser than the δ phase, the δ lattice must undergo considerable strain to accommodate the α′ martensite particles. After less than 25 percent of the δ phase has transformed to the α′ phase, the lattice becomes too strained to allow any more transformation to occur, and the transformation arrests.

In addition to its intriguing thermodynamics, the δ-to-α′ phase transformation has interesting kinetics, which are not yet well understood. Kinetics refers to the rate at which the transformation occurs. Martensitic transformations are common and relatively well understood in many steels. In most of these cases, the kinetics are considered "athermal," meaning the transformation occurs nearly instantaneously when the transformation temperature is reached—holding the material for longer times does not produce more martensite.

In the δ-to-α′ transformation in plutonium alloys, on the other hand, the martensite kinetics are considered "isothermal," meaning that the amount of α′ martensite formed depends on both the temperature and the time the material is held at that temperature—holding for longer times does produce more martensite. For typical isothermal transformations, a plot of temperature versus time shows a C-shaped curve, with the "knee" or "nose" of the C at the temperature where the transformation occurs most rapidly. In the 1970s, M. Faiers and his colleagues at the Atomic Weapons Establishment (AWE) in the United Kingdom found that some plutonium–gallium alloys had two temperatures where the transformation rate was maximized. Such "double-C" curve behavior is highly unusual.

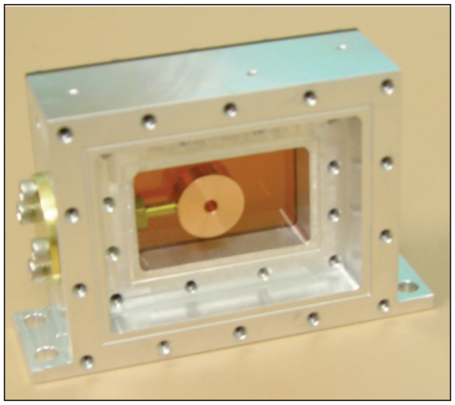
The reason for the double-C curve kinetics has puzzled plutonium scientists for more than thirty years. Several hypotheses have been proposed, but none has been fully confirmed. Faiers and his colleagues at AWE conjectured that the δ-to-α′ transformation was martensitic at lower-C curve temperatures and "massive" at upper-C curve temperatures (a massive transformation is a diffusionless transformation in which atoms move individually, rather than in the coordinated fashion that typifies martensites). However, microscopy shows no evidence of a massive transformation at any temperature.

A second possible reason for the double-C curve kinetics in the δ-to-α′ transformation is that different transformation mechanisms or paths are active in each C curve. More specifically, it is possible that the δ phase transforms to an intermediate phase before transforming to α′ at upper-C temperatures; at lower-C temperatures, the δ phase may transform to α′ directly, without any steps in between. An intermediate gamma phase (γ′) with a face-centered orthorhombic crystal structure was observed in some δ-to-α′ transformations by the French researcher Philippe Deloffre. More recently, Philippe Faure at France's Atomic Energy and Alternative Energies Commission (CEA) reported that the γ′ phase forms when the δ-to-α′ transformation occurs at elevated pressures; this was confirmed by William Evans and his colleagues at Lawrence Livermore National Laboratory (LLNL).

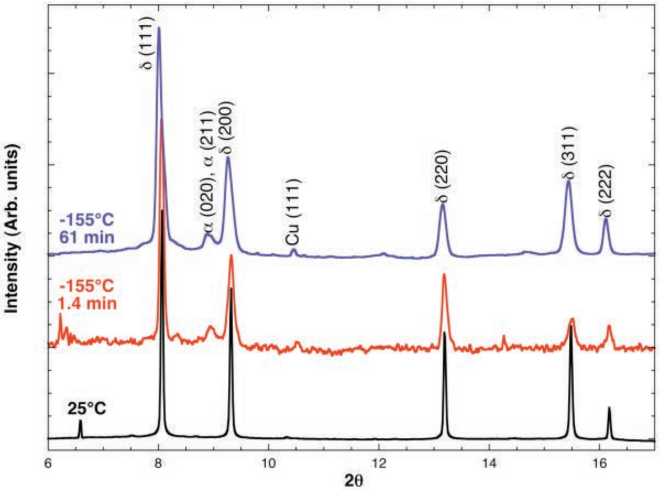
Jason Jeffries and his LLNL colleagues suggested a third hypothesis for the double-C curve kinetics several years ago. The group showed evidence for a "conditioning treatment" enabling δ-to-α′ transformation at temperatures within the lower-C curve. When Jeffries heated Pu-1.9 at.% Ga samples to 375 °C and then immediately quenched them to -155 °C (the nose of the lower-C curve), he found that very little transformation to α′ occurred, even when the sample was held for several hours. However, if he heated the sample to 375 °C and then held it overnight at ambient conditions, many α′ particles were observed when the sample was cooled to -155 °C. While the conditioning treatment seems like a plausible explanation for the double-C curve kinetics, Jeffries and his colleagues continue to investigate this behavior because they still do not fully understand what conditioning-caused events occur that later enable the δ-to-α′ transformation at low temperatures.

To look for a possible γ′ intermediate phase in the δ-to-α′ transformation, Kerri Blobaum and her colleagues at LLNL designed an experiment to monitor the phases present in a sample as it was slowly cooled to temperatures in the upper- and lower-C curves. Using high-brilliance X-rays at the Advanced Photon Source at Argonne National Laboratory, the brightest synchrotron source in the Western Hemisphere, the group was able to "see" through a Pu-1.9 at.% Ga alloy and measure diffraction patterns. These data provide information about the crystal structure of the sample, namely direct evidence for the presence of monoclinic, face-centered cubic, and face-centered orthorhombic phases corresponding to the α′, δ, and γ′ phases, respectively. By collecting X-ray diffraction patterns every few seconds as the sample cooled, the group could determine the transformation path of the material.

Because plutonium is radioactive and decomposes when exposed to air, collecting in situ X-ray diffraction data poses experimental challenges. The plutonium alloy sample must be contained behind three windows and polished to less than 90 micrometers (μm) thick to allow the X-rays to be transmitted through the metal. A sample holder was designed specifically for these experiments. The plutonium disc, approximately 3 millimeters (mm) in diameter, is mounted in a copper "lollipop" and then covered with a window made of polyester film.



A sample holder designed for in situ X-ray diffraction experiments at the APS with plutonium-gallium alloys. The plutonium disc sits on the copper "lollipop" and is contained behind three plastic windows (removed for illustrative purposes).



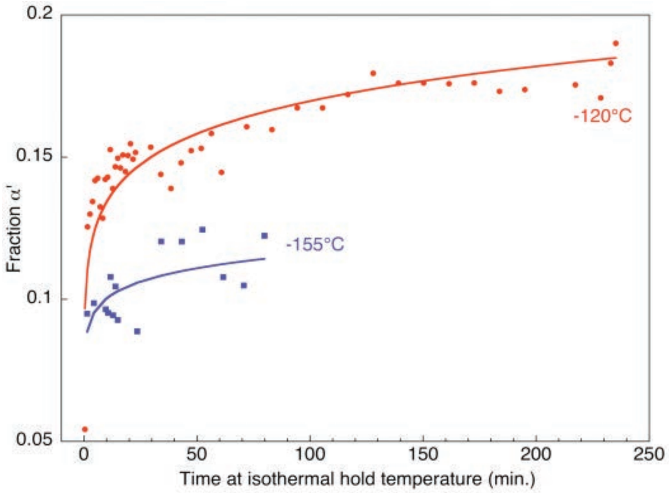
X-ray diffraction patterns showing the δ phase present before the sample was cooled and the δ + α′ phases present at -155 °C. The relative intensities and positions of the peaks provide a fingerprint for identifying which phases are present in the sample.

Additional polymeric plastic windows are secured with stainless steel frames and sealed with ductile indium wires squeezed behind the frames to prevent air from entering the sample holder and contaminant particles from exiting it.

Blobaum and her colleagues did not see any evidence of the γ′ phase at either upper-C or lower-C temperatures; the only phases observed during the experiment were δ and α′.

Because data were collected every few seconds, it is unlikely that the researchers missed the γ′ phase. The group feels confident that its work disproves the hypothesis about different paths being responsible for the double-C curve kinetics occurring during the low-temperature isothermal transformation. Analysis of the data yielded additional information about the rate of the δ-to-α′ transformation. Most of the transformation occurs in the first few minutes, and the amount of a′ continues to increase for several hours.

While the mystery of the double-C curve kinetics has not yet been fully solved, researchers are steadily gaining more scientific insight on the fundamentals of the curious δ-to-α′ transformation in plutonium–gallium alloys. Understanding the coupled thermodynamics and kinetics of this system will enable scientists to build models that help predict if and how the transformation might change as the plutonium ages with decades or centuries of self-irradiation. Such work is essential to the national laboratories' stockpile stewardship missions.

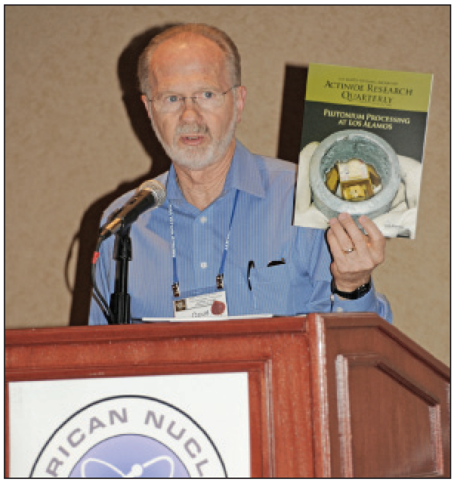


At both -120 °C and -155 °C, the majority of the α′ phase forms within a few minutes of reaching the isothermal hold temperature. However, the amount of α′ continues to increase for several hours.

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U. S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT is supported by CIW, CDAC, UNLV, and LLNL through funding from DOE-NNSA, DOE-BES, and NSF. HPSynC is supported as part of EFree, an Energy Frontier Research Center funded by DOE-BES under Grant No. DE-SC0001057. APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357.

DIFFUSE REFLECTANCE SPECTROSCOPY OF PLUTONIUM SOLIDS

This article was contributed by David Hobart and Kevin Boland of Chemistry Division, Los Alamos National Laboratory, United States. It details research presented in a conference poster, which was co-authored by Hobart, Boland, and Los Alamos colleagues Dominic Peterson, Stosh Kozimor, Marianne Wilkerson, and Jeremy Mitchell. Hobart was technical program co-chair for the conference and is the guest scientific editor for this issue of Actinide Research Quarterly. *The authors wish to thank Maida Trujillo of the Chemistry Division Office for her graphics support.*



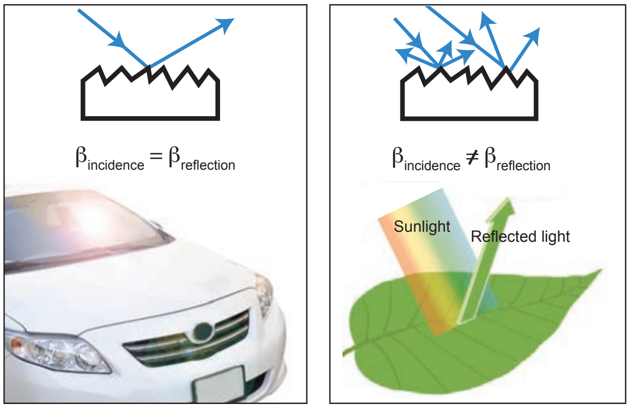
David Hobart pitches **ARQ** *to the audience.*

Conventional ultraviolet–visible–near-infrared (UV–Vis–NIR) absorbance spectroscopy involves light passing through a transparent or translucent material that absorbs at wavelengths corresponding to the electronic, vibrational, and translational transitions in the material. For analyzing samples that are completely opaque, diffuse reflectance spectroscopy (DRS) is the technique of choice. Reflectance spectrophotometers measure the intensity of light reflected by a surface as a function of wavelength to produce a reflectance spectrum.

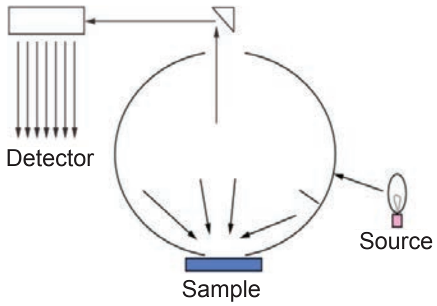
There are two types of light reflectance, and they are both familiar to us in everyday life. The first type is specular reflectance, in which white light striking a surface has an angle of incidence exactly equal to the angle of reflectance. In this instance, the light does not interact with the surface material, so there is no spectral interrogation of the surface. This is commonly referred to as “glare,” and an example is when sunlight reflects at the critical angle from a glass surface.

The second type is called diffuse reflectance, in which white light reflecting off a surface is observed at any angle except the angle of incidence. In this case the light effectively interacts with and spectrally interrogates the surface material. Color is the human eye’s perception of diffuse reflected radiation in the visible region of the electromagnetic spectrum (400–800 nanometers [nm]) as modified by the selective absorption of photons on the surface of the object. Diffuse reflectance allows us to visually perceive all the various colors and textures of the things in the world around us.

DRS is performed by directing a spectrometer beam onto the surface of a sample. Wavelengths that correspond to electronic and/or vibrational



Far left: Specular reflectance or glare (as shown on the car’s windshield), in which the angle of incidence of light is equal to the angle of reflectance and no interrogation of the surface is obtained. Left: Diffuse reflectance, in which the angle of incidence of light is not equal to the angle of reflectance and interrogation of the surface is obtained. Leaf adapted from Nancy Kiang, “The Color of Plants on Other Worlds,” *Scientific American*, April 2008.



Schematic diagram of an integrating sphere assembly for recoding diffuse reflectance spectra.

energy levels in the sample are absorbed during the analysis; other wavelengths are reflected without being absorbed. The reflected light is then collected from all angles except the incidence angle in a diffuse reflectance integrating sphere or similar device. The wavelength and intensity of the reflected light are measured, and the net result is a characteristic absorption spectrum of the surface of a completely opaque sample.

A standard UV–Vis–NIR spectrometer is used for diffuse reflectance measurements. It should have a bandwidth narrow enough to provide well-resolved spectral features yet wide enough to provide a sufficient energy level throughput for diffuse reflectance measurements. The spectrometer should of course have high-sensitivity optics and electronics and be able to physically accommodate the reflectance assembly. Recent advances include miniature fiber-optic probes and portable hand-held spectrophotometers.

DRS has been used in a wide variety of applications, including mineral identification, paint color identification, skin and blood pathology, metallurgy and corrosion, remote sensing, earth and extraterrestrial mapping and prospecting, meteorite studies, art attribution and forgery detection, counterfeit currency identification, textile analysis, archeology, thin-film deposition monitoring, agriculture, biology, and soil analysis.

There is recent renewed interest in DRS because of current advances in solid-state electronics, fiber optics, and the greater availability, portability, and lower cost of high-performance instrumentation. DRS is a particularly powerful analysis technique when combined with data from other modern analytical methods. Despite all of its advantages, DRS has been generally overlooked for analyzing f-elements. In the last twenty years—to the knowledge of the authors—fewer than forty articles have been published on DRS of the actinides. This article is a brief review of the field, some new results, and an effort to encourage greater application of this powerful technique for analyzing and characterizing the compounds, alloys, and metals of actinide elements.

Analysis of plutonium (Pu) metal, alloys, and compounds by DRS has many applications in corrosion studies, long-term storage of plutonium components, nuclear waste disposal, environmental protection, nuclear forensics, and the characterization of newly synthesized plutonium compounds and complexes.

DRS is particularly useful for analyzing and characterizing plutonium metals, alloys, and compounds. Although the f-electrons of plutonium are in general not strongly influenced by the local electronic environment, there are subtle ligand and matrix interactions that are enhanced in the solid state. Furthermore, the translational modes that broaden and smear electronic and vibrational spectra are generally "frozen out" in the solid state.

Changes in the positions, splitting, and intensity of the f-f, f-d, and charge-transfer absorption bands of f-elements can be exploited to provide rapid and unequivocal identification of oxidation state, compound, and matrix using this relatively simple technique. The metallic state of plutonium also exhibits a characteristic reflectance spectrum involving the transition of valence electrons to the conduction band.

Unlike conventional absorption/transmission spectroscopy, in which a known sample path length allows for acquiring accurate quantitative data, DRS is less quantitative but provides excellent qualitative data. It is possible, however, to obtain reasonably good semi-quantitative DRS data using well-characterized reference materials. DRS is particularly useful in characterizing solids with sharp, well-resolved spectral features in the UV–Vis–NIR regions, for example, the sharp f-electron spectra of plutonium and other actinide elements.

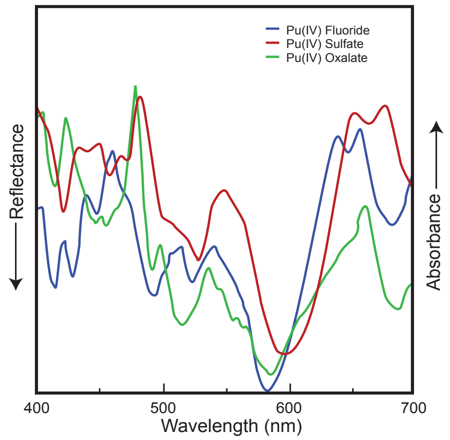
To our knowledge, 1970 was the first reported use of DRS on plutonium, and it involved recording the far infrared reflectance spectrum of plutonium dioxide (PuO_2). In 1985 the DRS of phosphine oxide and amide complexes of plutonium chlorides were reported. The DRS of plutonium(IV) fluoride, sulfate, and oxalate compounds was reported in 1987. In 1989 the DRS spectrum of high-fired plutonium dioxide was compared with the absorption spectrum of Pu(IV) polymer suspension, further confirming the close similarity of these species.

The DRS of crystalline plutonium(III)-potassium chloride salt electrorefining residues was reported in 1989. The intense purple of these salts became a sky blue when exposed to room light. The DRS spectrum showed that the color change was a result of color-center formation in the salts from radiation damage and not from a plutonium oxidation state change. In 1997 DRS was applied to the study of plutonium solubility and speciation in the separation of hydrothermal waste effluents. In 1998 the limiting species in the Pu(IV)-carbonate system was identified as $[Pu(CO_3)_5]^{6-}$ through the use of DRS.

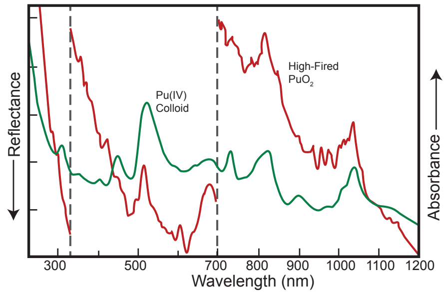
Later work involved the DRS analysis and characterization of coordination complexes of Pu(IV) pyridine N-oxide phosphoryl nitrates; Pu(III) tris trifluorosulfonate, $[Pu(H_2O)_9][CF_3SO_3]_3$; quaternary alkali metal plutonium thiophosphates; plutonium-doped zirconolites and perovskites; $[PuCl_6]^{2-}$ complex precipitated from the room-temperature ionic liquid [BuMeIm] [Tf_2N]; PuO_2CO_3; and inorganic PuO_2 and Pu(IV) bio-reduced by metal-reducing bacteria. In 2010 DRS was used to compare first-principle electronic structure and optical properties calculations with scarce experimental data for PuO_2. References for the above review can be found in the Further Reading recommendations below.

For the new results reported here, spectra were recorded with a Cary model 6000i double-beam, rapid-scanning, high-performance UV–Vis–NIR spectrophotometer with an internal DRA-1800 diffuse reflectance attachment. This spectrometer has a spectral range from 175 nm to 1800 nm. Cylindrical quartz or plastic cells 2 centimeters (cm) in diameter and 1.7 cm in length, with a polytetrafluoroethylene (nonstick) plug, were used to contain samples.

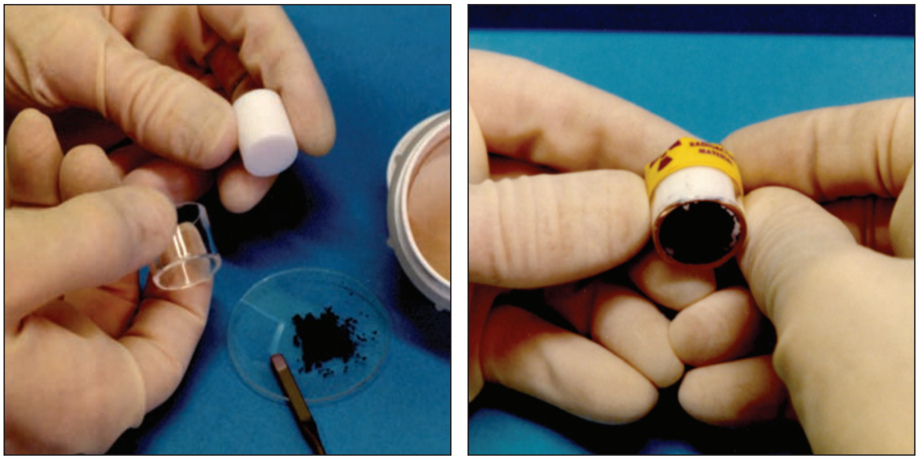
In a glovebox, samples were loaded into the sample cell, which was shrouded in a plastic paraffin shield. Only a thin layer of powder or crystals was required to cover the bottom of the cell. The sample cell was transferred out of the glovebox into a hood, where the plastic paraffin film was carefully removed and the cell handed off to a second worker with clean gloves who taped the cell closed. After a favorable survey for potential contamination, the cell was removed from the hood and stored in a second sealed container pending recording of spectra.



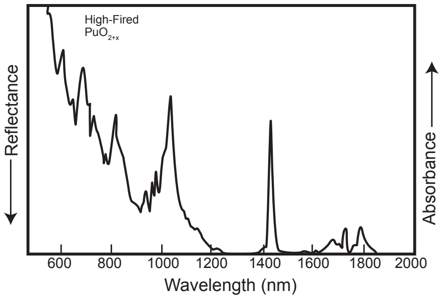
Diffuse reflectance spectra of plutonium(IV) fluoride, sulfate, and oxalate compounds. From “Formation, Characterization, and Stability of Plutonium(IV) Colloid,” D. Hobart, D. Morris, P. Palmer; Los Alamos National Laboratory report LA-UR-87-3504; 1987.



Diffuse reflectance spectrum of high-fired PuO_2 compared with the absorption spectrum of a plutonium(IV) polymer suspension, further confirming the close similarity of these species. “Formation, Characterization, and Stability of Plutonium(IV)-Colloid,” D. Hobart, D. Morris, P. Palmer; *FOCUS 89 Proceedings,* Las Vegas, Nevada; American Nuclear Society, 1989.



Diffuse reflectance cell components (right) and a cell loaded with PuO_2 with a nonstick plug insert that has been taped closed and that is free of contamination on the outside (far right).



High-resolution diffuse reflectance spectrum of non-stoichiometric PuO_2.

Plutonium samples are double-contained except when spectra are recording with single containment. The best DRS spectra are obtained from solid samples that are ground to a fine powder, but good spectra can also be obtained from coarse crystalline samples. In this case, background spectra were recorded using only the polytetrafluoroethylene plug or using white titanium dioxide powder.

In previous work, a plutonium-239 dioxide sample was prepared by precipitating Pu^{4+} from solution with oxalate and then heating the plutonium oxalate filtrate to high temperature in air. This formed a black non-stoichiometric oxide of the general formula PuO_{2+x}. The sample was finely ground and loaded into a DRS cell. The spectral features generally correlated with the solution absorption spectrum of aquo Pu^{4+}, but the DRS f-f transition peaks were much sharper and were split. This confirmed the oxidation state to be tetravalent, and the quality of the spectrum indicated that high-firing had “annealed” the solid into a well-ordered crystallization. This also provided a Pu(IV) oxide reference spectrum for comparison with the DRS of an unknown contaminant or interdicted nuclear materials.

As a suitable surrogate for the present study of plutonium metal corrosion, a small sheet of samarium (Sm) metal was polished and loaded into a DRS cell for analysis. Like plutonium metal, samarium metal is relatively easily oxidized in humid air. Samarium metal oxidizes to the stable, light yellow trivalent sesquioxide Sm_2O_3. The DRS spectra were obtained from polished samarium metal, after the metal was exposed to water-saturated air at room temperature for four days and from a Sm(III) nitrate reference compound. The oxidized metal spectrum had surface oxidation indicated by small peaks around 400 nm and 1000–1400 nm, characteristic of Sm_2O_3.

To study the oxidation behavior and electronic properties of plutonium-239 metal, a small sample of plutonium–gallium (Pu–Ga) alloy weighing approximately 100 milligrams was polished and loaded into a DRS cell. (A small percent of gallium metal in the plutonium alloy has negligible effect on the spectral properties of plutonium.)

The spectrum of the Pu–Ga alloy includes the reflectance spectra of samarium metal. The silver and gold metal reflectance spectra from the literature are included to demonstrate relativistic effects on the electronic structure of heavy elements. Gold is directly below its surrogate element, silver, in the periodic table and has the same electronic configuration as silver. Therefore, the physical-chemical behavior (that is, color and reflectance properties) of gold should be about the same as that of silver.

However, as the electrons of the larger gold atom approach the speed of light (in a "classical planetary" model of electrons orbiting a nucleus), strange things happen, so the properties of gold cannot be directly extrapolated from those of silver. This was demonstrated by the substantial shift in the band-gap peak from about 320 nm for silver metal to about 480 nm for gold metal. Without relativistic effects, these peaks would have been at about the same frequency.

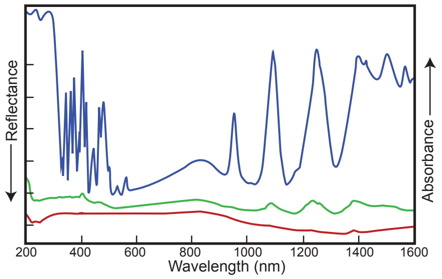
Although the band-gap peaks for samarium and plutonium metals are shifted to the ultraviolet region relative to silver and gold, it is clear that the peak for plutonium metal around 210 nm is shifted somewhat from the estimate of the peak for samarium metal, around 200 nm. (The samarium peak lies close to the ultraviolet cutoff for the instrument.) It should be noted that samarium also has relativistic behavior but not to the same extent as plutonium. The differences in the DRS spectra of silver and gold and of samarium and plutonium metals provide band-gap information that require invoking relativistic effects to explain their chemical differences. Additional research and quantitative analysis of these data are necessary to confirm these results.

DRS is a powerful tool for analyzing and characterizing plutonium solids, particularly when combined with data from other analytical techniques. DRS can provide unequivocal identification of the element, oxidation state, crystal structure, and matrix when compared with known reference spectra. DRS is particularly useful for studying surface oxidation products of plutonium metal and alloys and has applications for characterizing new, unknown, or interdicted plutonium solids.

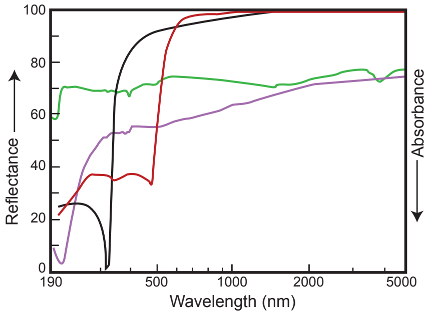
Further reading:

"Formation, Characterization, and Stability of Plutonium(IV) Colloid"; D. E. Hobart, D. E. Morris, and P. D. Palmer; Los Alamos National Laboratory report LA-UR-87-3505, 1987.

"Diffuse Reflectance Spectroscopy of Plutonium Metal, Alloys, and Compounds"; D. E. Hobart, D. S. Peterson, S. A. Kozimor, K. S. Boland, M. P. Wilkerson, and J. N. Mitchell; *Proceedings of the Plutonium Futures—The Science Conference,* Keystone, Colorado; American Nuclear Society Publication, 2010.



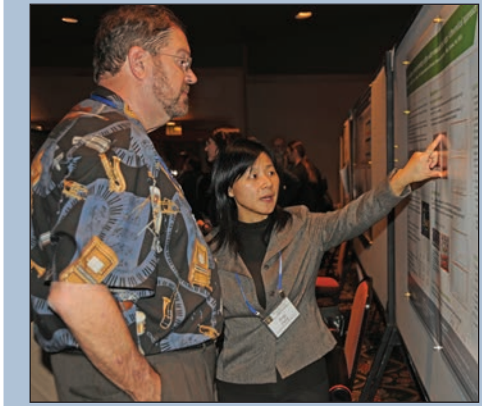
Diffuse reflectance spectrum of polished samarium metal (red), oxidized samarium metal (green), and samarium nitrate reference (blue). Note that the oxidized metal spectrum (green) has surface oxidation indicated by small peaks around 400 nm and 1000–1400 nm, characteristic of Sm_2O_3.



Diffuse reflectance spectra of samarium (green), plutonium (purple), silver (black), and gold (red). The shift in the band-gap absorbance peak between silver and gold and that between samarium and plutonium are evidence of relativistic effects. As a convention for metal reflectance, note that the y-axis has been inverted from previous spectra; reflectance is in the up direction in this figure. Gold and silver spectra adapted from Bob Mellis in *Handbook of Optics,* Vol. 2 (second edition), McGraw-Hill 1994.

FACES & PLACES

Johann Bouchet, CEA Arpajon, France



Rich Martin, Los Alamos National Laboratory, and Ping Yang, Pacific Northwest National Laboratory

Norman Edelstein (left) and Corwin Booth, Lawrence Berkeley National Laboratory

Roberto Caciuffo, Institute for Transuranium Elements, European Commission, Joint Research Center, Karlsruhe, Germany

Alan Handschuh, CEA Cadarache, France

Javier Gaona (left), Karlsruhe Institute of Technology–Institute for Nuclear Waste Disposal, Germany, and Chris Puxley, Atomic Weapons Establishment, Aldermaston, United Kingdom

Habib Latrous (left), University of Tunis, Tunisia, and Dick Haire, retired from Oak Ridge National Laboratory

Asok Ray (left), University of Texas, Arlington, and David Clark, Los Alamos National Laboratory

Faces & Places

Laurent Venault, CEA Marcoule, France

Maria Wallenius, Institute for Transuranium Elements, European Commission, Joint Research Center, Karlsruhe, Germany

Takasada Shibauchi, Kyoto University, Japan

Diyar Talbayev, Yale University

Narek Gharibyan, University of Nevada–Las Vegas

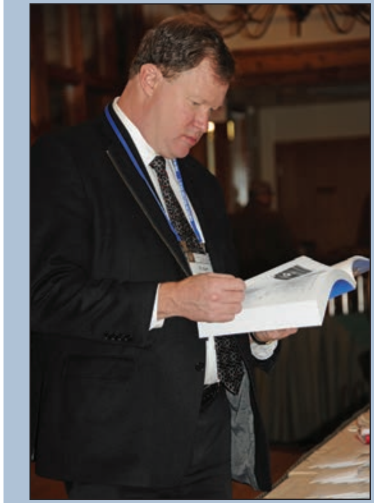
Sven Rudin, Los Alamos National Laboratory

P. R. Vasudeva Rao (left), Indira Gandhi Center for Atomic Research, India, and David Rossin, U.S. authority on nuclear energy technology

From left to right: Francois Delaunay, Philippe Faure, and Catherine Treimany, CEA Valduc, France, and Marie-Helene Nadal, CEA Saclay, France

Richard Wilson (left), Argonne National Laboratory, and Manuel Sturzbecher-Hoehne, Lawrence Berkeley National Laboratory

FACES & PLACES



Robert Hanrahan, U. S. National Nuclear Security Administration

Fuxiang Zhang, University of Michigan

David Clark (left), Los Alamos National Laboratory, and Nikolai Ponomarev-Stepnoy, Kurchatov Institute, Russia

Dominique Warin (left), CEA Marcoule, France, and Emory Collins, Oak Ridge National Laboratory

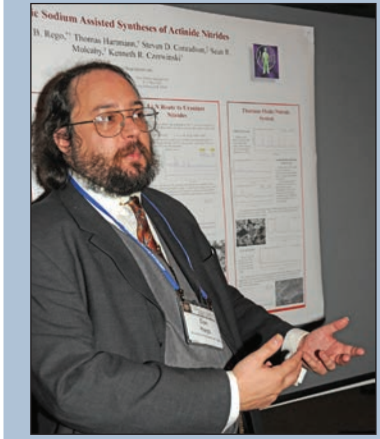
Shinsaku Kambe, Japan Atomic Energy Agency

Rebecca Flint, Rutgers University

FACES & PLACES

Kevin Moore, Lawrence Livermore National Laboratory

Trevor Hayton, University of California–Santa Barbara



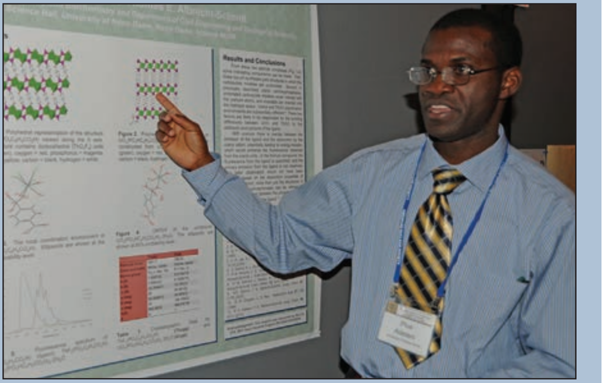
Dan Rego, University of Nevada–Las Vegas

Mark Sarsfield, National Nuclear Laboratory, Sellafield, United Kingdom

Tarik Saleh, Los Alamos National Laboratory

Carter "Buzz" Savage, U.S. Department of Energy

Olga Batuk (left), Los Alamos National Laboratory, and Annie Kersting, Lawrence Livermore National Laboratory

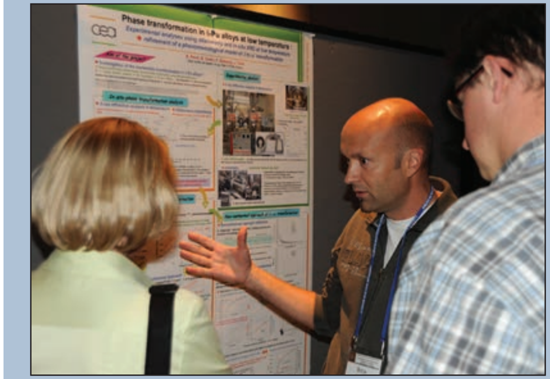


Pius Adelani, University of Notre Dame

Zhicheng Zhang (left), Washington State University, and Herman Cho, Pacific Northwest National Laboratory

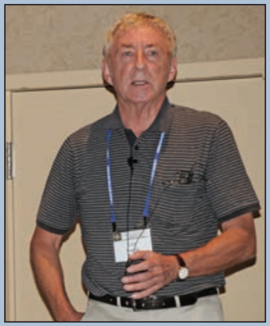
FACES & PLACES

Igor Izosimov, Khlopin Radium Institute, Russia, and Lidia Timofeeva, Bochvar All-Russian Scientific Research Institute for Inorganic Materials



Brice Ravat (center), CEA Valduc, France

Geoff Allen (left), University of Bristol, United Kingdom, and David Geeson, Atomic Weapons Establishment, Aldermaston, United Kingdom



Lou Vance, Australian Nuclear Science and Technology Organization

Clemens Walther, Karlsruhe Institute of Technology–Institute for Nuclear Waste Disposal, Germany

Christophe Jegou, CEA Marcoule, France

Thomas Fanghanel (left), Institute for Transuranium Elements, European Commission, Joint Research Center, Karlsruhe, Germany, and Herman Cho, Pacific Northwest National Laboratory

Vijay Manchanda (left), Bhabha Atomic Research Center, India, and Sean Reilly, Los Alamos National Laboratory

Tom Ricketts (left), Steve Schreiber (center), and John Berg, Los Alamos National Laboratory

End Notes

The Chemistry of the Actinide and Transactinide Elements

Editors Announce Publication of CATE Volume 6

Norman Edelstein of Lawrence Livermore National Laboratory, Jean Fuger of Belgium's University of Liege, and Lester Morss, recently retired from the Department of Energy, were on hand at Plutonium Futures to announce the publication of Volume 6 of *The Chemistry of the Actinide and Transactinide Elements (CATE)*. The three gentlemen served as editors for the new volume, as well as for the five-volume *CATE,* third edition, which premiered at the Plutonium Futures 2006 conference in Pacific Grove, California. The current six-volume set is considered the fourth edition; Springer publishes both it and the third edition.

Joseph Katz and Glenn Seaborg edited the first edition of *The Chemistry of the Actinide Elements,* which was published in 1957. Katz, Seaborg, and Morss (who was with Argonne National Laboratory at the time) edited the second edition, which was published in 1986. Planning for the third edition, now including the transactinide elements, began about 1996, and Seaborg and Katz expected to be among its editors, according to Morss. However, active writing and editing didn't begin until 2000, the year after Seaborg's death, and required six years. Katz was named honorary editor of the third edition. Planning for Volume 6 began in 2006 in collaboration with Springer Publishing editor Sonia Ojo, just after Volumes 1–5 were published. Writing and editing of Volume 6 occurred from 2007 through July 2010.

Volume 6 contains eight chapters covering a wide range of topics. Several of the authors were in attendance at Plutonium Futures 2010. Titles of the new chapters and their authors are as follows:

Chapter 32: "Actinides in the Geosphere," Wolfgang Runde and Mary P. Neu

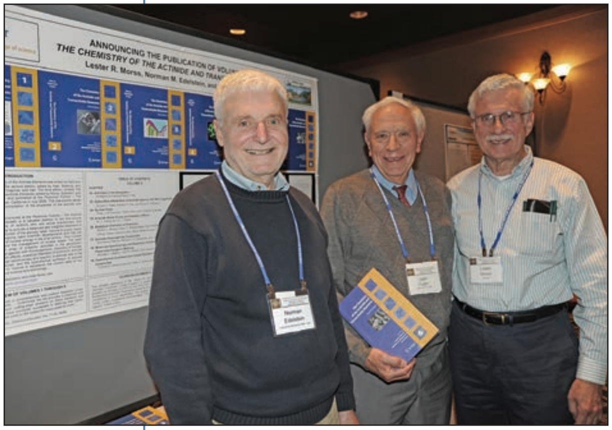
Chapter 33: "Subsurface Interactions of Actinide Species with Microorganisms," Donald T. Reed, Randhir P. Deo, and Bruce E. Rittmann

Chapter 34: "Nuclear Fuels," Rudy J. M. Konings, Thierry Wiss, and Christine Guéneau

Chapter 35: "Actinide Waste Forms and Radiation Effects," R. C. Ewing and W. J. Weber

Chapter 36: "Analytical Chemistry of Plutonium," Kenton J. Moody, Dawn A. Shaughnessy, Karin Casteleyn, Herbert Ottmar, Klaus Lützenkirchen, Maria Wallenius, and Thierry Wiss

Chapter 37: "Actinide Chalcogenide Compounds," Emmanouil Manos, Mercouri G. Kanatzidis, and James A. Ibers

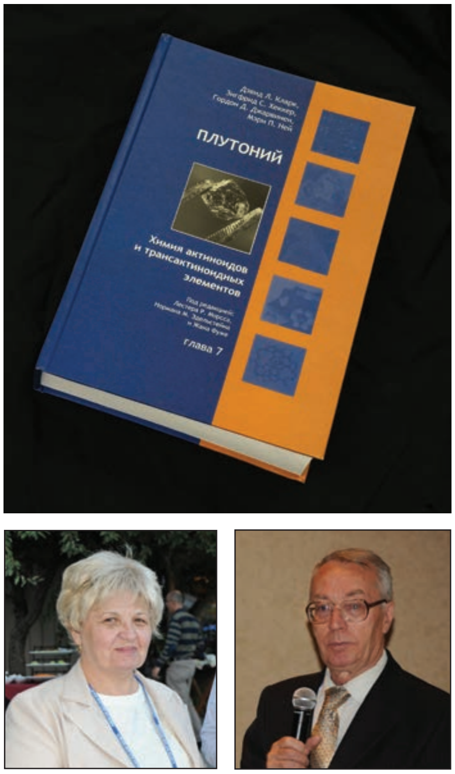


Norman Edelstein (left), Jean Fuger (center), and Lester Morss announced the publication of Volume 6 of The Chemistry of the Actinide and Transactinide Elements *at a poster session.*

Chapter 38: “Molecular Spectroscopy and Reactions of Actinides in the Gas Phase and Cryogenic Matrices,” Michael C. Heaven, John K. Gibson, and Joaquim Marçalo

Chapter 39: “Hydrothermal Synthesis and Crystal Structures of Actinide Compounds,” Thomas E. Albrecht-Schmitt, Peter C. Burns, and Sergey V. Krivovichev.

When asked if the editors were planning additional volumes, Morss said, “Younger actinide scientists may initiate a new edition of *CATE* someday, but editors Morss, Fuger, and Edelstein do not plan a fifth edition.”



CATE Chapter 7, “Plutonium” (top), has been translated into Russian by Lidia Timofeeva (above left) and Boris Nadykto (above right).

CATE “Plutonium” Chapter Translated into Russian

Lidia Timofeeva and Boris Nadykto have edited and translated Chapter 7, “Plutonium,” of *CATE,* third edition, into Russian. Both Timofeeva and Nadykto presented talks at Plutonium Futures 2010. Timofeeva is with the Bochvar All-Russian Scientific Research Institute for Inorganic Materials (VNIINM). Nadykto is with the Russian Federal Nuclear Center–All-Russian Scientific Research Institute of Experimental Physics (RFNC–VNIIEF). The chapter was authored by Los Alamos researchers David L. Clark, Gordon Jarvinen, Mary Neu, and director emeritus Siegfried Hecker and appears in Volume 2.

Russian readers are familiar with the first two editions of the handbook (1957 and 1986), which were translated into Russian in 1960 and 1991–1999, respectively. The introduction to Chapter 7, written by Timofeeva and Nadykto and translated from the Russian, reads in part as follows:

> *The publication of Chapter 7 in Russia is beneficial to the local scientific community in a number of ways. Plutonium is a substance of critical importance for both the nuclear energy and nuclear weapon programs. Being produced in a number of countries all over the globe, plutonium remains the most common artificial element (thousands of tons), whose world stocks are steadily growing by approximately 90 tons a year.*
>
> *Just as everywhere in the world, there is great interest in Russia in nuclear energy and problems related to the usage of plutonium, preparation of new plutonium alloys, storage, and radioactive waste management, which require development of new scientific technologies based on fundamental knowledge.*

Timofeeva and Nadykto acknowledge Springer Science+Business Media for providing the license to publish the chapter in Russian; authors Clark, Hecker, Jarvinen, and Neu for their help in preparing the Russian edition; and the staff of the VNIIEF Publishing House for their work on the book. The Russian editors also acknowledge L. V. Mazan for preparing the monograph, and I. D. Goncharov (Ph.D. in chemistry), T. V. Kazakovskaya (Ph.D. in engineering), and D. E. Pozdyaev (Ph.D. in chemistry) for reading separate parts of the book and making valuable comments to improve the quality of the translation.

Best Poster Wins CATE Volumes; Four Other Posters Also Win Awards

In keeping with tradition, the conference closed with recognition of student and postdoc poster awards. The grand-prize winner, Shuao Wang, University of Notre Dame, received the six-volume set of *CATE*. Wang was co-author of the poster "New Insights into Actinide (U, Np, Pu) Borate Materials Relevant to Nuclear Waste Storage." (See article beginning on page 24.) Four additional students/postdocs were recognized for their posters and received autographed copies of Pulitzer Prize–winning author Richard Rhodes's new book *The Twilight of the Bombs*.

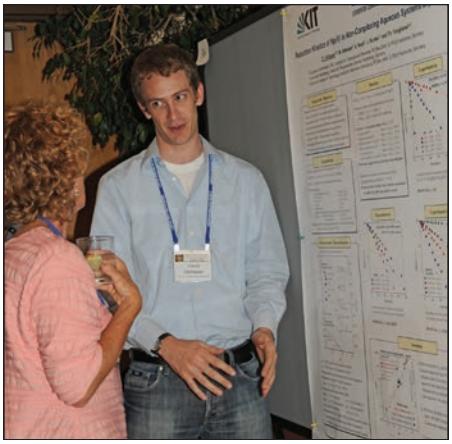
The four, and their posters, are Stefan Minasian, a current Seaborg Institute postdoc at Los Alamos National Laboratory, "A Spectroscopic Technique to Explore Covalency in Actinide-Oxygen, Bonds"; David Fellhauer of the Institute for Transuranium Elements, Germany, "Reduction Kinetics of Np(V) in Non-Complexing Aqueous Systems at pH 5–10"; Andrea Alsobrook of the University of Notre Dame, "Cubic and Rhombohedral Heterobimetallic Networks Constructed from Uranium, Transition Metals, and Phosphonoacetate"; and Paul Tobash, a former Seaborg Institute postdoc and now a staff member at Los Alamos National Laboratory, "Physical Properties of the New Intermetallic Compound $Pu_2Ni_3Si_5$."

Shuao Wang (right) discusses his grand prize–winning poster with Albert Migliori (left) of Los Alamos National Laboratory and P. R. Vasudeva Rao of the Indira Gandhi Center for Atomic Research.

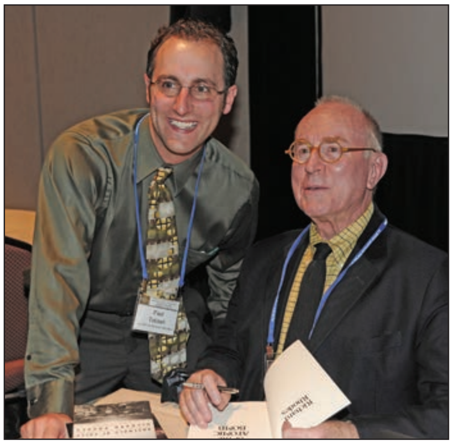
Andrea Alsobrook has a rapt listener in John Auxier of Los Alamos National Laboratory.

AUTHOR RICHARD RHODES DELIVERS BANQUET ADDRESS

Pulitzer Prize–winning author Richard Rhodes delivered the banquet speech on the last evening of the conference. Rhodes discussed his latest book, *The Twilight of the Bombs: Recent Challenges, New Dangers, and the Prospects for a World without Nuclear Weapons.* The book is the fourth and final volume in his

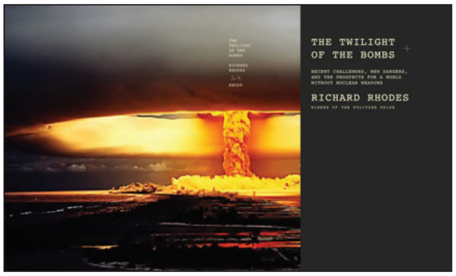


David Fellhauer explains his research to Annie Kersting of Lawrence Livermore National Laboratory.



Paul Tobash (left) gets an autograph from Pulitzer Prize–winning author Richard Rhodes.

Stosh Kozimor (left) of Los Alamos National Laboratory discusses a fine point with Stefan Minasian.



Top: The jacket of Richards Rhodes's latest book. Middle: Claude Guet (left), Sig Hecker (center), and Richard Rhodes have a moment of conversation after Rhodes's speech. Bottom: During dessert, banquet diners scaled Mount Chocolate—an artistic confection of chocolate genoise and raspberry mousse capped by a snow-white peak.

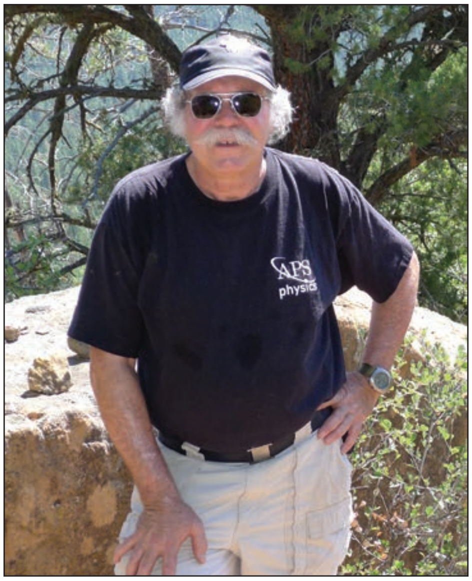
nuclear history series; the other three volumes are *The Making of the Atomic Bomb,* which won a Pulitzer Prize in nonfiction; *Dark Sun: The Making of the Hydrogen Bomb;* and *Arsenals of Folly: The Making of the Nuclear Arms Race.* Rhodes was making a return appearance at Plutonium Futures; he was the banquet speaker at the inaugural conference in 1997 in Santa Fe, New Mexico.

MIGLIORI NAMED LOS ALAMOS SEABORG INSTITUTE DIRECTOR

Albert Migliori has been named director of the G. T. Seaborg Institute at Los Alamos National Laboratory. He received his Ph.D. in condensed matter physics from the University of Illinois at Urbana-Champaign in 1973 and has spent his entire career at Los Alamos, most recently as a staff member in Condensed Matter and Magnet Science (MPA-CMMS). Gordon Jarvinen will continue serving as Seaborg Institute associate director.

"In my thirty-seven-year career at a single national laboratory, I have focused on scientific problems that for the most part required team building and collaborations that span more technical capabilities than the typical single-investigator project might involve," said Migliori. "This is the tremendous personal attraction that a national laboratory has for me and is an essential quality of the Seaborg Institute."

Because the science of renewable and nuclear energy and of safeguarding nuclear weapons is a national priority, Migliori sees the need for collaboration even more strongly. "The Seaborg Institute is positioned to provide substantial guidance for future directions of actinide science at Los Alamos, and it is my great honor to have been given the opportunity to direct those efforts," Migliori continued. "I look forward to working with all the people who have made the Seaborg Institute so valuable to the nation."



Albert Migliori

Hoffman Receives Seaborg Actinide Separations Award

Darleane Hoffman

Darleane Hoffman of Lawrence Berkeley National Laboratory's (LBNL) Nuclear Science Division and professor emerita, Department of Chemistry, UC Berkeley, has been awarded the 2011 Glenn T. Seaborg Actinide Separations Award.

The award, established in 1984, recognizes outstanding and lasting contributions to the development and application of actinide separation processes and methodology. It is presented at the annual Actinides Separations Conference. The award is named for Glenn Seaborg, co-discoverer of nine actinide elements, who was the first recipient of the award.

Hoffman's career has spanned the disciplines of nuclear chemistry, actinide and transactinide chemistry, radiochemistry, environmental chemistry radionuclide migration, atom-at-a-time chemistry, and actinide separation science. Her "scientific and educational achievements and public service bear witness to a career of remarkable innovation, insight, and sustained contributions," according to a published announcement.

Hoffman is the first woman to receive the award. She was the charter director of the Seaborg Institute at Lawrence Livermore National Laboratory (see "History of the Seaborg Institute," *Actinide Research Quarterly* 2nd Quarter, 2009) and is a former researcher and division leader at Los Alamos National Laboratory.

"It was a special honor for me to receive the Seaborg Award because I shall never forget what a wonderful mentor he [Seaborg] was for me when I left my position as division leader at Los Alamos in 1984 to become professor of chemistry at Berkeley and leader of the Heavy Element Nuclear and Radiochemistry Group at LBNL," said Hoffman.

"I was well acquainted with the national laboratory system but not with the university campus," Hoffman continued. "Prof. Seaborg introduced me to the campus community and colleagues there, advised me on committee assignments, took me with him to important meetings, and at the reception for new graduate students, suggested they join my newly forming group. In spite of his legendary accomplishments, he always found time for discussions on current topics and remained a cherished advisor and friend until his death in 1999."

Gordon Jarvinen, associate director of the Seaborg Institute at Los Alamos and scientific editor of *Actinide Research Quarterly,* received the award in 2008 for his innovative research on processes that can be used to recycle plutonium and other actinides.

Global Roundtable

Experts from around the world participated in a roundtable discussion of the future of nuclear energy and concerns about the spread of nuclear weapons. Panelists (shown below clockwise from upper left) included Nikolai Ponomarev-Stepnoy, Kurchatov Institute, Russia; Maegon Barlow, U.S. Department of Energy; Claude Guet, CEA Headquarters, France; and Vijay Manchanda, Bhabha Atomic Research Center, India. Sig Hecker of Stanford University served as the moderator.

Plutonium Futures
The Science 2012

July 15–20, 2012, University of Cambridge, UK

Plutonium Futures—the Science 2012 will be held in Cambridge, United Kingdom, and is the seventh in a series of open conferences established by the US national laboratories. The organizers of the 2012 conference are AWE, CEA, the ITU, and the UK's NNL.

This series of conferences provides an international forum for the presentation and discussion of current research on the physics, chemistry, and materials science of plutonium and other actinide elements, with an emphasis on the fundamental properties and behaviors of plutonium and their technological consequences.

Conference topics will include:

- condensed matter physics
- detection and analysis
- materials science
- nuclear fuel cycle
- environmental behavior

Timeline:

Second announcement/ call for abstracts:	November 15, 2011
Registration open:	November 15, 2011
Abstract deadline:	January 13, 2012
Early registration deadline:	April 13, 2012
Registration deadline:	May 18, 2012

www.PuFutures2012.co.uk

AWE

cea

energie atomique • energies alternatives

itu Institute for Transuranium Elements

National Nuclear Laboratory

ACTINIDE RESEARCH QUARTERLY
is published by Los Alamos
National Laboratory

ACTINIDE RESEARCH QUARTERLY
is a publication of the
Plutonium Science and Manufacturing
Directorate (ADPSM).
The directors of the Seaborg Institute for
Transactinium Science serve as the magazine's
scientific advisors. *ARQ* highlights progress
in actinide science in such areas as process
chemistry, metallurgy, surface and separation
sciences, atomic and molecular sciences,
actinide ceramics and nuclear fuels,
characterization, spectroscopy, analysis,
and manufacturing technologies.

Address correspondence to
Actinide Research Quarterly
c/o Meredith Coonley
Mail Stop E532
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.

Phone (505) 667-0392
Fax (505) 665-7895

PSM Associate Director, acting
Timothy George

Plutonium Science Strategy Leader
David L. Clark

Scientific Advisors, Seaborg Institute
Gordon D. Jarvinen
Albert Migliori

Guest Editor
David E. Hobart, C-AAC

Editor
Meredith S. Coonley, IRM-CAS

Contributing Editor
Eileen Patterson, IRM-CAS

Designer
Kelly L. Parker, IRM-CAS

Photography
Mick Greenbank, IRM-RMMSO

Photo Support
Joe Riedel, IRM-RMMSO
Susan Ramsay, Institutes Office

Printing Coordinator
Lupe Archuleta, IRM-RMMSO

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396.

LALP-11-028

Los Alamos
NATIONAL LABORATORY
EST. 1943