ACTINIDE RESEARCH QUARTERLY

Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

First Quarter 2020

COMMEMORATIVE ISSUE

9 ARTICLES FROM THE ARCHIVES

Foreword

This quarter we are celebrating the 25th anniversary of Actinide Research Quarterly. The publication was established in 1995 by the former Nuclear Materials Technology Division of TA-55 at Los Alamos National Laboratory (LANL), before later becoming part of the Glenn T. Seaborg Institute and the National Security Education Center. A total of 64 issues have been produced, covering the full spectrum of topics related to actinide science and research, including contributions from esteemed scientists such as Glenn Seaborg and Siegfried Hecker. This back catalog is available electronically at www.lanl.gov/arq.

On this occasion, we thought this would be a great opportunity to look back and reprint a selection of articles from the past 25 years that represent a wide cross-section of topics from the archives. Several of these articles describe projects or policies which are ongoing, and therefore we have provided short updates that bring the reader up-to-date on current developments, where appropriate.

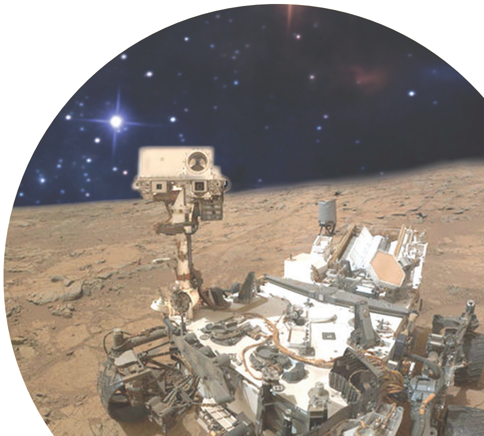
Our anniversary issue begins with a historical article from 1997, "Source of the Actinide Concept," in which the late Glenn Seaborg recounts the discovery and naming of the actinide elements. Another piece of remarkable history is recounted in 2005, "From Heat Sources to Heart Sources," which describes the technological use of plutonium as a heat source in pacemakers. The restoration of Rocky Flats in Colorado, as part of the bigger remediation of the Department of Energy weapons complex, was the focus of ARQ First Quarter 2006—a portion of this issue is reproduced in an abbreviated form on p10.

One of our most popular issues over the years has proven to be the 2007 Fourth Quarter, which brought the field of nuclear forensics into the spotlight. The cover story from this issue, "CSI: Karlsruhe," is included on p18. Joseph Martz contributed a valuable piece on capability-based nuclear deterrence in 2011 and taken from the same issue, the late Lester Morss wrote an authoritative 7000 word history of US-based actinide research, essential reading for any actinide scientist today.

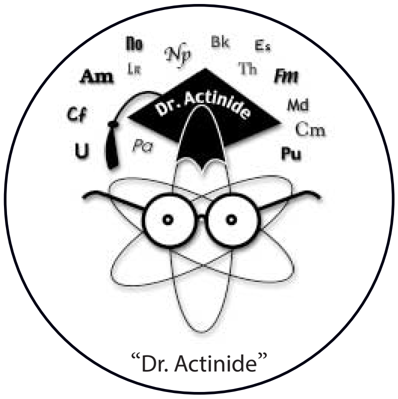
A 2012 article by Doug Kautz and David Gubernatis illuminates the issue of "swarfology," or waste turnings during the machining of radioactive metals as it relates to the Lab mission. The role of plutonium in extra-terrestrial planetary exploration is introduced by Amanda Bean in an article from 2013 on the Mars Curiosity Rover. Finally, a 2015 article by Albert Migliori and Franz J. Freibert, the previous and current directors of the Seaborg Institute, respectively, discuss the history of the notoriously complex and important issue of elemental plutonium's many crystal structures.

Owen Summerscales *Editor*

Contents



25 Years of ARQ



“Dr. Actinide”

Winter 1994

Los Alamos National Laboratory • A U.S. Department of Energy Laboratory

The Actinide Research Quarterly
of the Nuclear Materials Technology Division

In This Issue

1 Introducing The Actinide Research Quarterly

2 NMT Develops Acid Recycling Process

3 Milliwatt Surveillance Program Ensures RTG Safety and Reliability

4 Low Temperature Sublimation Separation

6 NMT Division Science and Technology Assessment

7 Recent Publications and Reports

8 Newsmakers
-LDRD Funding
-Staff Member completes Ph.D.
-NMT Top Three Technical Accomplishments for 1994

Introducing
The Actinide Research Quarterly

My first year as Division Director has been a challenging yet rewarding experience. Although the Division has faced many challenges, I am gratified by the “can do” attitude our personnel continually exhibit. The foundation of NMT Division's science and technology excellence is our capabilities of actinide process chemistry, plutonium metallurgy, surface and separation sciences, actinide ceramics, actinide characterization and analysis, and manufacturing technologies. This new periodical is aimed at communicating NMT's technical progress to TA-55 workers, to peers at Los Alamos, and to customers.

Our latest NMT Division Science and Technology Assessment, just completed in October, is proof of the enormous scientific and technological resources within our Division. Several examples from the Division Review are highlighted in this issue.

K.C. Kim, NMT's chief scientist, has agreed to coordinate and edit *The Actinide Research Quarterly*. I encourage all NMT employees to contribute news items, recent publication titles, and any other materials that will keep our publication informative and interesting.

RB93-059-01

Bruce Matthews, Director of NMT Division

B1883-25

Professor Darryl DesMarteau, an External Review Committee member from Clemson University, discusses a poster presentation with Pam Benicewicz.

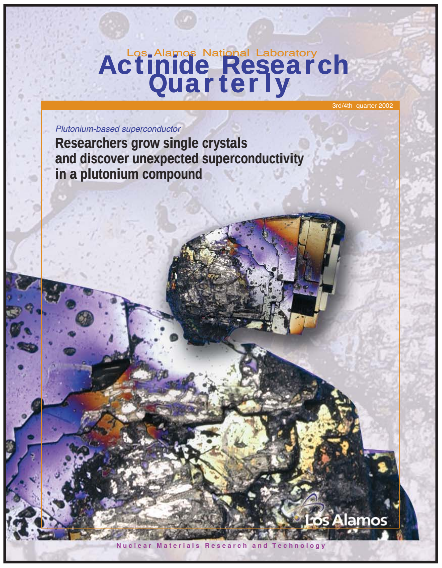
Nuclear Materials Technology Division/Los Alamos National Laboratory 1

The first issue front cover of "The Actinide Research Quarterly", winter 1994/1995.

1995 The publication is established by the former Nuclear Materials Technology (NMT) Division of TA-55 at Los Alamos National Laboratory (LANL). K.C. Kim served as its first scientific editor. *“The Actinide Research Quarterly is published to highlight recent achievements and ongoing programs of the NMT division.”*

1997 Themes in the late 90s include stockpile reduction and opening up the previously secretive Laboratory to the media. The late Glenn Seaborg contributed an exclusive article *“Source of the Actinide Concept,”* reproduced here on p4. The same year, the Glenn T. Seaborg Institute was established at LANL; David L. Clark was named as its inaugural director. The Plutonium Futures conference series was established in a collaboration between LANL and the American Nuclear Society. ARQ continues to communicate highlights from this biennial series. “Dr. Actinide” character appears in rhetorical interviews with K.C. Kim.

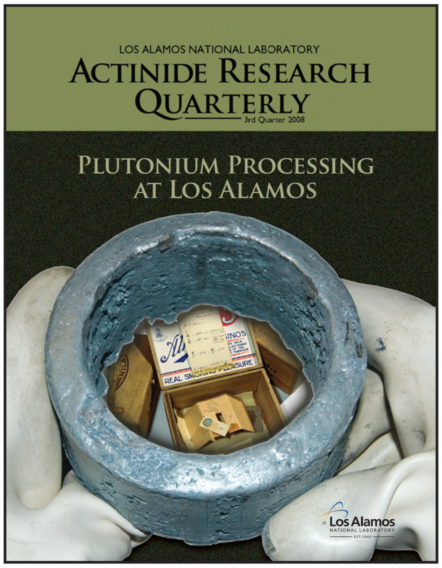
2001–02 Meredith “Suki” Coonley assumes position of editor and brings a more people-focused approach. The publication undergoes a facelift with color photography and earns several awards from the Society of Technical Communications.



Los Alamos National Laboratory
Actinide Research Quarterly
3rd/4th quarter 2002

Plutonium-based superconductor
Researchers grow single crystals and discover unexpected superconductivity in a plutonium compound

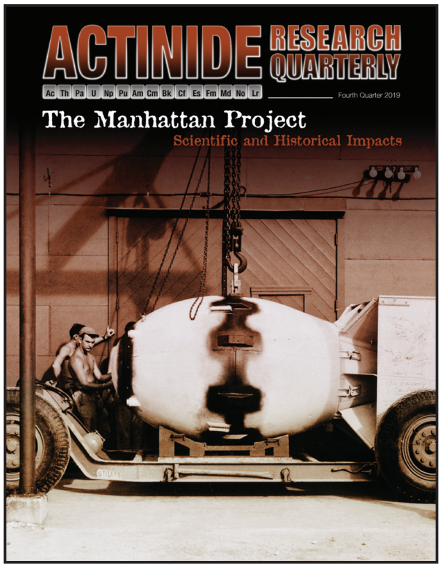
Los Alamos
Nuclear Materials Research and Technology



LOS ALAMOS NATIONAL LABORATORY
ACTINIDE RESEARCH QUARTERLY
3rd Quarter 2008

PLUTONIUM PROCESSING AT LOS ALAMOS

Los Alamos NATIONAL LABORATORY



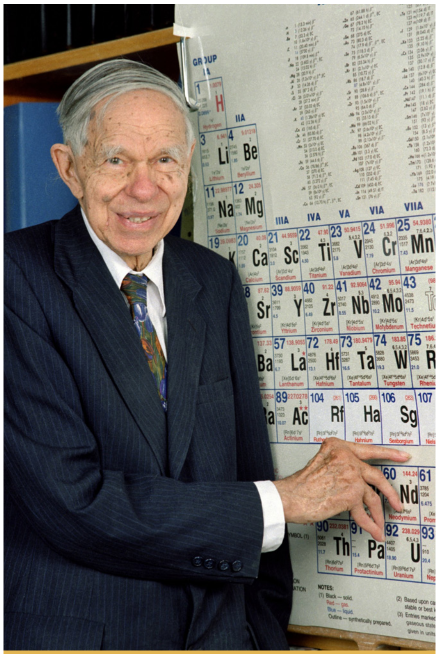
ACTINIDE RESEARCH QUARTERLY
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Fourth Quarter 2019

The Manhattan Project
Scientific and Historical Impacts

2007 The quarterly editions begin to move away from internal and news-based subjects and focus on bigger topics in the actinide research world. An edition devoted to nuclear forensics proves to be one of our most successful issues. One of the featured articles, *"CSI: Karlsruhe,"* is reproduced on p18.

2019 The popular Fourth Quarter issue covered a recent student symposium on the Manhattan Project held at LANL. It included a range of both historical and contemporary topics by notable scientists such as Siegfried Hecker and James Smith, and featured recently-declassified photographs from the era.

2010–13 A series of retrospective articles are a few of the treasures to be found in a set of quarterlies from this period. A collection of reminiscences from the early days of LANL is collated in the Second Quarter 2010, from the INC-4 reunion conference. Lester Morss recounts the history of actinide science in a detailed article from the First Quarter 2011, and a collection of heartfelt remembrances of Bob Penneman, a "legendary Los Alamos chemist," are found in the First Quarter 2013.



ARQ Second Quarter 1997:

"This issue of the Actinide Research Quarterly is blessed with the guest article "Source of the Actinide Concept" by Dr. Glenn Seaborg. One could not ask for a more significant and timely introduction to the "Plutonium Futures—The Science" conference than the personal perspective of the discoverer of the element. The Santa Fe conference will also feature Dr. Seaborg's plenary lecture videotaped in April this year. In reminiscing about the past and anticipating the future, we hope that this conference helps to herald a new beginning in the future science of actinides.

– K. C. Kim"

ARQ SECOND QUARTER 1997

Source of the Actinide Concept

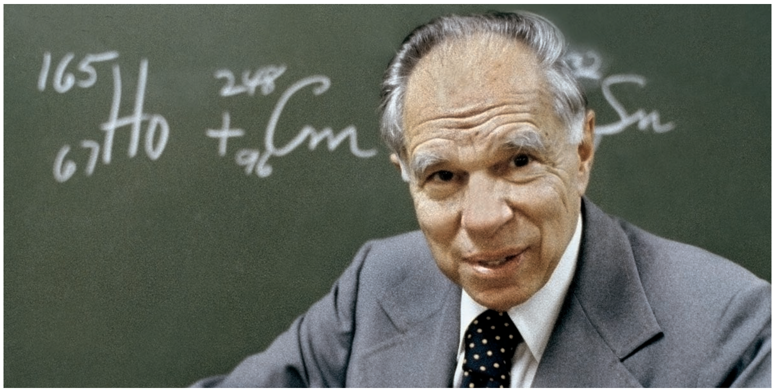
Glenn T. Seaborg

My romance with the transuranium elements started 63 years ago, in 1934, soon after I became a chemistry graduate student at the University of California, Berkeley. These were the undiscovered elements with atomic numbers greater than 92 (the atomic number of uranium), the heaviest naturally occurring element.

We (the transuranium elements and I) were first introduced at the weekly chemistry seminar on nuclear science held in venerable Gilman Hall. Actually, I was introduced to what were thought to be the transuranium elements. I read articles by Enrico Fermi and coworkers about the induced radioactivities observed when elements such as uranium were bombarded with neutrons. Since some were published in their native Italian, they were a challenge to decipher.

These induced radioactivities were, of course, produced in trace (unweighable) quantities, so radiochemistry methods were needed. For guidance, researchers predicted the chemical properties using the periodic table as it was then known. The heaviest natural elements, thorium, protactinium, and uranium (atomic numbers 90, 91, and 92), were placed in that table just below the sixth-period "transition elements"—hafnium, tantalum, and tungsten (in these elements, the "5d" electron shell is being filled). Thus it was assumed that the 6d electron shell was being filled in these heaviest elements, and the chemical properties of the transuranium elements, the undiscovered elements 93, 94, 95, and 96, would be homologous with the 5d elements immediately above them in the periodic table, rhenium, osmium, iridium, and platinum. The limited chemical identification experiments of Fermi and coworkers seemed consistent with this view. The work of Otto Hahn, Lise Meitner, and Fritz Strassman in Berlin seemed to further confirm it. Little did we know then how we were being misled by accepting what was easiest to accept. I bought this interpretation "hook, line, and sinker." In the fall of 1936, I described the work and interpretation of Otto Hahn and coworkers during a required graduate student talk to the chemistry faculty, staff, graduate students, and visiting scientists.

Then in January 1939, the bubble burst! At the physics journal club meeting, we heard something extraordinary. Niels Bohr, who had arrived in New York the previous week, brought news from Otto Hahn's laboratory that the neutron-bombardment of uranium produced isotopes of light elements, like barium and lanthanum. The meaning was simple: the uranium had been split approximately in half, and all the radioactive "transuranium" isotopes studied by Hahn, Strassman, and Meitner during the previous four years were actually isotopes from the middle of the periodic table. This was exciting! After the seminar, I walked the Berkeley streets for hours, chagrined that I hadn't recognized that the "transuranium elements" in which I had been so interested were nothing of the kind. I felt stupid for failing to admit the possibility. Subsequent work showed that the radioactivities that had been ascribed to transuranium elements were actually due to fission products!



“ This bold revision of the periodic table was a hard sell. When I showed it to some world-renowned inorganic chemists, I was advised not to publish it—such an act would ‘ruin my scientific reputation’. ”

With poetic justice, the actual discovery of the first transuranium element resulted from experiments aimed at understanding the fission process. In 1940, Edwin M. McMillan and Philip H. Abelson showed that a radioactive product of the bombardment of uranium with neutrons was an isotope of element 93, with a mass number 239 ($^{239}93$). The isotope $^{239}93$, a negative beta-particle emitter, should decay to the product $^{239}94$, but they were unable to observe this daughter product because of its long half-life.

McMillan then started looking for a shorter-lived isotope of element 94 through the deuteron bombardment of uranium. When McMillan was called to MIT for war work, I continued this quest with the help of my graduate student Arthur C. Wahl and another instructor in chemistry at Berkeley, Joseph W. Kennedy. We succeeded on the night of February 23–24, 1941, in chemically identifying (i.e., discovering) element 94 (the isotope $^{239}94$) in room 307, Gilman Hall (designated as a National Historic Landmark on the 25th anniversary of the discovery). Most importantly, we found that the chemical properties of element 94 weren’t like those predicted from the periodic table of that time (i.e., not like osmium), but were chemically similar to uranium. Joined by physicist Emilio Segrè, we soon identified $^{239}94$ and, most importantly, demonstrated that it was fissionable by slow neutrons.

Following McMillan’s suggestion for naming element 93 “neptunium” (after Neptune, the first planet beyond Uranus), with the chemical symbol Np, Wahl and I suggested “plutonium” (after Pluto, the next planet) for element 94. We first debated whether the name should be “plutium” or “plutonium,” the sound of which we liked better. Although the chemical symbol might have been “Pl,” we liked the sound of “Pu,” for the reason you might suspect, and therefore decided on “Pu.”

I had the pleasure of meeting for the first time Clyde Tombaugh, the discoverer of the planet Pluto, in Albuquerque, New Mexico, on June 9, 1991. At that time, he told me he had also considered naming his planet after the Greek god Cronus or Roman goddess Minerva (rather than after Pluto). In that case, I suppose we would have given element 94 the name “cronium” or “minervium,” and therefore, people throughout the world would never have heard the word “plutonium” which is so much in the news today.

The chemical properties of neptunium and plutonium were found to be similar to those of uranium and quite unlike those of rhenium and osmium, which, according to the existing periodic table, they should have resembled. Thus we concluded that a new series of 14 rare-earth-like elements, starting at uranium, would be the "uranide" (uranium-like) series, just as the 14 rare-earth elements were known as the "lanthanide" (lanthanum-like) series. Wrong again!

Soon after Pearl Harbor and the U.S. entry into World War II, I moved to the wartime Metallurgical Laboratory of the University of Chicago. Here, we solved many of the problems attendant with plutonium-239 production, and I turned my attention to the quest for the next two transuranium elements, 95 and 96. I was joined in the endeavor by my colleagues Albert Ghiorso, Ralph A. James, and Leon O. (Tom) Morgan. But when we predicted the chemical properties on the basis of the "uranide" concept, we failed to make any identification of our transmutation products. We weren't successful until I suggested that we needed a bold revision of the periodic table in order to make correct predictions of the chemical properties of elements 95 and 96. I wrote a secret report in July 1944, suggesting that thorium, protactinium, and uranium be removed from the body of the periodic table and placed as the beginning of a "transition" series, analogous to the lanthanide (rare-earth) elements, in a separate row at the bottom.

Thus the 14 elements beginning with thorium (elements 90–103), would become the "actinide" elements (by analogy with the "lanthanide" elements). They would then show the necessary element-by-element analogy with the lanthanide elements (58–71). Thus element 95 would be chemically similar to the lanthanide element europium (63) and element 96 would be chemically similar to gadolinium (64). Using this concept, in 1944 and 1945, we synthesized and chemically identified elements 95 and 96, by analogy with their rare earth homologues, europium (63) and gadolinium (64). The new elements were subsequently named americium (95) and curium (96) by analogy with the naming of their homologues.

This bold revision of the periodic table was a hard sell. When I showed it to some world-renowned inorganic chemists, I was advised not to publish it—such an act would "ruin my scientific reputation." However, I did publish it after the war, and it became a guide for the chemical identification of most of the subsequent members of the actinide series. The series was predicted to end at element 103, and the subsequent investigations confirmed this. At element 104 (now known as rutherfordium), we jumped back up to the body of the periodic table, and rutherfordium took its place under hafnium (element 72). (This spot had been occupied by thorium before I moved it to a separate row at the bottom of the periodic table). Then we proceed across the periodic table along now-known elements 105–112, to undiscovered elements 113–118; element 118 will be a noble gas.

This form of the periodic table is accepted throughout the world and is now ubiquitous in wall charts and chemistry books. I am, needless to say, proud that US chemists recommended that element 106, which is placed under tungsten (element 74), be called "seaborgium." I am looking forward to the day when chemical investigators will refer to such compounds as seaborgous chloride, seaborgic nitrate, and perhaps, sodium seaborgate. Fortunately, this name, after initial rejection, is now being accepted by the Commission on Nomenclature on Inorganic Chemistry of the Union of Pure & Applied Chemistry (IUPAC). This, then, is a brief account of the origin of the actinide concept for the placement of the fourteen elements beyond actinium (atomic numbers 90–103) in the periodic table.

ARQ FIRST QUARTER 2005

From Heat Sources to Heart Sources

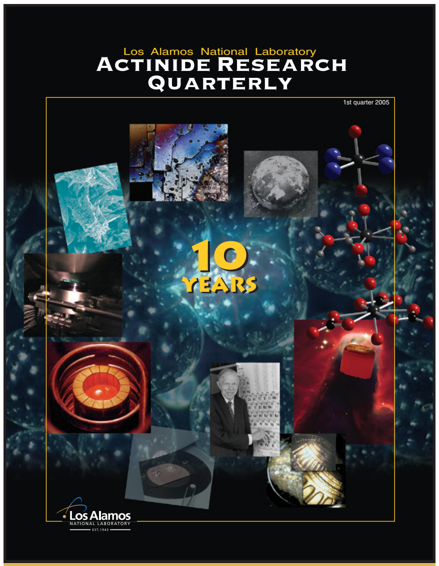
Kathy DeLucas, Jim Foxx, Robert Nance

Los Alamos Made Material for Plutonium-Powered Pumper

Be still my beating heart. In a novel program that started in the 1960s, the Laboratory began a project to help those faint of heart. In 1967, Los Alamos Scientific Laboratory explored a new mission: developing a self-contained energy source that would last for decades to power a conceptual artificial heart. The energy source would be powered by the same material developed in 1963 for the space program—plutonium-238. The heat from the radioactive decay of the plutonium-238 can readily be used directly or used to produce electric power for space probes, etc. In a joint effort between the National Heart and Lung Institute (NHLI) and the Atomic Energy Commission (AEC), the Department of Energy's predecessor agency, Los Alamos researchers began the endeavor to balance the hazards of plutonium-238 with the benefits. Researchers believed that they could minimize the element's neutron radiation effects while supplying future artificial heart recipients with a long-life power source. Members of Chemistry-Metallurgy "Baker" Division's CMB-11 fabricated the source with 50 watts of energy—enough to drive the artificial heart—and focused on reducing the radiation while George Matlack and Joe Bubernak of CMB-1 analyzed the radiation properties. Researchers considered two or three different isotopes but finally chose plutonium-238 because of its half-life of eighty-seven and a half years, which was long enough to provide power with no significant loss of energy during the lifetime of the mechanical heart. The idea came from the Lab's active space program. More than thirty years ago [1975], NHLI concluded that an external power source needed to run the implanted device would be as large as a telephone booth, somewhat impractical for artificial heart recipients.

Scientists at Los Alamos believed that they could make a plutonium-238 heat source small enough to implant into the human body. The heat source would power a stirling-cycle engine that would pump the blood. But the conundrum was if the plutonium-238 was powerful and long-lasting enough to save the patient, would the radiation effects end up killing the heart recipient? Another drawback to using plutonium-238 metal was that it has a relatively low melting point, so if a deceased patient was cremated, the crematorium might become a radiological cleanup site. The research team considered using an alternative form with 3 percent gallium, which raised the melting point, but it still didn't prevent the melt that could occur in a crematorium.

Researchers experimented with plutonium-238 oxide from Savannah River, but the radiation levels were hard to measure at the time, and several light-element impurities produced an alpha-neutron reaction. Plutonium-238 is relatively easy to shield because its gamma rays are mostly of low energy and it produces a low amount of spontaneous neutrons. However, in the presence of other light-element isotopes such as nitrogen-14, oxygen-17, oxygen-18, carbon-12, or fluorine-19, the neutron emission is much higher because of the interaction of alpha particles (produced by plutonium-238 radioactive decay) with the other elements. A heavy but energetic



ARQ First Quarter 2005:

"This article was contributed by Kathy DeLucas of the Public Affairs Office; Jim Foxx of the Nuclear Materials Technology Division; and Robert Nance, formerly with the Chemistry-Metallurgy 'Baker' Division and now retired."

Clockwise from left: Larry Mullins records data during a direct oxide reduction experiment; Art Beaumont measures the outside diameter of a gauge tube with a micrometer; Beaumont compares a mock-up welded capsule and the gauge tube; Carl Peterson transfers plutonium oxide inside an inert-atmosphere glove box from a storage container in preparation for pressing a fuel pellet; Jim Foxx (left) and Larry Mullins discuss a helium release experiment with a vented plutonium-238 oxide heat source; the heat source capsule had to be handled inside a glove box with forceps because of the high temperature of the unit (generated by the alpha radioactive decay of plutonium-238).

alpha particle (helium ion), which can be shielded with a piece of paper, would hit an atom like fluorine and cause a neutron to escape. Neutrons are very difficult to attenuate and cause significant potential radiological doses to employees and candidate artificial heart recipients.

Scientists reduced this threat of the induced neutrons by two steps. In the original process, the first step was to convert the plutonium oxide to metal, which was historically done by means of a plutonium-fluoride intermediate with excessive alpha-induced neutrons. From the health-physics standpoint, this was quite undesirable for workers in the immediate area. Researchers therefore came up with the direct-oxide reduction process. In this process the plutonium oxide is mixed with calcium chloride-calcium fluoride or only calcium chloride, along with calcium metal, and heated to produce plutonium metal. A variation of the direct-oxide reduction (DOR) process today is the mainstay of producing plutonium-239 for the weapons program.

Researchers prepared the metal and removed nonradioactive light elements from it through electrorefining. The pure metal ingot was then converted to finely divided metal particles by reacting it with hydrogen and subsequently removing the hydrogen three times—a hydride-dehydride cycle. The purified finely divided metal was then ready for reaction with oxygen-16 water vapor, in the second step.

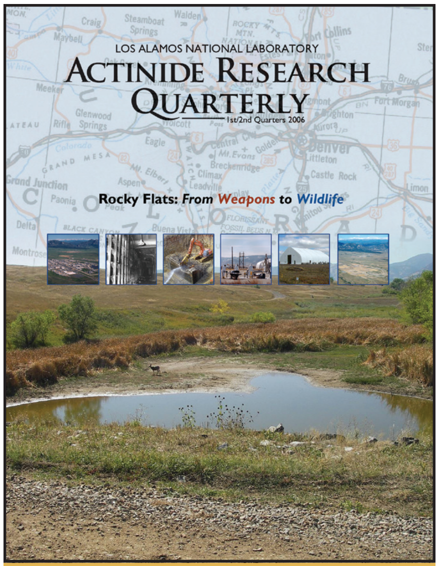
Normal water contains three oxygen isotopes: ^{16}O, ^{17}O, and ^{18}O. The oxygen-17 and -18 isotopes are susceptible to alpha-neutron reactions, but the oxygen-16 isotope is not. High-purity water vapor enriched at Los Alamos in the oxygen-16 isotope was reacted with the finely divided plutonium-238 metal to prepare plutonium oxide that had minimal alpha-induced neutron radiation. The techniques for the hydride-dehydride cycle and preparation of the plutonium-238 oxygen-16 oxide fuel were developed by Robert Nance.

The process of reacting oxygen-16 water with plutonium oxide to produce isotopic exchange is still used today to reduce the alpha neutron reactions in heat sources for the space program. The recently highly successful Cassini space probe to Saturn and its moon, Titan, is a good example. A number of earlier, spectacular, landmark deep-space explorations such as Voyagers I and II were powered by specially processed plutonium-238.

Because Congress was funding dual-track research programs, it decided to proceed with NHLI research, so the AEC's program was dropped and the project ended in 1977. Even if the project had continued, there were some real challenges to overcome. Insurance companies surely would have balked at the $200,000 price tag. The plutonium was encapsulated with three layers of metals: first tantalum, then tantalum-10 tungsten, and finally an outermost capsule of platinum-20 rhodium. These metals provided shielding and protected the heat source from oxygen. Three of the "D" cell sized 50-watt plutonium heat sources were made for testing.

Another drawback was discovered when rigorous tests were conducted. Researchers found that the encapsulation would not survive a .30-06 gunshot, which could cause a radioactive contamination threat if a recipient was shot through the heart. Finally, there was a problem at that time identifying pump materials that would not cause coagulation during long-term contact with blood.

While the program demonstrated many firsts at the Lab, some of which are still used in actinide processing today, there was also a successful spin-off. The Lab produced 63 grams of high-purity plutonium-238 metal for the pacemaker program. Medtronics made about 250 of the plutonium-powered pacemakers, and about 22 were still stimulating human heart more than 25 years after they were manufactured, a feat that no battery-powered pacemaker could match. The Nuclear Regulatory Commission maintains strict guidance for hospitals conducting patient monitoring and how to dispose of the pacemaker when the patient no longer needs it. The pacemaker is clearly stamped with the radioactive symbol and is labeled as containing plutonium-238. Other successful technologies that are still used today as a result of the program include the minimization of neutron radiation and the methods of accurately measuring the radiation from plutonium-238 materials.



LOS ALAMOS NATIONAL LABORATORY
ACTINIDE RESEARCH QUARTERLY
1st/2nd Quarters 2006
Rocky Flats: *From* Weapons *to* Wildlife

ARQ First Quarter 2006:

“This article was contributed by David L. Clark (PMT-DO), David R. Janecky (ENVP-AQE), Leonard J. Lane (EES-ACED and USDA-Agricultural Research Service, retired), and Gregory R. Choppin (Florida State University).”

ARQ FIRST QUARTER 2006

Scientific Understanding Aids Rocky Flats Cleanup

David L. Clark, David R. Janecky, Leonard J. Lane, Gregory R. Choppin

Rocky Flats Environmental Technology Site (RFETS) was a DOE environmental cleanup site located about 16 miles northwest of downtown Denver. Today [2006] more than 2.5 million people live within a 50-mile radius of the site, and 300,000 of those live in the Rocky Flats watershed. From 1952 to 1989, the Rocky Flats Plant made components for the nation’s nuclear weapons arsenal using various radioactive and hazardous materials, including plutonium and uranium, toxic metals such as beryllium, and hazardous chemicals such as cleaning solvents and degreasers.

The key component produced at Rocky Flats was the plutonium pit, commonly referred to as the “trigger.” The pit provided energy to fuel the explosion of a nuclear weapon. In 1989, the FBI and the Environmental Protection Agency (EPA) abruptly halted nuclear production work to investigate environmental and safety concerns, and the site was added to the Superfund list later that year. In 1993, the Secretary of Energy announced the end of the Rocky Flats nuclear production mission. Nearly 40 years of nuclear weapons production left behind a legacy of contaminated facilities, soils, surface water, and groundwater. Accordingly, RFETS was designated as an EPA Superfund cleanup site.

THE DENVER POST
Voice of the Rocky Mountain Empire
★★★★ 50 cents
June 7, 1989

Federal Agents Raid Rocky Flats

By Tom Graph, Peter G. Chronis, Mark Obmascik, Alan Gottlieb
Denver Post Staff
Copyright 1989, The Denver Post Corp.

JEFFERSON COUNTY – The Federal Bureau of Investigation raid Rocky Flats, the Energy Departments plutonium trigger plant near Denver.

The sudden shutdown left large quantities of plutonium and other hazardous substances in various stages of processing and storage. Because plutonium is dangerous to human health, even in minute quantities, the cleanup of plutonium-contaminated materials is complex, tedious, labor intensive, and slow. In March 1995, DOE estimated the cleanup for Rocky Flats would cost in excess of $37 billion and take 70 years to complete. By 1996 DOE and Kaiser-Hill had initiated efforts that eventually resulted in a credible plan to accelerate the closure of Rocky Flats by December 31, 2006, at a contracted cost of $7 billion. After a troubled start, Kaiser-Hill completed the task nearly a year ahead of schedule.

Many around the US Nuclear Weapons Complex are analyzing the factors that led to the turnaround. Without question, contributing factors included the incentive-laden contract, strong support and stable funding from Congress, high-level DOE support that mobilized the entire complex to assist in the cleanup, technological and operational innovation, and scientific understanding. Much has been made of the contractor’s fee of more than $500 million, but less has been said about the role that scientific understanding played in guiding key cleanup decisions and facilitating good project management.

From 1952 to 1989, the primary mission of the Rocky Flats Plant was making components for nuclear weapons. A raid in 1989 by the FBI and the EPA for alleged environmental violations resulted in an abrupt halt to nuclear material production. Large quantities of plutonium and other hazardous materials were left in various stages of processing and storage, as shown in the above photo of the Building 707 storage area. The environmental cleanup was originally estimated to cost more than $37 billion and take more than 70 years to accomplish.

The drive to understand the science behind plutonium contamination gained momentum in 1995 when intense rainfall and wet spring conditions raised concerns among site personnel and stakeholder groups about the potential for increased plutonium mobility and off site transport. There was a hypothesis that the plutonium was soluble in surface and groundwater, which would account for increased plutonium concentrations at onsite monitoring locations.

Modeling efforts and site data at the time predicted no or very limited movement of plutonium. The prediction of no plutonium mobility coupled with the observation of plutonium transport at surface-water monitoring stations led to public mistrust and lack of confidence. When coupled with other questions regarding the mobility of different actinide elements (uranium, plutonium, and americium) at different site locations, DOE and Kaiser-Hill established the Actinide Migration Evaluation (AME) advisory group in 1995 to provide advice and technical expertise on issues of actinide behavior and mobility in the air, surface water, groundwater, and soil.

Through a combination of expert judgment supported by state-of-the-art scientific measurements, it was shown that under environmental conditions at Rocky Flats, plutonium and americium form insoluble oxides and colloids that adhere to small soil and mineral particles. These particles can migrate in the Rocky Flats environment by wind and surface-water resuspension and sedimentation processes.

The scientific understanding showed that soluble transport models were not appropriate and led to the development and application of erosion and sediment transport models. The scientific understanding developed through these integrated studies provided the basis for the negotiation of plutonium and americium cleanup levels selected by the Rocky Flats Cleanup Agreement (RFCA) parties of 50 picocuries per gram (pCi/g) of plutonium in surface soils. A curie is a measure of the amount of radiation emitted by a radionuclide. It is the quantity of a radionuclide that undergoes 37 billion disintegrations every second.

Actinide Migration Evaluation team members gather at the Site in October 2005. From left to right are Gregory Choppin (Florida State University), David Clark (Los Alamos), Ian Paton (Wright Water Engineers), David Janecky (Los Alamos), Leonard Lane (US Department of Agriculture, retired), Robert Nininger (Kaiser-Hill, LLC), and Christine Dayton (Kaiser-Hill, LLC).

Three decades at the Central Operable Unit of Rocky Flats, where 800 structures once stood.

Top: A 1995 aerial photo of Rocky Flats Environmental Technology Site shows the Industrial Area and the surrounding controlled open space.

Middle: A photo from a similar angle shows the site in 2007 immediately following the cleanup.

Bottom: The site in 2011. This 1,300 acre parcel is held by the DOE for legacy management including long-term site maintenance and to ensure the cleanup is functioning as designed.

Did it save a lot of taxpayer dollars? That's more difficult to determine. What everyone agrees on is that it provided clarity and focus on the real issues surrounding plutonium and americium in the RFETS environment, and that allowed for good project management to move forward on site cleanup. It helped all parties focus remediation efforts on surficial contamination and transport pathways that posed the greatest risk to human health and the environment. It helped guide selection of surface-specific removal technologies, and future land configuration strategies.

The reconfigured Walnut Creek basin functional channel shows the heavily armored channel and extensive erosion-control measures on stream banks. The measures included straw bales, wattles, and crimping; silt fences; mats; hydromulch and Flexterra™; and rip-rap (rock) lining of drainage channels. The inset shows a remediated area of the 903 Pad covered with coconut matting. The biodegradable matting prevents wind and water erosion and allows native vegetation time to take hold.

Thus, scientific understanding, through advanced measurement techniques, was developed into science-based communication and decision-making for Kaiser-Hill and DOE that helped focus Site-directed efforts, aided the DOE in its effort to close RFETS in December 2005—one year ahead of schedule, and most certainly helped shave decades and billions of dollars off initial cleanup estimates.

The scientific understanding developed through the integrated studies provided clarity and focus on the real issues surrounding plutonium and americium migration in the RFETS environment. Once Kaiser-Hill, DOE, EPA, Colorado, and the concerned citizens' groups reached an understanding of the technical issues surrounding plutonium and americium migration at the site, then these groups were able to reach long sought-after agreements on how to proceed with cleanup. The common understanding that plutonium and americium were predominantly in particulate and colloidal forms led to the recognition that environmental migration occurs through sedimentation and resuspension of small particles by action of wind and surface water at the site. This knowledge helped all parties focus remediation efforts on surface contamination and wind and surface-water transport pathways that posed the greatest risk to human health and the environment. It also helped guide selection of surface-specific removal technologies and future land configuration strategies.

In recognition of the new understanding, site operators responded with a major shift in emphasis to erosion and the need to control it. The most poignant illustration of this shift was a Management Directive (NRT-011-04) from Kaiser-Hill President Nancy Tuor, which discussed the importance of erosion control in all site activities.

This temporary water-detention pond was constructed to collect and store dust-suppression water used during the decontamination and decommissioning of Building 371. The pond was used to ensure that plutonium and americium contaminants did not enter the streambeds during remediation of the site. This is an example of the extraordinary efforts employed by site personnel to control erosion—and hence actinide transport—during decontamination and decommissioning operations at the site.


Cleanup excavation of the 903 Pad took 13 months, during which approximately 32,000 tons of contaminated soil and asphalt were removed. Two 90-by-100-foot tents were erected over the site; sampling, excavation, waste loading, and backfill were conducted inside the tents to prevent wind dispersal of contaminants during remediation.

The recognized need for erosion controls “close in space and close in time” helped prevent movement of contaminants during site remediation activities and reduced the transport of plutonium and americium to the site’s stream channels and ultimately off-site. The additional protection provided by soil-erosion control measures allowed site remediation to proceed rapidly and thus meet or exceed the project deadlines.

In 1996, the Rocky Flats Cleanup Agreement radionuclide soil action level for plutonium cleanup was 651 pCi/g, and was based on dose. In 2002, armed with improved understanding of plutonium behavior, the DOE, Colorado Department of Public Health, and EPA released reports that formed the basis for a new surface soil-action level of 50 pCi/g that was based on risk and resulted from unprecedented community involvement. Because plutonium contamination was generally confined to surface soils, the greatest risk to public health was from dispersal due to action of wind and surface-water erosion processes. This new risk-based agreement focused on removal of surface soil contamination at a more aggressive 50 pCi/g standard to three feet below the surface, with the trade-off that contaminated soil below three feet could remain in place at higher concentrations.

The site developed a Storm Water Pollution Prevention Plan that encouraged minimum soil disturbance, which resulted in control and minimization of erosion and sedimentation and minimization of runoff across the site. Each project was reviewed for impacts to surface water with a specifically designed control system. Erosion-control measures included straw bales, wattles, and crimping; silt fences; mats; hydromulch and Flexterra™; and rip-rap (rock) lining of drainage channels. In addition, some new wetland areas were created. Several of these methods have expected useful lifetimes of a few months to a few years, and will require regular maintenance until the location is stabilized and vegetation well established.

In actual decontamination, demolition, and remediation work, the site employed a combination of tents, comprehensive dust- and erosion-control measures, and general environmental protection during cleanup activities. As a result, surface-water and air monitoring stations at the site boundary showed little change in actinide migration as a result of the site cleanup activities.

Two views of Rocky Flats' Central Avenue.

Actinide Migration Evaluation projects

The Actinide Migration Evaluation (AME) projects were commissioned at Rocky Flats in 1995 to address how actinide elements move in the environment. Initially, AME advisors were recruited to evaluate and provide guidance on environmental conditions (including actinide chemistry, geochemistry, migration, and erosion) at RFETS. The charter was rapidly expanded to include recommendations of paths forward for long-term protection of surface-water quality as the primary technical and regulatory measure of remedial action quality.

Over 10 years, the group was led by Christine S. Dayton (formerly Kaiser-Hill), and the following served as advisors: Sumner J. Barr (Los Alamos), Gregory R. Choppin (Florida State University), David L. Clark (Los Alamos), Arokiasamy J. Francis (Brookhaven National Laboratory), Bruce D. Honeyman (Colorado School of Mines), David R. Janecky (Los Alamos), Annie B. Kersting (Lawrence Livermore National Laboratory), Leonard J. Lane (USDA Agricultural Research Service), D. Kirk Nordstrom (US Geological Survey), and Peter H. Santschi (Texas A&M University). The following overriding technical questions and priorities were identified:

Urgent: What are the important actinide migration sources and migration processes that account for surface-water quality standard exceedances?

Near-term: What will be the impacts of actinide migration on planned remedial actions? To what level do sources need to be cleaned up to protect surface water from exceeding action levels for actinides?

Long-term: How will actinide migration affect surface-water quality, airsheds, and impact on downstream areas (e.g., what soil-action levels will be sufficiently protective of surface water)?

A central principle of AME, from its inception, was to have ongoing interaction with the public. As actinide-migration related studies were performed and completed, meetings were held with representatives from the regulatory agencies, neighboring communities, and citizens' groups to discuss study results and the implications for remedial actions at the site. When warranted, additional personnel were brought in to provide technical expertise as necessary (for example, chemists experienced with specialized analytical techniques). Discussion of issues occurred in the public forums and prompted additional research to be conducted to address unanswered questions.

The expansive prairie at Rocky Flats consists of grasslands, wetlands, and shrublands. The Xeric Tallgrass Prairie is a rare grassland type believed to be a remnant from the ice age and is perhaps the largest contiguous remnant of this grassland type in North America.

Rocky Flats National Wildlife Refuge

The Rocky Flats National Wildlife Refuge Act of 2001 began a process to finalize the reclamation of the land and secure its natural state into the future. In April 2005, a Comprehensive Conservation Plan was published in the Federal Register; it outlined habitat restoration plans for the next 15 years. The refuge is scheduled to partially open next year and be in full operation about 2012. It will have hiking trails, interpretive signs, and limited hunting. Approximately 1,000 acres in the center of the site will be maintained by DOE for long-term surveillance and maintenance while the remaining 5,200 acres will be transferred to the Department of the Interior.

The Xeric Tallgrass Prairie is a rare grassland type believed to be a remnant from the ice age and is perhaps the largest contiguous remnant of this grassland type in North America. This area is identified by species such as big bluestem, little bluestem, prairie dropseed, Indian grass, and switchgrass. Because of the prairie's proximity to the mountains, the species composition is influenced by mountain muhly, Porter's aster, blazing star, scurfpea, and Canada bluegrass.

The site:
- 6,266 acres within 50,000 acres of publicly owned open space

Habitat zones:
- Tallgrass prairie
- Mixed prairie grasslands (mixed-mesic grassland, xeric needle and thread grassland, reclaimed mixed grassland)
- Riparian corridors and wetlands (marsh, wet meadows, upland shrublands)

The wildlife:
- Preble's meadow jumping mouse, Black-tailed Jack Rabbit, Black-tailed Prairie Dog, Mule Deer, Whitetail Deer
- Painted Turtle, Prairie Rattlesnake
- Red-tailed Hawk, Northern Harrier, Peregrine Falcon, Western Meadowlark, Killdeer, Warbler
- Aragos Skipper (rare butterfly)

Summary

Superfund sites such as RFETS are environmental problems of national significance. As such, we in the scientific community hope that our best science is brought to bear on decision making to improve its technical basis and to make it more transparent, repeatable, and thus, scientifically defensible. This came about at RFETS because of several factors, including the willingness of the integrating contractor to seek outside scientific advice and guidance; the acceptance through time, down to the project level, of the value of scientific advice in avoiding pitfalls and improving operations; and the gradual acceptance of the independence and veracity of the AME scientific advisors by the stakeholders. This willingness and acceptance allowed DOE, the integrating contractor, the regulators, and other stakeholders to focus on specified goals and objectives.

Making the case for particle-transport mechanisms, rather than aqueous sorption-desorption processes, as the cause of plutonium and americium mobility established a successful scientific basis for the dominance of physical transport processes by wind and water. The scientific basis was successful because it was in agreement with general theory on insolubility of PuO_2 in oxidation state IV; results of ultrafiltration analyses of field water and sediment samples; and X-ray absorption fine structure (XAFS) analyses of soil, sediment, and concrete samples.

It was also in general agreement with on-site monitoring data. This understanding in turn allowed site contractors to rapidly move to adopt soil erosion and sediment-transport models as the means of predicting plutonium and americium transport, which led to design and application of sitewide soil erosion control technology to help control downstream concentrations of plutonium and americium in streamflow.

Finally, good scientific understanding in the public interest helped bring clarity and focus to real issues of actinide migration at RFETS. This in turn helped to develop a more defined scope with a clearer endpoint that allowed the most extensive cleanup in the history of Superfund legislation to finish one year ahead of schedule, ultimately resulting in billions of dollars in taxpayer savings and removing a $600-million-plus annual liability from the DOE budget forever.

Acknowledgments

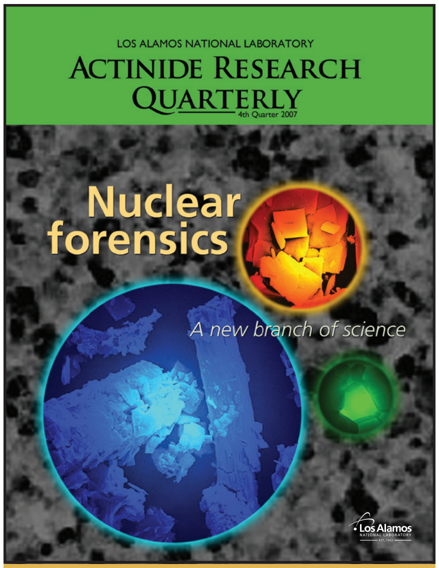
The authors are grateful to Kaiser-Hill, LLC, and DOE for their support of AME studies between 1995 and 2005. We acknowledge the Office of Basic Energy Sciences, and the Office of Biological and Environmental Research at the DOE for their support of actinide and synchrotron radiation science that assisted RFETS cleanup activities. We also acknowledge the Stanford Synchrotron Radiation Laboratory (SSRL) for its support of X-ray absorption studies that aided RFETS cleanup.

Further reading:

1. *Actinide Migration Evaluation Pathway Analysis Summary, Kaiser-Hill, Rocky Flats Environmental Technology Site, Report ER-108, 2002.*
2. *S.D. Conradson, B.D. Begg, D.L. Clark, C. den Auwer, M. Ding, P.K. Dorhout, F.J. Espinosa-Faller, P.L. Gordon, R.G. Haire, N.J. Hess, R.F. Hess, D.W. Keogh, L.A. Morales, M.P. Neu, P. Paviet-Hartmann, W. Runde, C.D. Tait, D.K. Veirs, and P. M. Villella, J. Am. Chem. Soc., 126(41), 13443-13458, 2004.*
3. *P.H. Santschi, K.A. Roberts, and L. Guo, Environmental Science and Technology, 36(17), 3711-3719, 2002.*

2020 Update

The Rocky Flats National Wildlife Refuge was established in 2007 and is managed by the US Fish and Wildlife Service. In 2018, it opened to the public with 10 miles of trails for hiking, cycling, and horseback riding; there are plans to connect these trails to Rocky Mountain Arsenal, Two Ponds National Wildlife Refuges, and Rocky Mountain National Park via the Rocky Mountain Greenway trail system. The 15,000-acre Rocky Mountain Arsenal National Wildlife Refuge site was transferred to US Fish and Wildlife Service from the US Army after cleanup completion in 2010. The DOE maintains 1,300 acres of the original Rocky Flats site as part of their legacy management for long-term site maintenance and to ensure the cleanup is functioning as designed. These lands are not part of the refuge.



ARQ Fourth Quarter 2007:

"ARQ thanks Klaus Mayer, Maria Wallenius, Ian Ray, and Klaus-Richard Lützenkirchen of the Institute for Transuranium Elements (ITU) for their contributions to this article."

ARQ FOURTH QUARTER 2007

CSI: Karlsruhe

Klaus Mayer, Maria Wallenius, Ian Ray, Klaus-Richard Lützenkirchen

Nuclear forensics sleuths trace the origin of trafficked material

When the former Soviet Union broke up, the new independent states couldn't control their supplies of nuclear material and some of it got "lost." In 1994 alone, 45 confirmed cases of nuclear material trafficking were reported, according to the International Atomic Energy Agency (IAEA). The numbers have decreased to around 10 reported incidents a year, but poorly guarded and easily stolen nuclear materials still pose a serious problem because of the radiological hazards associated with improper transport, handling, and storage. And while the dumping of nuclear material in a landfill or salvage yard is very serious, even more dire consequences could occur if the material ended up in the hands of a terrorist.

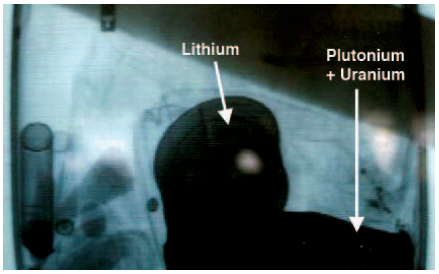
When a cache of stolen or dumped nuclear material is intercepted, routine forensics techniques are used to answer the questions of who and how and what. Answering what the material is, where it came from, and what it could be used for is a nuclear whodunit worthy of the "CSI" television series and has resulted in the development of a new branch of science called nuclear forensics.

Since the early 1990s the Institute for Transuranium Elements (ITU) in Karlsruhe, Germany, has been involved in developing the methodology of nuclear forensics to answer the questions of chemical makeup, origin, and use. Tracing where the material came from will help governments improve physical protection of the site of origin and prevent future thefts or illegal disposal. The science is based on analytical techniques related to the nuclear fuel cycle: radiochemistry, nuclear physics, reactor physics, and materials science.

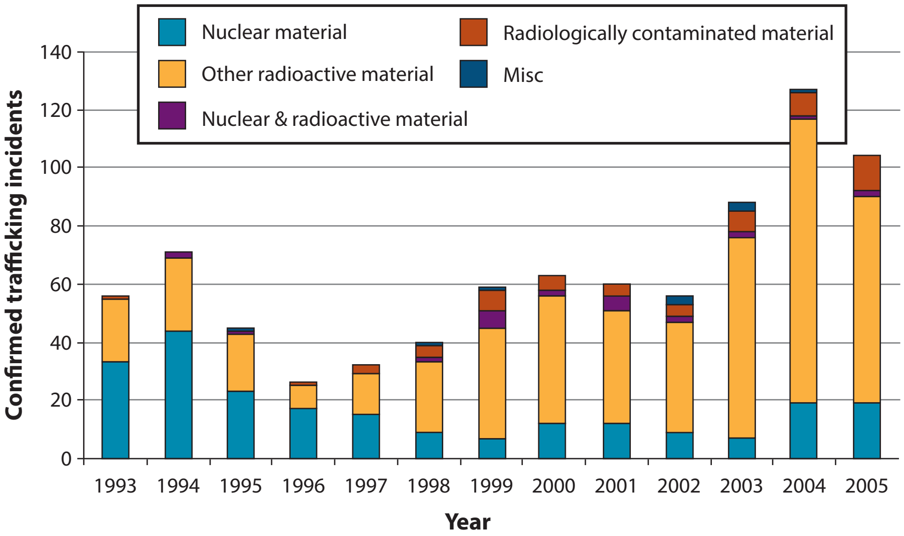
Klaus-Richard Lützenkirchen of ITU's Nuclear Safeguards and Security Unit recently visited Los Alamos [2007] and gave a talk on nuclear forensics activities at ITU. The Seaborg Institute sponsored his visit for Transactinium Science. Lützenkirchen discussed typical cases that have been analyzed at ITU and described the various analytical techniques that led to the successful determination of where the materials, specifically plutonium and uranium, came from. Three of the cases are discussed below.

ITU's nuclear forensics methodology takes data from analytical methods from safeguards, material science, and isotope geology to determine the isotopic composition, elemental composition, impurities, macroscopic appearance, microstructure, and age. The data reveal into two types of results: endogenic, or self-explanatory (age, intended use, production mode), and exogenic, which requires reference data (place of production, last legal owner, and smuggling route). Twenty-one seizures analyzed at ITU between 1992 and 1997 included natural uranium, low-enriched uranium fuel pellets, highly enriched uranium, plutonium, and contaminated scrap metal.

First case: One of four uranium-oxide fuel pellets seized in Lithuania. Nuclear forensics sleuths determined that the pellets were manufactured by MZ Electrostal in Moscow for the RBMK-1500 reactor known as Ignalina Unit 2 in Lithuania. The pellets probably came from a fresh fuel assembly that had been stolen from the Ignalina power plant in 1992.



Second case: X-ray of a suitcase that contained nuclear material. In August 1994, three men who were expected to be carrying plutonium arrived in Munich from Moscow. Gamma-ray detectors did not respond when their luggage was checked, but X-rays showed a stainless steel container and tin cans.



First case: Uranium pellets

Uranium dioxide (UO_2) pellets are used as fuel in nuclear power reactors. In June 2003, ITU received four uranium pellets from Lithuania. The pellets were analyzed for uranium content and isotopes; chemical impurities, which would point to the source of the raw product; age, which would point to the production time; and microstructure, which would point to the production process.

All of the pellets showed identical geometry; they had a central hole and they were dished. The pellets were weighed and their dimensions measured. The four pellets were measured individually with a high-resolution gamma spectrometer for the first indication of the isotopic composition. The spectra showed gamma lines belonging only to uranium, and analysis showed an average uranium-235 enrichment of 2%. Because the pellets were identical in dimensions as well as in isotopic composition of the uranium, only one of them was dissolved for further analysis.

Information that can be obtained from nuclear material (uranium, U, plutonium, Pu)

Parameter	Information	Analytical technique
Appearance	Material type (e.g., powder, pellet)	Optical microscopy
Dimensions (pellet)	Reactor type	Database
U, Pu content	Chemical composition	Titration, HKED, IDMS
Isotopic composition	Enrichment → intended use; reactor type	HRGS, TIMS, ICP-MS, SIMS
Impurities	Production process; geolocation	ICP-MS, GDMS
Age	Production date	AS, TIMS, ICP-MS
$^{18}O/^{16}O$ ratio	Geolocation	TIMS, SIMS
Surface roughness	Production plant	Profilometry
Microstructure	Production process	SEM, TEM

HKED: hybrid K-edge densitometry, IDMS: isotope dilution mass spectrometry, HRGS: high-resolution gamma spectrometry, TIMS: thermal ionization mass spectrometry, ICP-MS: inductively coupled plasma mass spectrometry, SIMS: secondary ion mass spectrometry, GDMS: glow discharge mass spectrometry, AS: alpha spectrometry, SEM: scanning electron microscopy, TEM: transmission electron microscopy.

The isotopic composition of uranium was determined by mass spectrometry. Mass spectrometry techniques are able to provide accurate results for minor abundant isotopes (uranium-234 and -236), which is not the case with gamma spectrometry. The measurement technique routinely used for uranium and plutonium isotope analysis is thermal ionization mass spectrometry (TIMS). An inductively coupled plasma mass spectrometer with multi-collector detection system (MC-ICP-MS) was used to compare the accuracy and precision between these two methods.

The uranium content in solution was determined by three different methods: potentiometric titration, hybrid K-edge densitometry (HKED), and isotope dilution mass spectrometry (IDMS). All three methods determined that the uranium content corresponded to the stoichiometry of uranium dioxide (UO_2) whose theoretical value is 88%. Impurities in the sample were determined after complete dissolution by sector-field ICP-MS using rhodium-103 as an internal standard.

Determining the age of the material, and thus the date when the material was produced, helps identify the production campaign or batch. The radioactive decay of the uranium isotopes provides a unique chronometer that is inherent to the material. This clock is reset to zero each time the decay products (daughter nuclides) are chemically separated from the uranium. The half-life of the uranium isotopes in question is very long, therefore the short periods between the preparation of the uranium fuel and the seizure of the material generated extremely minute amounts of daughter nuclides. Nevertheless, the age could be determined from these parent/daughter ratios. The age of the uranium was calculated using the equation of radioactive decay and its derivatives.

The sample solution was spiked with thorium-228 and uranium-233 before the uranium/thorium separation. The amount of uranium-234 and thorium-230 was determined using the isotope dilution technique, i.e., relative measurements against the (known amount of) spike isotope. The age of the material was determined to be 12.6 ± 0.8 years. Thus, the pellets had been produced at the end of 1990 (remember that the test occurred in 2003). Only the uranium-234/thorium-230 parent/daughter ratio could be used this time for the age determination because of the long half-life of uranium-235 and consequently the very small amounts of built-up daughter nuclides.

At this point, the investigators knew the dimensions of the pellets as well as the isotopic composition and age of the material. For the next step—determining where the pellets came from—the team used a relational database at ITU that contains data from several nuclear fuel manufacturers (including most of Western Europe and Russia). The database contains dimensions of pellets, uranium-235 enrichment, and typical impurities. Besides commercial reactor fuels, the database also contains information on research reactor fuels and information acquired from open literature. Additionally, results of old findings are introduced into the database for a comparison with future cases.

In the case of the four pellets from Lithuania, the database gave a very unambiguous answer. The pellet dimensions and enrichment already were enough to identify them as being made for an RBMK-1500 reactor, which is a Russian-type, water-cooled, graphite-moderated reactor. There are two models of the RBMK reactor: the 1000 and 1500. The 1000 model is older and more widely distributed, while there is only one 1500 model reactor in the world: Ignalina Unit 2 in Lithuania, which started up in August 1987 and is still operational.

Furthermore, there is only one manufacturer for this type of fuel: MZ Electrostal near Moscow. The measured impurities of the pellet material were below the maximum values given in the manufacturer's specifications and they also agreed with the experimental data from earlier findings of the same fuel. The last confirmation parameter was the age, which fit with the production data of the manufacturer (start of fuel production: December 1989). The information contained in the nuclear materials database proved to be essential for the attribution of the material.

ITU's nuclear forensics team was able to further deduce from the absence of uranium-236 that the fuel had been enriched from natural uranium (meaning there was no reprocessed material) and, because the pellets contained no traces of plutonium, that the fuel had never been in a reactor.

The IAEA database on trafficking of nuclear and other radioactive materials and some other open source information reported a case of a fresh fuel assembly being stolen from the Ignalina power plant in 1992. The four pellets under investigation definitively originated from Electrostal, and probably came out of that stolen assembly. This kind of fuel assembly contains about 110 kilograms of uranium. Between 1994 and 1997 more than 100 kilograms of pellets have been confiscated in several seizures; the greater part of the material has been recovered. The material itself is not usable for nuclear weapons because the uranium-235 enrichment of 2% is far too low. However, what makes this case spectacular is the amount of the material that was stolen. Efforts have been undertaken to improve the physical protection at nuclear power plants and other storage facilities for nuclear material in the former Soviet Union.

Nuclear material seized at the Munich airport. The suitcase contained 560 grams of plutonium- and uranium-oxide powder (left) and 210 grams of lithium metal (center). The structure of the mixed-oxide powder was determined by scanning electron microscopy (SEM). The micrograph (right) shows the three distinct shapes of the powder: plutonium-oxide platelets, plutonium-oxide rods, and uranium-oxide hexagons.

Second case: Mixed-oxide (MOX) powder

In August 1994, three men were stopped at the Munich airport carrying a suitcase containing 560 grams of plutonium- and uranium-oxide powder and 210 grams of lithium metal. The powder consisted of 64.9 wt.% of plutonium and 21.7 wt.% of uranium. The plutonium-239 enrichment was about weapons-grade quality, whereas the uranium had a low uranium-235 enrichment. The piece of lithium metal was enriched to 89.4% lithium-6. The MOX powder consisted of three different particle types: plutonium-oxide (PuO_2) platelets, rod-shaped PuO_2, and hexagonal uranium-oxide (U_3O_8); see image above, right.

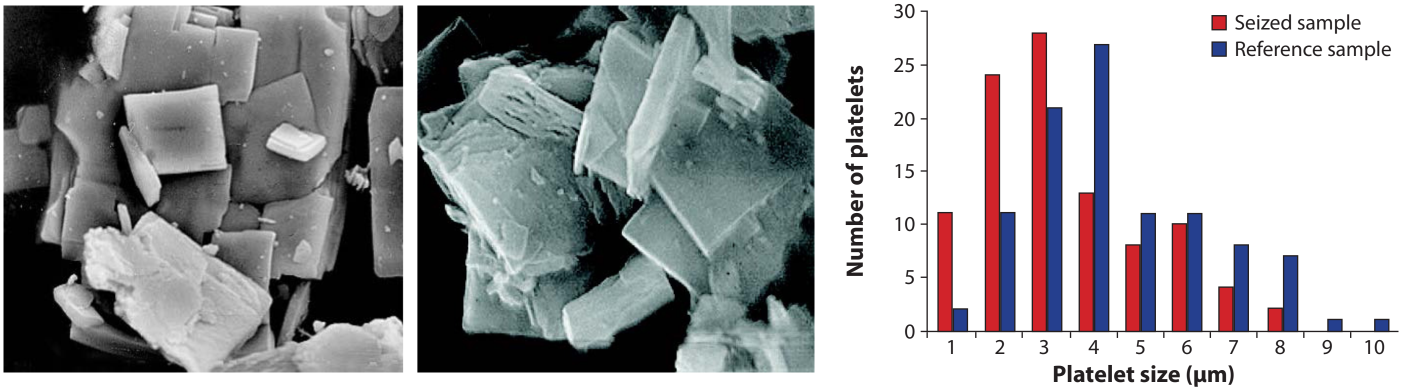
Light-water reactors (PWR, BWR, and VVER) were excluded as the origin of the plutonium because the isotopic composition of plutonium after a typical irradiation period of three years in these reactors would have been significantly different. Materials-testing reactors using 36–90% enriched uranium-235 were also excluded because a higher plutonium-238 abundance would have been expected in this case. Most likely, a reactor type with a softer neutron spectrum (e.g., heavy-water or graphite-moderated) was used for production.

In this case, the nuclear reactor would have operated with an initial fuel enrichment of 1.8% uranium-235 to yield the uranium composition, assuming of course that the uranium and plutonium were from the same reactor. This scenario was also proposed by plutonium isotopic correlation. However, the plutonium-238 and -242 abundances were too high to originate from the low-burn-up spent fuel of an RBMK-1000 reactor. Thus, most likely, the plutonium was a mixture of different spent fuels (e.g., a low-burn-up or weapons-grade plutonium and a high-burn-up fuel) and had no direct connection with the uranium present.

Because the powder consisted of two different plutonium particle types, individual microparticles were analyzed by SIMS to determine if their isotopic compositions were identical or if the earlier determined isotopic composition for the bulk material was a result of mixing two different compositions. The plutonium-240/-239 ratios in the platelets and the rod-shaped particles were slightly different (0.1159 ± 0.0012 and 0.1245 ± 0.0026, respectively). However, the difference was much too small to conclude that one plutonium particle type originated from weapons-grade plutonium (plutonium-240/-239 < 0.05) and the other type from high-burn-up fuel (plutonium-240/-239 ~ 0.4–0.7). Therefore, the mixing must have taken place before the particles were produced.

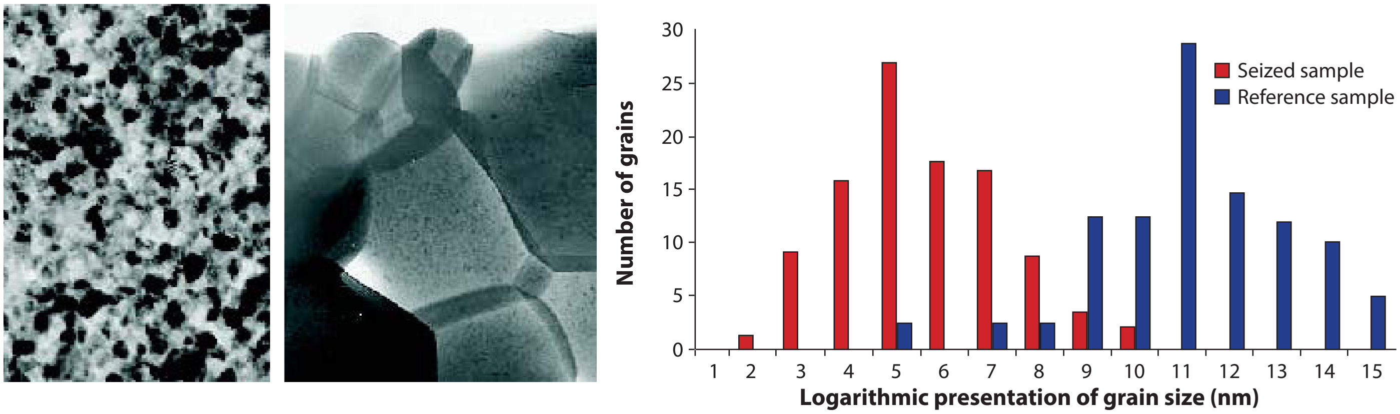
The age of the plutonium material was determined by gamma spectrometry (bulk sample) and by SIMS (both particles types). The adjacent uranium particles interfered in the SIMS measurements, leading to biased results for the

Platelet analysis. The plutonium-oxide (PuO_2) platelets in the seized Munich mixed-powder were examined in detail by scanning electron microscopy (SEM), top row, to determine platelet-size distribution, and by transmission electron microscopy (TEM), bottom row, to determine grain-size distribution:



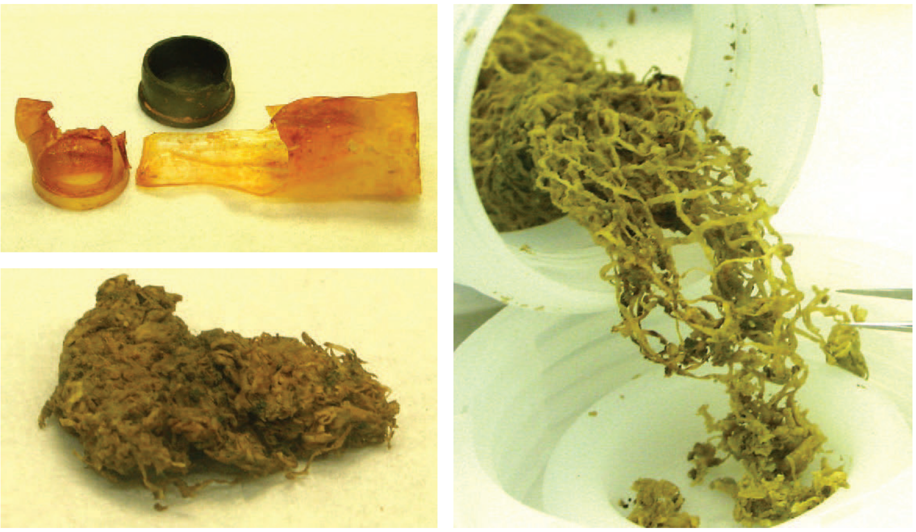
Above: The SEM analysis shows a reference sample of PuO_2 from a known fabrication plant (left) and the PuO_2 platelets from the sample seized at the Munich airport in 1994 (center). SEM analysis (right) does not show a significant difference between the two samples.

Below: The TEM analysis shows a reference sample of PuO_2 from a known fabrication plant (left) and the PuO_2 platelets from the sample seized at the Munich airport in 1994 (center). It is interesting to note that both of the TEM pictures were taken at the same magnification. The TEM analysis (right) reveals a remarkable difference in grain-size distribution, indicating that a different production process was used for manufacturing the PuO_2.



plutonium-238/uranium-234 and the plutonium-239/uranium-235 ratios (isobaric interferences for uranium-238 and plutonium-238, for uranium-235 from uranium particles, and uranium-235 from plutonium-239 decay). Because uranium-236 is a minor isotope in the uranium material, its interference with the grown-in uranium-236 from plutonium-240 decay was negligible. The ages determined for different particle types from the plutonium-240/uranium-236 ratio were similar (within the uncertainties) and were consistent with the age obtained from the bulk measurement of the plutonium-241/americium-241 ratio by gamma spectrometry. Both methods gave a production time around the end of 1979±0.5 years.

Even though the plutonium-239 enrichment is somewhat too low for military purposes, it is not impossible to produce a nuclear device with plutonium of this quality. With regard to the lithium metal, its high enrichment in lithium-6 of 89.4% is noteworthy. One of the possible uses of lithium-6 is to generate energetic tritons via the $^6Li(n,\alpha)^3T$ reaction. Such energetic tritons would then be able to initiate deuterium-tritium nuclear fusion in a thermonuclear weapon. Therefore, it may not be a coincidence that plutonium and lithium-6 were found together.



Third case: Theft of radioactive waste. A plastic vial containing a liquid and a swipe cloth, which were stolen from a decommissioned reprocessing plant in Karlsruhe, Germany, were first analyzed by gamma spectrometry. The vial was found to contain plutonium-238, -239, and -241; americium-241; cesium-134 and -137; and antimony-125. In addition to these elements, europium-154 was also found in the swipe cloth (cellulose fibers from the swipe cloth are shown at bottom left and nylon fibers at right). To quantify the uranium and plutonium isotopes, parts of the samples were dissolved in nitric acid and measured by thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS).

Third case: Radioactive waste

In July 2001, plutonium was found in a routine urine analysis of an employee who had been working in a shut-down reprocessing plant under decommissioning in Karlsruhe, Germany. His car and apartment were also found to be contaminated. In addition, his girlfriend and her daughter had incorporated americium and cesium. The employee was arrested and confessed that he had stolen a plastic vial containing a liquid and a swipe cloth. He had managed to get both items out of the reprocessing plant about half a year earlier.

The analytical task was two-fold: first, to confirm that the reprocessing plant in question was really the source of the material; second, to verify whether the two stolen items were the only sources of the contamination and the incorporation. Besides the two stolen items, analyzed samples included vacuum cleaner bags from the contaminated apartments, household gloves used to handle the stolen items, and clothing.

All samples were first measured by gamma spectrometry. The plastic vial contained plutonium-238, -239, and -241; americium-241; cesium-134 and -137; and antimony-125. In addition to these elements, europium-154 was also found in the swipe cloth. The other items contained the same nuclides in slightly lower activities. To quantify the uranium and plutonium isotopes, part of the samples was dissolved in nitric acid and measured by TIMS and ICP-MS.

The isotopic compositions of plutonium and uranium were similar in all samples and resembled the spent fuel last reprocessed in the plant before shutdown. The large amount of cesium ingested by the thief's girlfriend was difficult to explain from the activity found in the two stolen items. However, the items were most probably washed before being transferred for the investigations. Because cesium is fairly soluble in water, most of the cesium might have been lost at this stage. The thief was sentenced to prison for breaking the security regulations of the reprocessing plant and for unauthorized possession of radioactive material. Decontaminating the two apartments cost about $2.5 million.

Current developments

The examples presented here are typical cases analyzed at ITU. A pellet case is often easier to solve than a powder case because information on commercial nuclear fuels is available in ITU's database. Powder is usually not a final product but is an intermediate product or not from a commercial production cycle. To make the origin determination more accurate, researchers are continuously studying samples of known origins.

Existing analytical techniques, as used in material science, nuclear materials safeguards, and environmental analysis, have been adapted to the specific needs of nuclear forensic investigations. Characteristic parameters (e.g., isotopic composition, chemical impurities, and macro- and microstructure) can be combined into a "nuclear fingerprint" pointing at the origin of the material. Further research is being carried out aimed at identifying other useful material characteristics to reduce the ambiguities often remaining in the interpretation of the data and in the source attribution.

The new science of nuclear forensics has also required a change in how police conduct investigations. Using classical forensics techniques on contaminated items must be done in a controlled environment and with proper radiological protection. ITU has helped the police develop procedures for crime-scene management and has set up a dedicated glove box for taking DNA samples and fingerprints from contaminated items.

Response to trafficking of nuclear material

Nuclear forensics is a crucial component of a comprehensive response to nuclear material trafficking. The response measures require a collaborative effort on an international level. ITU, together with several eastern countries of the European Union and countries in the Commonwealth of Independent States (CIS), has set up projects to increase the efficiency in combating trafficking. A comprehensive approach has been developed that involves all competent authorities in the individual countries.

Assistance is offered to develop a national response plan that is consistent with the Model Action Plan recommended by the Nuclear Smuggling International Technical Working Group (ITWG) on combating nuclear terrorism. The concept of a national response plan has been taken over by the IAEA, put on a broader basis, and promoted for implementation. Training sessions have been offered to law enforcement officers and scientists and demonstration exercises have been carried out in different countries to test the implementation of the Model Action Plan. In a final step, joint analyses of seized samples have been conducted by ITU and requesting countries to demonstrate the preparedness and usefulness of nuclear-forensic analysis.

Classical forensics on contaminated items. The nuclear forensics team at the Institute for Transuranium Elements (ITU) in Karlsruhe is helping police departments learn how to perform investigations on radiologically contaminated evidence. The classical technique of taking fingerprints or DNA samples from evidence becomes even more challenging when it has to be performed in a glovebox.

These efforts are coordinated with other international activities, in particular by the United States and the IAEA, to make efficient use of available resources. On the scientific level, the ITWG serves as a forum for the exchange of experience, advancing nuclear forensics, and interacting with regulatory bodies, law enforcement, and measurement scientists. Nuclear forensics provides an element of sustainability in the fight against trafficking of nuclear material.

Further reading:

1. *K. Mayer, M. Wallenius, I. Ray, "Nuclear forensics—A methodology providing clues on the origin of illicitly trafficked nuclear materials," The Analyst 130 (2005).*
2. *M. Wallenius, K. Mayer, I. Ray, "Nuclear forensic investigations: Two case studies," Forensic Science International 156, (2006).*
3. *M. Wallenius, et al., "Nuclear forensic investigations with a focus on plutonium," Journal of Alloys and Compounds 444-445 (2007).*

2020 Update

In 2016, the organization formerly known as the Institute for Transuranium Elements was renamed to the Joint Research Centre (JRC) in Karlsruhe, which serves the European Union with a focus on nuclear safety and security. As a field, nuclear forensics continues to grow in importance. The International Atomic Energy Agency (IAEA) encourages coordinated research programs between its member states, and provides technical assistance on the conduct of nuclear forensics examinations.

ARQ FIRST QUARTER 2011

Reconstitution as Deterrence: Advantages and Challenges of the Strategy

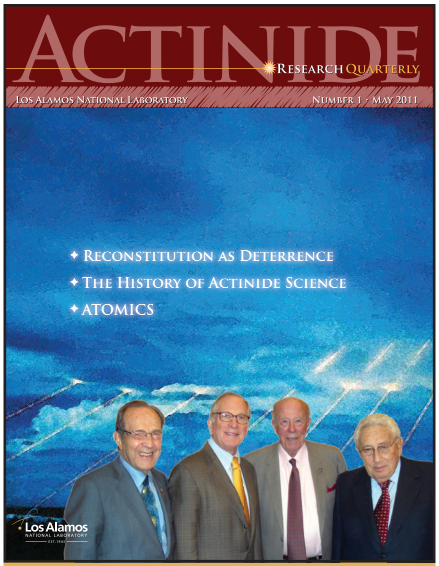
Joseph C. Martz

Many people, including senior statesmen and political leaders, have suggested over the years that establishing and maintaining the capacity for reconstituting nuclear weapons may be a safer form of deterrence than retaining a large stockpile of weapons. In addition, in a widely read 2007 Wall Street Journal editorial, former Secretary of Defense William Perry joined former secretaries of state George Shultz and Henry Kissinger and former senator Sam Nunn in calling for a recommitment to achieving a world without nuclear weapons. Two years later Secretary Shultz addressed the issue in the forward to “A World Without Nuclear Weapons: End-State Issues” by Sidney Drell and James Goodby. Shultz wrote: “The fact is nuclear deterrence is increasingly hazardous and decreasingly effective. We have to change our way of thinking about it … including ways of stretching out time for decision making during a nuclear crisis and relying increasingly on an ability to reconstitute nuclear forces as a safer form of nuclear deterrence.” And as early as the 1980s, author Jonathan Schell was discussing what has become known as “capability-based deterrence” in his book The Abolition. “The capacity for retaliation would consist less and less of the possession of weapons and more and more of the capacity for rebuilding them, until, at the level of zero, that capacity would be all.” The current objective of capability-based deterrence is to accomplish two simultaneous goals: continue to preserve a strategic deterrent to aggression while enabling reductions in nuclear weapons stockpiles. To do this, the nuclear weapons complex must demonstrate agility, capacity, confidence, security, and transparency.

Characteristics of an effective deterrent

The United States’ capability for producing nuclear weapons as a form of deterrent was robustly exercised during the Cold War to counter the threat of the Soviet Union. Looking forward, the desire is to preserve security in an environment of nuclear stockpile reductions, with a long-term vision of “Global Zero,” in which the retention of deployed nuclear weapons isn’t necessary to preserve the strategic security of the United States and its allies.

In support of the Global Zero vision, the Defense Department’s 2010 Nuclear Posture Review (NPR) has embraced the idea that the reconstitution of nuclear forces can serve as a growing portion of deterrence in an environment of stockpile reductions. The Obama administration has backed up this policy decision with a recommendation to reinvest and revitalize the US nuclear weapons infrastructure. What remains to be decided are specific objectives and goals that address the strategy of further stockpile reductions and a move toward capability to preserve US strategic security interests.



ARQ First Quarter 2011:

“Joseph C. Martz of the Seaborg Institute contributed this article, which is based on a talk he gave last fall [2010] to the Los Alamos Committee on Arms Control and International Security. The topic is capability-based deterrence, which was the focus of Martz’s recent research at Stanford University.”

Senior statesmen have joined with political leaders in calling for a recommitment to a world without nuclear weapons. Author Joe Martz took this photo of the senior diplomats, left to right: former Secretary of Defense William Perry, former senator Sam Nunn, former Secretary of State George Shultz, and former Secretary of State Henry Kissinger.

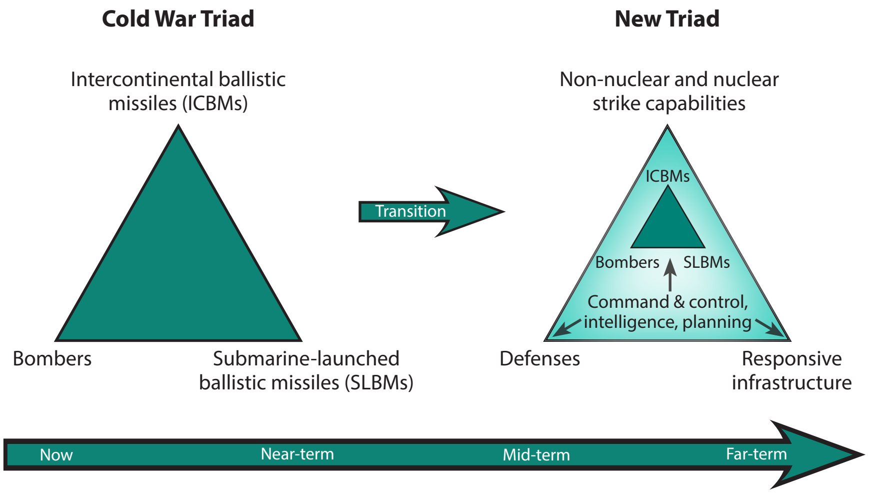
Some statesmen have begun to address this issue with specific proposals. Former Secretary Perry's "2020" vision establishes a concrete goal for stockpile reductions by the year 2020 (500 deployed weapons each for the United States and Russia), followed by a reexamination of the deterrence landscape. This proposal sets an intermediate goal that both preserves strategic security and makes substantial progress toward the Global Zero vision. As the Nuclear Posture Review points out, the largest portion of the US nuclear stockpile is not its deployed strategic forces; it is the reserve and backup forces, which are retained as a hedge against technical or geopolitical surprise. A vision of stockpile reductions can begin with a strategy that addresses possible reductions in these reserve forces. The Nuclear Posture Review has suggested that the ability to reconstitute nuclear forces can begin to augment, and eventually replace, the need to retain reserve and hedge forces.

Building a capability-based deterrent

The essential questions for a capability-based deterrent are timing (agility) and capacity. There is no consensus on either of these issues at present, nor is there a ready answer to "how fast" and "how many" weapons or components should be reconstituted should the need arise.

Numerous studies in support of complex modernization have examined the structure of US forces, the anticipated lifetime of various weapons and components, and the overall size of the deterrent. These studies have concluded that production capacities ranging from 50 to as high as 400 warheads per year are sufficient. These numbers are dramatically lower than the historic production capacities of the US nuclear weapons complex, which produced as many as 8000 warheads per year in the late 1950s during the buildup of the Cold War. Nonetheless, a production capacity of even 100 warheads per year is challenging, and key elements of the US nuclear weapons complex are not presently configured to support this modest number.

These issues can be complex, and exact capacities will vary depending upon the urgency and need. For example, in a true national crisis, the "surge" capacity for pit (or other component) production could be substantially higher, given a willingness to modify safety and security rules. Furthermore, the required capacity for reconstitution in a geopolitical crisis could be substantially larger than the capacity calculated from stockpile size and lifetime considerations.



The advent of long-range missiles gave rise to the nuclear triad for deterrence. This diagram, from the 2001 Nuclear Posture Review, shows the evolution of nuclear deterrence. Historically, each leg (delivery system) of the triad has unique abilities in support of deterrence. Intercontinental ballistic missiles (ICBMs) are land based and provide a visible counterforce target; submarine-launched ballistic missiles (SLBMs) provide survivable, secondstrike assuredness; and bombers (with air-carried bombs and cruise missiles) are flexible, recallable, and ideal for "posturing" during a crisis. The historic triad remains as part of offense strike capabilities and is supplemented by both defense and infrastructure components.

The question of agility (timing) is equally challenging to address. Recent experience in the weapons complex has demonstrated the capability to produce key components (such as pits) and complete weapons systems (life-extension programs) but arguably not on agile timeframes. For example, the first certified pit for the W88 was produced at Los Alamos in 2006, nearly 11 years after the program began. Much of this extended time was required to certify the newly built pit using the tools of stockpile stewardship (and most important, while conducting no further nuclear tests). If the United States is to rely upon reconstitution as a form of deterrence, the agility of the complex clearly must be improved.

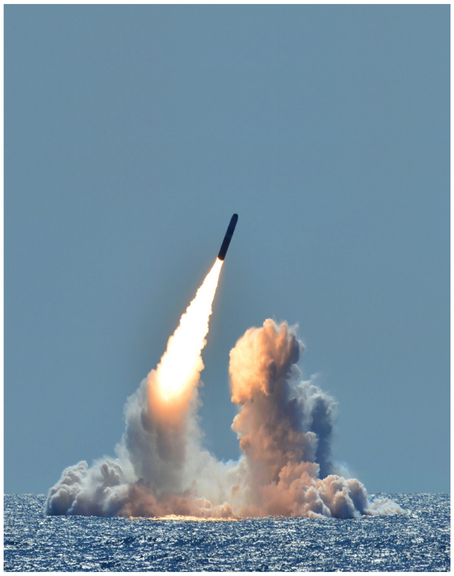
Here, actinide science plays a crucial role in support of national security. The key elements of production and certification of pits intimately involve understanding the process–properties–performance relationship. This understanding encompasses physics performance and dynamic materials properties, as well as the engineering stability of the pit across the stockpile-to-target sequence, including critical performance in mechanical and chemical stability over decades.

As recent experience in W88 pit production and in several life-extension programs has shown, there is a continuing need for further advancements in the scientific understanding and assessment of plutonium (and other actinides). On an optimistic note, the complex has demonstrated substantial agility in several key programs. For example, the Reliable Replacement Warhead (RRW) feasibility study saw two independent teams conceive next-generation warhead designs and conduct substantial computational and experimental assessment of those designs in less than eighteen months.

Historically, the degree of design, computation, and assessment demonstrated by RRW would have taken four to five years. This shows the advantage of both modern engineering and modern design practices when applied to the nuclear weapons complex. It also shows the success and maturity of the Stockpile Stewardship Program in accomplishing its core function of assessing the safety, security, and effectiveness of the nuclear stockpile.

RRW exercised the front end of the design–certify–develop–manufacture cycle, which represents the spectrum required for a reconstitution strategy. Critically, the back end of this cycle, especially development and production, has been dormant

Technicians inspect two Trident D5 missiles, which contain the W88 warhead. The first certified rebuilt pit for the W88 was produced at Los Alamos in 2006, almost 11 years after the program began. Much of this extended time was required to certify the newly built pit using the tools of stockpile stewardship.



A Trident missile is part of the SLBM "leg" of the nuclear deterrence triad. This photo shows a Trident D5 after launching from a British Royal Navy submarine.

for nearly two decades for many, if not most, of the materials and components in today's weapons. Capability cannot exist by assertion alone; it must be exercised to be credible.

Thus, the environment today consists of four key elements. We have the recently ratified New START [April 8, 2010], which commits the United States and Russia to a maximum of 1550 deployed warheads. The United States retains several thousand additional warheads as a reserve and hedge force. The administration and Congress have made a commitment to revitalize the nuclear weapons complex as a form of reconstitution-based deterrence. Finally, recent policies have embraced a path to further stockpile reductions, beginning with the Nuclear Posture Review.

Strategy recommendations

An examination of these elements leads to a simple set of recommendations in the near term. We should formally and quantitatively adopt a strategy in which a growing demonstration of a capability-based deterrent begins to replace the reserve and hedge forces in the US stockpile. Specifically, we should adopt a series of goals that when met allow the downsizing of US reserve and hedge forces. These goals should be negotiated among all involved parties (NNSA, DOE, military, nuclear policy offices, Congress, and the nuclear weapons complex, with input from impacted allies) with specific dates, deliverables, resources, and associated numbers for reductions.

As the nuclear weapons complex demonstrates the ability to reconstitute specific—or functionally equivalent—weapons systems, the reserves for those weapons can be reduced. For example, a goal of delivering some number (a few

A W87 is part of the ICBM "leg" of the nuclear deterrence triad. This is a time exposure shot of eight W87 Peacekeeper reentry vehicles launched from a single missile. The Air Force refers to these as reentry vehicles (RVs); the Navy refers to them as reentry bodies (RBs).

dozen, perhaps) of a specific tail number (B61, W78, etc.) by some date would then trigger a reduction in the reserves for that weapon. The negotiation of these specifics will answer the questions of timing and capacity, resolving a key question in the formulation of a reconstitution strategy.

In support of this negotiation, the administration might appoint a group, co-chaired by the US Strategic Command and the NNSA, to develop specific goals, schedules, and resources. The timing of this recommendation is consistent with objectives in the Nuclear Posture Review, which states that replacing reserve and hedge forces with reconstitution capability is possible in the next decade.

Advantages of the strategy

The advantages of this approach are many. Foremost, establishing a robust capability to provide a strategic deterrent should the need arise is potentially more flexible than continuing the current US strategy of maintaining Cold War–era weapons designed and built more than 30 years ago. Indeed, should a new threat emerge that requires a different balance of characteristics in the deterrent, the United States has few options available today to address this threat.

To cite one example, Russia has recently [2010] deployed a next-generation strategic warhead with terminal maneuverability on reentry. Such advances may require modifying or adapting US forces to develop an adequate response. A robust capability provides this flexibility. More generally, the experience gained by the United States in its policy and leadership communities by addressing specific questions of timing, capacity, security, and confidence in constituting this capability will be critical as the country moves toward a future of fewer weapons and a more capability-based deterrent.

Another advantage is the experience gained in trading reserve forces for reconstitution capability. In the longer term, it may be desirable to extend the contribution of a capability-based deterrent to provide functions that are currently served by deployed forces. This is a challenging assignment, and constraints on agility, capacity, survivability, confidence, and transparency will have a greater negative impact as more of our strategic security is vested in a capability. The experience gained from an initial move from reserve forces to capability will be an essential stepping-stone toward further transition in the US nuclear force posture.

The B-61-11, often called an "aircarried" platform, is shown being loaded into a B-52 bomber.

Yet another key advantage is the concrete revitalization of the nuclear weapons complex, especially the training and mentoring of the next generation of personnel and the concurrent advances in related scientific disciplines, notably actinide science. RRW is relevant here because it provided an opportunity for generational transfer of expertise. The experiences in that study showed the irreplaceable nature of doing actual design work as opposed to focusing stockpile stewardship activities on assessment and certification. It is imperative to extend this experience to the development and manufacturing elements of the complex—and well before the loss of critical expertise makes rebuilding capability considerably more difficult. RRW provided an additional lesson. It showed that the nuclear weapons complex responds best when it is given a specific assignment with concrete resources, milestones, dates, and the support of a broad spectrum of the community. A challenging assignment can serve to revitalize and motivate the national labs and production complex, just as RRW did for the nuclear weapons design enterprise.

Finally, the advantages of this approach in the international community are considerable. Establishing concrete goals and milestones for reducing reserve and hedge forces offers a powerful signal to the international community of our commitment to nonproliferation treaty objectives. Much of this can be accomplished unilaterally, with a powerful message to other nuclear states and the international community at large. The transparency of these operations will be key in showing our security partners that our capability is robust and that their security is protected. Transparency will also play a role in showing that US actions match our words with respect to the Global Zero vision as well as to other policy elements presented in the Nuclear Posture Review and other venues. Experience gained with the international community in transitioning from stockpile numbers to a more capability-based approach may form the basis for further arms-control efforts in which reserve forces and possibly even production capacity come under the umbrella of future agreements. Trust gained among partners and the wider community may lay further groundwork for a greater transition to a capability-based approach in the distant future, helping to replace even-larger numbers of deployed forces.

Challenges of the strategy

The approach suggested here poses several challenges as well. The three most substantial are sustaining a commitment to a robust capability, maintaining confidence in this capability without additional nuclear testing, and addressing negative perceptions the international community may have of this capability if not convinced of the influence it can have on the nonproliferation and arms control regimes.

A sustained commitment to the nuclear weapons complex is essential to ensure a robust capability over the long term. Over the last two decades, much of the capability in the nuclear weapons complex has eroded, and most of the production capacity has been closed or radically downsized. The need to revitalize the nuclear weapons complex has arisen due to this loss of capability and capacity.

Commitment is intrinsically a political and policy issue. Given the role that a revitalized complex will play in further stockpile reductions, and given a clear elucidation of a strategy and roadmap to Global Zero, the result of a cost-benefit analysis for investments in the nuclear weapons complex is compelling. Establishing the linkage between investments in capability and stockpile reductions may go a long way to ensuring this commitment. Confidence in a rebuilt stockpile in the absence of additional testing is another challenge. The Stockpile Stewardship Program has developed confidence in rebuilt and life-extended components, although the timeframe has been less than agile in many examples. Execution of a large-scale project such as development of an agile reconstitution capability (the design–certify–develop–manufacture cycle) can be viewed as having three critical, interrelated components: scope, schedule, and resources.

Because scope is defined by process (the capacity and types of systems for reconstitution) and schedule is determined by agility constraints (several years, certainly not more than a decade), resources are a critical variable. Here, prior investments in the Stockpile Stewardship Program are crucial, as is the modernization of antiquated facilities, especially those that process nuclear material.

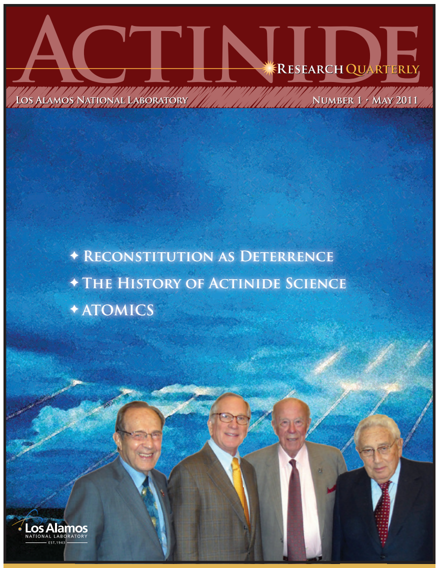
Confidence will come down to the breadth and scope of analysis for life-extended systems and, in some cases, improvements in the "performance margin" for certain system components during this process. Committing sufficient resources and support for the science-based tools of stewardship is absolutely essential to ensuring confidence in the absence of additional nuclear testing.

A final challenge is raised by the perceptions of the international community, perceptions that can be changed by the influence of this strategy on the nonproliferation and arms-control regimes. Viewed in isolation, establishing the capacity for reconstituting nuclear weapons may be seen as provocative. Conversely, when linked with substantial stockpile reductions and shown as part of a strategy for further advancing Global Zero objectives, reconstitution may be acceptable.

Linkage and transparency are the key tools in this arena. During informal discussions the author had at Stanford University with a wide spectrum of international nuclear policy experts (including those from Sweden, Mongolia, the United Kingdom, India, Pakistan, and China), participants showed an interest in and acceptance of this approach if it is concretely tied to stockpile reductions. Formally establishing milestones that link reductions to development of reconstitution capability will powerfully serve this function.

2020 Update

Nuclear defense remains at the forefront of today's social and political dialogue. Today as the US implements a 30 pit-per-year production mission and seeks the capacity to triple that production rate by decade's end, science-based stockpile stewardship is as important as ever. In an era absent of nuclear testing and an ever-aging nuclear stockpile, a skilled, well-prepared technical workforce conducting purposeful research and development with state-of-the-art scientific tools enabled to address challenging technological problems remains the basis for success. Since 2011, US and Russia have made gradual progress in their reductions over the lifetime of the New START Treaty and by February 2018, both parties had reached their reduction goals. A capability-based deterrent remains important for both.



ARQ First Quarter 2011:

"Lester R. Morss began his scientific career in inorganic chemistry and radiochemistry by carrying out research on the actinide elements uranium through californium under Professor Burris B. Cunningham. He joined the Chemistry Division of Argonne National Laboratory in 1980, where he resumed his primary research focus on solid-state and thermochemistry of the transuranium elements. Morss retired from Argonne in 2002 and then served until 2010 as program manager for Heavy Element Chemistry in the Office of Basic Energy Sciences of the Department of Energy.

The author acknowledges helpful comments from John Burnett, Norman Edelstein, Richard Haire, Robert Penneman, and Elliot Pierce."

ARQ FIRST QUARTER 2011

Tracing the Evolution of Actinide Science Research in the United States

Lester R. Morss

Many scientists entering a research field assume that the science has been funded steadily and has had broad public support for many decades. But the genesis of public support of science, the tradition of government support of basic research, and the maintenance of research support must not be taken for granted. Actinide science has a rich and dynamic history in the United States, but it is also an example of a research field that has seen government and public support wax and wane throughout the course of seventy years.

The field of actinide science was born with the discovery of neptunium and plutonium—within the memory span of some living scientists. The US federal government has supported research on the physical, chemical, and nuclear properties of the actinides, with a focus on the transactinides, since the early days of World War II. Actinide research has been carried out under the auspices of the Department of Energy (DOE) and its predecessor agencies: beginning with the Uranium Committee in 1939 and the numerous groups that evolved into the Manhattan Project, the Atomic Energy Commission (AEC), and the Energy Research and Development Agency (ERDA).

The now-obscure growth and maturation of physical chemistry, of which actinide science is a part, is illuminated in a recent book, Cathedrals of Science: The Personalities and Rivalries That Made Modern Chemistry. The book's title is based on the preface to the 1923 textbook, Thermodynamics and the Free Energy of Chemical Substances, which reads in part:

> *"There are ancient cathedrals which, apart from their consecrated purpose, inspire solemnity and awe. Even the curious visitor speaks of serious things … The labor of architects and artisans has been forgotten, the scaffolding erected for their toil has long since been removed, their mistakes have been erased, or have become hidden by the dust of centuries. … But sometimes we enter such an edifice that is still partly under construction; then the sound of hammers … enable[s] us to realize that great structures are but the result of giving to ordinary human effort a direction and a purpose."*

Actinide science before World War II

European university laboratories advanced the field of nuclear science with early studies of the chemical properties of radioactive elements and the chemical effects of ionizing radiation. German chemist Martin Heinrich Klaproth discovered uranium in the 1780s, more than a century before French physicist Henri Becquerel discovered radioactivity in uranium minerals. Swedish chemist Jöns Jacob Berzelius discovered thorium in 1828. Actinium and protactinium are also found in nature because they have isotopes that are decay products of long-lived thorium and uranium ores; several

Pioneers of nuclear science (*left to right*): Marie and Pierre Curie; Henri Becquerel, who shared the 1903 Nobel Prize in physics with the Curies; and G. N. Lewis, who mentored twenty Nobel Prize winners.

of their isotopes were chemically separated by Marie Curie and other radiochemists working in France, Germany, and England between 1898 and 1909. By 1941, chemical and physical properties of the first four actinide elements (actinium, thorium, protactinium, and uranium) were known, although neither the concept nor the terminology of an actinide series of elements had been expressed.

Nuclear science in the United States was practiced by a relatively small number of chemists. Theodore William Richards—an analytical chemist, not a radiochemist—made precise measurements that provided strong evidence that differences in the atomic weight of lead samples taken from different minerals (for example, pitchblende and thorite) were due to different isotopic ratios caused by radioactive decay. Richards was the first American to be awarded the Nobel Prize in chemistry, which he received in 1914. Harold Urey—also not a radiochemist but a physical chemist—was inspired by a 1931 paper on differences in the atomic weights of hydrogen to search for a heavy hydrogen isotope, which he discovered and named deuterium. His studies of deuterium were an example of nuclear chemistry but not radiochemistry because neither deuterium nor heavy water involved radioactivity. He was awarded the Nobel Prize in chemistry in 1934.

Similarly, G. N. Lewis, already famous as a physical chemist but without a Nobel Prize, decided in 1935 to study the chemistry of heavy water and other deuterated compounds, perhaps as a “short and sure route to the Nobel Prize,” says Patrick Coffey in Cathedrals of Science. Although Lewis published twenty-six communications within less than two years on this topic, the Nobel Prize continued to elude him. He was nominated for the prize more than thirty times but never received it. He did, however, mentor twenty future Nobel Prize winners during his career. Aristid von Grosse was a notable pre–World War II radiochemist who is considered by many to be the first US actinide chemist. Educated in Germany, von Grosse came to the United States in 1930 and studied protactinium at Lindsay Light and Chemical Co. in West Chicago, Illinois, and at the University of Chicago in the 1930s. (Protactinium is a decay product of uranium.) Von Grosse developed techniques to recover and purify the element from uranium ores, isolated milligram amounts of the protactinium oxide Pa_2O_5, reduced it to the metal, determined its atomic weight, and prepared several compounds.

Glenn Seaborg was the quintessential actinide chemist. He received his doctorate in 1937 from the University of California, Berkeley (UC Berkeley), under chemist George Gibson. Seaborg served as Lewis's research assistant in generalizing the theory of acids and bases from the Arrhenius concept of protonic acids and from Lewis's earlier concept of electron-pair acceptor "Lewis" acids. The result was a generalized acid-base concept in nonaqueous systems, organic chemistry, and catalysis. Seaborg then began to work in the field of nuclear chemistry. In 1939 Seaborg began a tenure-track career, first as an instructor and then as an assistant professor at Berkeley. He was thus able to begin an independent research career. The Los Alamos and Livermore Glenn T. Seaborg Institutes and the G.T. Seaborg Center at UC Berkeley/Lawrence Berkeley National Laboratory would later be named in his honor.

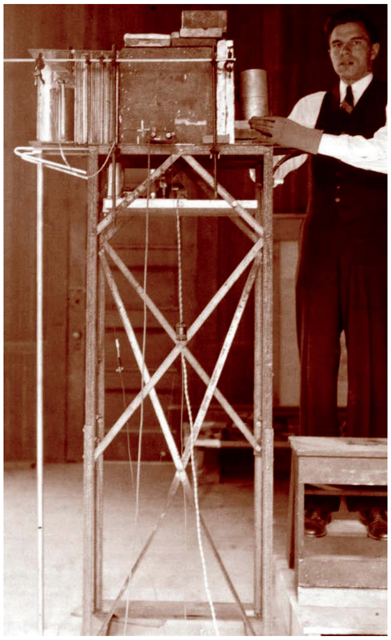
Seaborg recalled a Journal Club meeting (probably in January 1940) of the Physics Department at which an announcement was made about the Otto Hahn–Fritz Strassmann fission paper (*"On the detection and characteristics of the alkaline earth metals formed by irradiation of uranium with neutrons,"* published in Naturwissenschaften in 1939). Seaborg wrote, *"Somebody got up and said, 'You know, all of these transuranium elements … are due to the splitting of uranium in half …' Before he had finished the sentence, I said to myself, 'My God, how stupid we have been! Obviously, that should be the explanation.'"* The fissionability of uranium-235 and the potential of a critical mass leading to a chain reaction and a nuclear explosion were tempered by the difficulty of separating the small concentration of uranium-235 from uranium-238 in natural uranium.

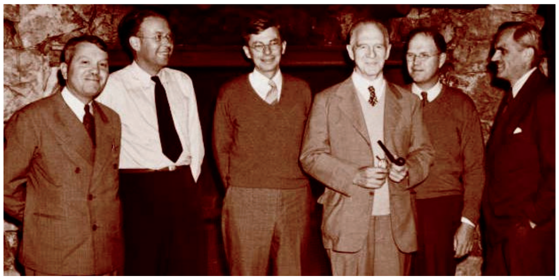
Meanwhile, Berkeley physicists Edwin McMillan and Philip Abelson had begun studies in nuclear chemistry. In 1937–9 they irradiated natural uranium with neutrons and succeeded in producing two radioisotopes, one with a half-life of 23 minutes and the other with a half-life of 2.3 days. McMillan identified the 23-minute isotope as uranium-239, previously identified by Austrian physicist Lise Meitner and others. Subsequently, in a few days' research during a May 1940 visit to Berkeley, Abelson discovered that uranium-239 decays by beta decay to a unique isotope: neptunium-239, the first isotope of a transuranium element.

It should be noted that Enrico Fermi and collaborators at the University of Rome carried out neutron bombardments of many elements, succeeding in inducing artificial radioactivity from many of them. Using careful radiochemical "carrier" chemistry, they ruled out most known elements as representing some of the artificial radioactivity and claimed discovery of transuranium elements. Fermi was awarded the 1938 Nobel Prize in physics in part for these discoveries, which turned out to be erroneous. What he thought were transuranium elements were subsequently found by Hahn and Meitner to be fission products. Fermi emigrated to the United States after receiving the Nobel Prize and extended his work in nuclear physics and reactor physics at Columbia University and the University of Chicago.

During the summer of 1940, McMillan tried unsuccessfully to identify the decay product of the 2.3-day isotope, neptunium-239. (The decay product is plutonium-239, but its long half-life, 24,110 years, prevented its detection at that time.) With permission of McMillan, who left Berkeley and moved to MIT to join the radar project, Seaborg and coworkers continued studying deuteron-irradiated uranium, discovering first (in late 1940) the much more radioactive plutonium-238 (half-life 87.7 years) and, early in 1941, the longer-lived plutonium-239 and its fissionability.

None of this pre-World War II chemistry research on actinide elements was supported by government grants or contracts. There were no such grants or contracts until 1940, except for applied research related to military needs. Other than the War





and Navy Departments, only the National Bureau of Standards and the Department of Agriculture had established research programs. But in 1939 nuclear scientists took the first steps to establishing the tradition of government support for research applied to national needs.

Evolution of the Manhattan Project

In the years immediately preceding the United States' entry into World War II, while researchers investigated the new science of fission, decisions were being made in Washington, D.C., that would evolve into a full-scale bomb project—the Manhattan Project.

In 1939, in response to the famous letter of Albert Einstein warning President Franklin Roosevelt of the military potential of nuclear fission, Roosevelt established the Advisory Committee on Uranium to consider the feasibility of an atomic bomb. He appointed Lyman J. Briggs, director of the National Bureau of Standards, to head the advisory committee, which included both military and civilian members. The committee met for the first time on October 21, 1939, and several months later recommended that the government fund research—$6,000 was budgeted for research on fission chain reactions and isotope separation.

In June 1940 the Uranium Committee was transferred to the newly created National Defense Research Committee (NDRC), chaired by Vannevar Bush, an MIT physicist and president of the Carnegie Institution. Bush would become one of the most influential forces in the establishment of not only the nascent Manhattan Project but also early US atomic-energy policy.

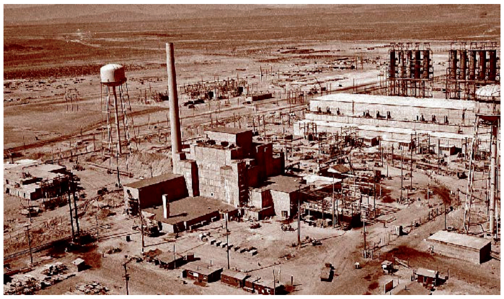
With Roosevelt's approval, Bush reorganized the Uranium Committee into a strictly scientific committee and eliminated the military membership. In June 1941 Roosevelt appointed Bush as director of another new agency: the Office of Scientific Research and Development (OSRD). Bush reorganized the Uranium Committee into the Section on Uranium, code name S-1, at which time jurisdiction for it was transferred from the NDRC to the OSRD. Bush now had responsibility for all fission research, and Briggs reported to Bush.

Left to right: Glenn Seaborg was the quintessential actinide chemist. This photo from 1937 shows him with neutron scattering apparatus in the East Hall at UC Berkeley.

Edwin McMillan in the lab in 1940, the year he discovered neptunium. He and Glenn Seaborg would share the 1951 Nobel Prize in chemistry for "their discoveries in the chemistry of the transuranium elements."

Vannevar Bush became one of the most influential forces in the establishment of Manhattan Project and early US atomic-energy policy.

The S-1 Executive Committee in 1942. From left to right: Harold Urey, E. O. Lawrence, James Conant, Lyman Briggs, Eger Murphree, and Arthur Compton.



Left to right: Site W: Hanford B-reactor area;
Site X: Oak Ridge Y-12 shift change;
Site Y: Los Alamos main technical area.

James B. Conant, a chemist and president of Harvard University, replaced Bush at the NDRC. While the NDRC technically still existed after the creation of the OSRD, its authority was reduced from actually funding research to serving as an advisory body to the OSRD. The NDRC would cease to exist after its last meeting, in January 1947.

In early July 1941 the British MAUD Committee issued a report concluding that a uranium bomb was feasible. (MAUD is often assumed to be an acronym, but it was actually the name of the governess of Danish physicist Niels Bohr's children.) A report by the US National Academy of Sciences later that year agreed with the MAUD Committee's conclusion. In December 1941 Bush organized a meeting to accelerate research into uranium-235. Arthur Holly Compton, Nobel Prize winner and physics professor at the University of Chicago, was in charge of the project to investigate gaseous diffusion and electromagnetic enrichment of uranium-235. Urey headed heavy water and isotope separation research, and Fermi headed theoretical studies. The S-1 project now focused on developing an atomic bomb.

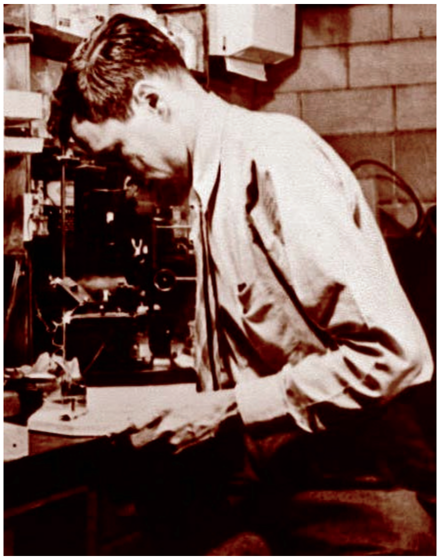
In June, 1942, Bush dissolved the original S-1 and created the S-1 Executive Committee, whose members included Conant (chairman), Briggs, Compton, Urey, E.O. Lawrence (winner of the Nobel Prize in physics in 1939 for his work on the cyclotron), and Eger Murphree (a chemist with Standard Oil). Cooperation between the OSRD and the Army was strengthened, and the project was put under the management of the US Army Corps of Engineers. On August 13, 1942, the Manhattan Project (formally called the Manhattan Engineer District because its first offices were in New York City) was created, and on September 17, 1942, General Leslie R. Groves assumed command. Three primary secret research and production sites were established: Site W at the Hanford Site in eastern Washington state for plutonium production; Site X at Oak Ridge, Tennessee, for uranium isotope separation; and Site Y in Los Alamos, New Mexico, for bomb design. Berkeley theoretical physicist J. Robert Oppenheimer was named scientific director at Los Alamos. By May 1943 the Army had assumed full control over OSRD's research projects, and the S-1 Executive Committee became inactive. The Manhattan Project would later involve more than 30 sites, including universities, and 130,000 people.

Actinide science during World War II

While Washington was consolidating the institutional structure that would lead to development of the atomic bomb, scientists were making major discoveries. NDRC leaders realized that the key to a uranium fission weapon was separating the rare isotope uranium-235 from the more abundant uranium-238. Processes to accomplish isotope separation were then, and still are, physical processes (such as diffusion or centrifugation) rather than chemical processes. When Seaborg succeeded in proving that plutonium-239 was fissionable, an alternative "chemical" route to a fission weapon became possible.

The first fission reactor Fermi constructed at the University of Chicago might have had sufficient neutron flux to produce multigram quantities of plutonium-239. Plutonium could be separated from uranium-238 by a chemical rather than a physical process. In 1941, Compton chaired the National Academy of Sciences Committee to Evaluate Use of Atomic Energy in War. Surprisingly, it was Compton—a physicist—who favored pursuing the plutonium-239 "chemical" route to nuclear fission, whereas Conant—a chemist—preferred only the uranium-235 "physical" route. Compton's influence led directly to the plutonium chemistry research program at the University of Chicago Metallurgical Laboratory (Met Lab), to the Oak Ridge and Hanford reactors, and to the Trinity Site and Nagasaki plutonium nuclear explosions.

Actinide chemistry research that focused on a plutonium bomb option was initiated in the spring of 1942, primarily in Section C-1 at the Met Lab under Seaborg's leadership. A secondary site was at the UC Berkeley Chemistry Department under Wendell Latimer, Robert Connick, Leo Brewer, and John Gofman. Almost all of this research focused on plutonium chemistry. Plutonium metallurgy was carried out first at the Met Lab and expanded at Los Alamos.



Glenn Seaborg looking at the first pure plutonium produced at the University of Chicago Met Lab, 1942.

Chemist Frank H. Spedding led important wartime research at Iowa State College (now Ames Laboratory of Iowa State University). Spedding developed technology to make high-purity uranium metal in sufficient quantities for reactors. He also developed ion-exchange separation of rare-earth elements, a technique that would later be applied to separate and chemically characterize all transplutonium actinide elements.

Although elements heavier than plutonium were in a strict sense peripheral to the mission of the Manhattan Project, both nuclear physicists and chemists were aware that reactor production of plutonium would also result in elements of higher atomic number, created by the beta decay of plutonium isotopes (for example, plutonium-241 forming americium-241 and plutonium-243 forming americium-243), followed by additional neutron capture. These transplutonium isotopes would degrade weapon performance, so their physics and chemistry had to be studied. The first transplutonium isotopes were actually prepared in the summer of 1944 by alpha-particle bombardment of plutonium-239 to make curium-242 and, later that year, by neutron bombardment of plutonium-239 to make americium-241. However, the isotopes' isolation and identification remained elusive because no one anticipated that their +3 ions would be the most stable.

During the Manhattan Project years, Seaborg hypothesized that these elements might form an "actinide series" with stable +3 ions. Seaborg enunciated the "actinide concept" in classified Met Lab papers in 1944. In talks and papers, he frequently mentioned that, for example, "when I showed [the actinide concept] to some world-renowned inorganic chemists, I was advised not to publish it—such an act would 'ruin my scientific reputation.'" (See p4 for more information.)

Seaborg's first public description of the transplutonium elements was on a "Quiz Kids" radio program in Chicago on November 11, 1945, a few days before his paper on the subject was presented at an American Chemical Society symposium and immediately published. The phrase "heavy-element chemistry" traces its origin to studies of "heavy elements" or "heavy isotopes" during and immediately after World War II. (For more on Seaborg, see ARQ, Second Quarter, 2009.)

President Truman, with several senators looking on, signs the Atomic Energy Act of 1946, which established the US Atomic Energy Commission.

The frantic pace of wartime actinide research culminated in the production of three atomic bombs: one uranium gun-type assembly, in which a subcritical mass of uranium-235 is shot at another subcritical mass of fissile material, and two plutonium-triggered implosion devices, in which a core of plutonium is compressed to critical mass by a high-explosive charge. The scientists had little doubt that the uranium gun assembly would work but were concerned about the implosion concept. For that reason, they chose to test the plutonium device, nicknamed “The Gadget”—the world’s first atomic bomb—at Trinity Site in Alamogordo, New Mexico, on July 16, 1945. (A test of the implosion device rather than the gun-type one was also prudent because there was much more plutonium available than uranium-235.) The implosion test was a success. The first nuclear device used as a weapon, “Little Boy,” was the uranium-based bomb, dropped on Hiroshima, Japan, on August 6, 1945. Three days after that, the second plutonium weapon, “Fat Man,” was exploded over Nagasaki, Japan. (For more on the Manhattan Project, see ARQ, Fourth Quarter, 2019.)

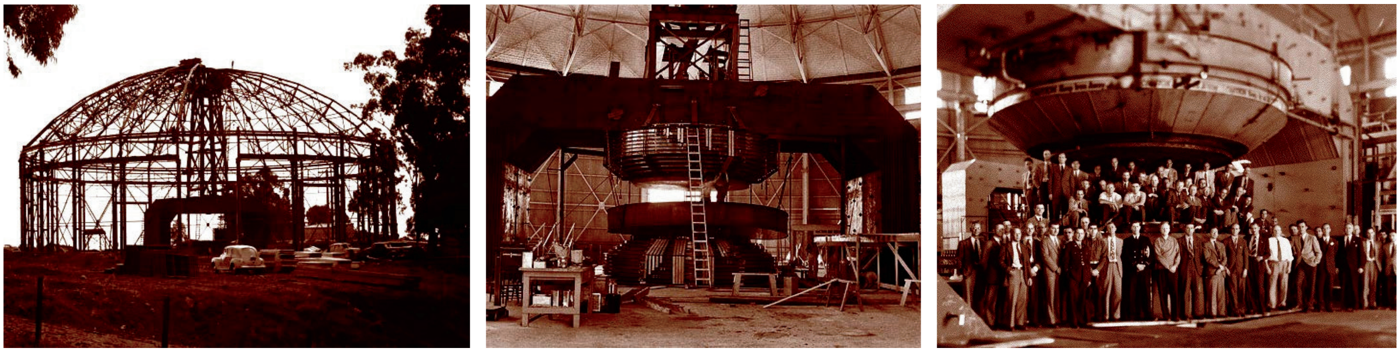
Postwar actinide science

The Atomic Energy Act was introduced in Congress on December 20, 1945, during a time when there was much debate (mostly out of public view) over whether atomic energy should be under military or civilian control. The bill established civilian control, with many restrictions on dissemination of information, even to US wartime allies. It was signed by President Harry Truman on August 1, 1946, and became law on January 1, 1947. Manhattan Project assets were transferred to the new Atomic Energy Commission (AEC) at midnight on December 31, 1946. The AEC exercised governmental control over military, regulatory, and developmental aspects of atomic energy until 1975 when the agency was disestablished.

The AEC was formally led by five commissioners and supported by technical management led by a general manager. The first AEC general manager was Carroll L. Wilson, a 1932 MIT graduate, who was nominated by Truman (and subsequently confirmed by the Senate) even though he had little more than a decade of MIT and government management experience. The AEC’s first director of research was James B. Fisk, a colleague of Wilson’s. Fisk had taught physics at MIT and came to the AEC in 1947, after having served as wartime director of research at Bell Laboratories. Although at the AEC only until August 1948, Fisk initiated research in high-energy accelerators and expanded support of science at universities.

Meanwhile, the first AEC director of biology and medicine, Shields Warren, was able to initiate basic research in biological sciences because the Division of Biology and Medicine was parallel to, rather than under, the Division of Research. Warren had been chief pathologist at the New England Deaconess Hospital and professor of pathology at Harvard Medical School. The second AEC director of research, Kenneth Pitzer, served from January 1949 through June 1951. Pitzer came from the chemistry faculty at UC Berkeley and returned there after his AEC tenure. He initiated AEC support for physical science research at the national laboratories and guided a transition from university contracts with Office of Naval Research interim support to those with AEC support.

The AEC’s authority to issue research contracts outside the national laboratory system was tenuous: its legal staff concluded that Pitzer could legally participate in evaluating and selecting research projects as long as the Commission determined the total allocation for such research. However, in December 1950, at the height of the Korean War, Pitzer “believed that the Commission could take a more daring



Construction of the 184-inch cyclotron at U.C. Berkeley's Rad Lab began in 1941. The magnet yoke was set in place and the building erected around it. E.O. Lawrence and his staff pose with the magnet at the cyclotron, which was converted from a calutron to a synchrocyclotron after the war.

approach" to focus AEC research on applied research on military topics (as noted in *"A History of the United States Atomic Energy Commission,"* by Richard Hewlett and Oscar Anderson), clear scientists for classified research, and take steps so that "universities should be prepared to undertake classified research."

By law, Congress limited research to reactor physics, metallurgy, and related reactor science and to weapons development. Almost all research was carried out at the national laboratories: first Argonne National Laboratory (the first national laboratory, chartered in 1946 and arising out of the Met Lab) and then Oak Ridge. Thus, postwar actinide science suffered from the exodus of many Manhattan Project scientists back to universities, where they could not seek AEC support. Robert Penneman, leader of the actinide group at Los Alamos Scientific Laboratory, was able to initiate americium chemistry there with the laboratory director's informal approval but without the AEC's formal approval. ("Scientific" was added to Los Alamos Laboratory's name in 1947, and in 1980 the name changed again to Los Alamos National Laboratory.) The Radiation Laboratory at Berkeley was established before World War II with private and university support; it became a federal laboratory in 1942 and an independent national laboratory in 1959. Actinide chemistry research there was led by Seaborg and Burris Cunningham, who both returned to Berkeley in 1946 after leaving the Met Lab.

Seaborg served on the first General Advisory Committee of the AEC from January 1947 to August 1950, along with chairman Oppenheimer; Fermi; Conant; Isidor Rabi, a physicist and Nobel laureate; and Lee A. DuBridge, a physicist and founding director of the Radiation Laboratory at MIT. The General Advisory Committee advised the AEC to initiate a program of support for basic research in US universities and colleges. The Atomic Energy Act did not permit issuing contracts or grants for such research; nevertheless, Pitzer was able to initiate a few non-national-laboratory contracts.

The National Science Foundation, proposed by Bush in 1945 in the influential report *"Science: The Endless Frontier"* and finally enacted into law in 1950, provided a model for independent support of scientific research based on peer-reviewed proposals from researchers rather than directed-research contracts awarded to national laboratories.

Lawrence (left), Glenn Seaborg (center), and J. Robert Oppenheimer at the controls to the magnet in early 1946, while it was being converted from its wartime use.

President Eisenhower delivers his Atoms for Peace address to the United Nations General Assembly, December 8, 1953.

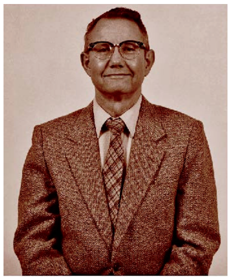
The ’50s: Focus on the national laboratories

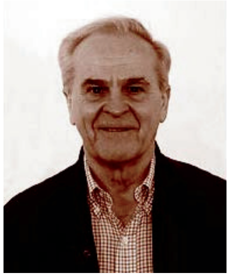
President Dwight Eisenhower’s Atoms for Peace address to the United Nations General Assembly in December 1953 and the resulting Atoms for Peace program removed the cloak of secrecy from much basic actinide research. The Atomic Energy Act was modified in 1954 to permit a limited number of level-of-effort contract awards to outside organizations (for example, academic institutions). The modified act did not require merit (peer) review of proposals, although the AEC followed the National Science Foundation example by requesting proposals from universities and subjecting them to written merit review.

Among the scientists involved in pioneering research projects at Argonne National Laboratory, Paul Fields carried out nuclear and atomic spectroscopy, Joseph Katz studied actinide oxides and fluorides, Dieter Gruen studied molten salts, and Sherman Fried and Leonard Katzin synthesized new actinide compounds. Fields led the Argonne heavyelement group for many years, then served as Chemistry Division director in the 1960s and 1970s.

At the University of California Lawrence Radiation Laboratory (LRL), Seaborg continued nuclear chemistry research that led to the discoveries of berkelium (1949), californium (1950), einsteinium (1952), fermium (1953), mendelevium (1955), and nobelium (1958) and determination of their nuclear and chemical properties. These elements were separated as tripositive ions by cation exchange by Seaborg and colleagues, in particular Gregory R. Choppin, who continued his actinide research at Florida State University into the twenty-first century.

Seaborg’s colleague Albert Ghiorso was first author on the papers that announced the discoveries of einsteinium, fermium, mendelevium, and nobelium, as well as that of lawrencium in 1961, when Seaborg was chairman of the AEC. Seaborg chaired the session “Heavy Element Chemistry” at the first Conference on the Peaceful Uses of Atomic Energy in Geneva in 1955. He gave a plenary lecture, *“Recent Developments in the Field of Transplutonium Chemistry,”* at the second conference in 1958. The vast scope of these two conferences was manifested by the publication





Left to right: **William Carnall** spent his scientific career at Argonne National Laboratory, where he pioneered work in interpreting lanthanide spectra in solutions. After his death in 2003, the Handbook on the Physics and Chemistry of Rare Earths, Volume 37, was dedicated to him. **Albert Ghiorso** was a co-discoverer of a dozen elements, more than were discovered by anyone else. His research career spanned more than five decades, most of which was spent at Lawrence Berkeley Laboratory. **Robert Penneman** was leader of the actinide group at Los Alamos Scientific Laboratory. The group was one of only a few that carried out most of the pioneering transplutonium research in the United States. **Gregory Choppin**, a co-discoverer of mendelevium while at Lawrence Berkeley Laboratory, continued his actinide research at Florida State University into the twenty-first century.

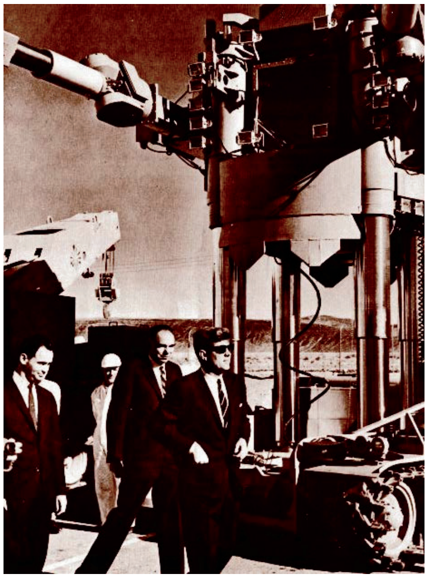
of research papers in twenty-six and thirty-two volumes, respectively. (For more on Ghiorso, see ARQ, First Quarter, 2007.)

Seaborg was influential in the initiation of the US National Transplutonium Production Program that led to construction of the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. As americium and heavier actinide metals and compounds became available in microgram or larger quantities, Cunningham pursued microchemical syntheses of these actinides to determine thermodynamic, magnetic, spectroscopic, and electrochemical properties. During this and adjacent decades, the Cunningham group at Berkeley, the Penneman group at Los Alamos, and the Fields–Carnall group at Argonne carried out most of the pioneering transplutonium research in the United States. The Los Alamos actinide program, led by Penneman, characterized americium chemistry both in solids and solution. (For more on Penneman and the history of isotope chemistry at Los Alamos, see ARQ, Second Quarter, 2010.)

Eisenhower appointed Seaborg to the President's Science Advisory Council in January 1959. The Advisory Council commissioned a study of the interactions among US funding agencies and institutions that carried out basic research. Seaborg chaired the committee that conducted the study. The final report, *"Scientific Progress, the Universities, and the Federal Government,"* known as the 'Seaborg Report,' made an immediate impression on Eisenhower in the final month of his presidency and had long-lasting influence. Seaborg wrote, *"Perhaps the report's most famous recommendation was … that basic research and the education of scientists go best together as inseparable functions of universities [and] that federal support for basic research and graduate education should be continued and flexibly increased, so as to support excellence where it already exists and to encourage new centers of outstanding work."*

The '60s: The golden post-Sputnik years

Seaborg, who served as chancellor of UC Berkeley from 1958 through 1961, was nominated by President-elect John F. Kennedy to succeed John McCone as chairman of the AEC. He served in that position for 10 years (1961–1971), being reappointed



President Kennedy and Glenn Seaborg tour the Nuclear Rocket Development Site at the Nevada Test Site in December 1962. As president-elect, Kennedy nominated Seaborg as chairman of the Atomic Energy Commission, a position he held for ten years.

The High Flux Isotope Reactor at Oak Ridge, completed in 1968, was commissioned to isolate and purify transplutonium isotopes from the reactor's irradiation targets. At peak production levels in the 1980s, two fuel-rod-separation campaigns were conducted annually, producing berkelium-249, californium-252, einsteinium-254, and fermium-257.

by Presidents Lyndon Johnson and Richard Nixon. During McCone's tenure, the AEC expanded its role in producing nuclear materials, in particular, long-lived isotopes of the transuranium elements curium through fermium for research studies. Seaborg was instrumental in negotiating both international agreements on peaceful uses of atomic energy and the limited nuclear test ban treaty with the Soviet Union. He served as head of the US delegation to the fourth United Nations Conference on the Peaceful Uses of Atomic Energy in Geneva in 1961.

Alexander VanDyken was assistant director for Chemistry Programs, Division of Research, at the AEC in the 1960s. In late 1964, the Transplutonium Program Committee was officially formed as an advisory body to the director of the Division of Research to allocate Radiochemical Engineering Development Center products to US national laboratories and to oversee the research carried out with them. VanDyken served as chairman.

Heavy-element chemistry continued at Berkeley, led by Cunningham, who in the late 1950s helped develop ultra-microchemistry using single cation exchange resin beads. This technique led to synthesis of pure compounds of berkelium-249, californium-249, and einsteinium-253 in microgram or smaller amounts by Cunningham and his students, followed by characterization of the physical and chemical properties of these compounds. The first research with products from the High Flux Isotope Reactor (HFIR)–Transuranium Element Processing Plant (TRU) would be carried out at Berkeley and Oak Ridge in 1967.

Seaborg had proposed Oak Ridge's HFIR in 1957. The AEC authorized it in 1958, and construction was completed in 1964. The companion TRU was authorized in 1958 and completed in 1965; it was later renamed the Radiochemical Engineering

Development Center. The facility, which included heavily shielded gloveboxes and "caves," was commissioned to isolate and purify transplutonium isotopes from other components of the reactor's irradiation targets.

At the peak HFIR production level in the 1980s, two fuel-rod separation campaigns were conducted annually, producing about 50 milligrams of berkelium-249,500 milligrams of californium-252, 3 micrograms of einsteinium-254, and 1 picogram of fermium-257. Heavier actinide and transactinide isotopes cannot be produced by neutron irradiation in reactors. Alfred Chetham-Strode, and later O. Lewin Keller, Jr., led Oak Ridge's actinide chemistry program. Inorganic chemists Russ Baybarz and Richard G. Haire advanced the understanding of actinides in low oxidation states and in colloids.

Haire led research thrusts in heavy actinide metal, oxide, and halide thermodynamic systematics, especially under high pressure. He also expanded upon Cunningham's ingenious syntheses of transplutonium materials at the milligram and microgram scale, coupling the syntheses of pure materials to measure and interpret their properties by systematic studies as a function of atomic number, f-electron configuration, temperature, and high pressure. Haire fostered collaborations with domestic and foreign laboratories, especially with the Institute for Transuranium Elements, Karlsruhe, Germany. (See p18 for more.) Argonne opened its "hot" laboratories (M-Wing of Building 200) in 1963, with hot cells for remote-handled high-level spent fuel examination and separations and fiberglass gloveboxes and hoods for f-element solid-state chemistry, spectroscopy, and solvent extraction separations.

At the Savannah River Site, Clark H. Ice, who later became director of Savannah River Laboratory, was influential in encouraging the separation of transplutonium isotopes, in particular curium-244 and californium-252, from Savannah River reactor targets before the startup of Oak Ridge's HFIR. David Karraker was the chemist most responsible for transuranium research there, carrying out magnetic susceptibility measurements of americium compounds and synthesis of organoactinide compounds.

Among the few university researchers in actinide chemistry, Choppin, who was codiscoverer of element 101 (mendelevium) at Berkeley, carried out coordination chemistry and thermodynamic measurements at Florida State University from 1956 through 2008. James W. Cobble of Purdue University had a contract for thermodynamic studies that included uranium, neptunium, and plutonium. Joseph R. Peterson of the University of Tennessee had a contract for studies of transplutonium compounds from 1969 through 2000.

The '70s and '80s: Transition to DOE

AEC research activities that eventually became the Office of Basic Energy Sciences (BES) were originally in the Division of Research. In December 1971 the Division of Research was renamed the AEC Division of Physical Research to help distinguish it from an expanding program in biological, health, and medical research. The AEC became part of the new Energy Research and Development Administration (ERDA) as a result of the Energy Reorganization Act of 1974.

In 1975 Congress created the Nuclear Regulatory Commission (NRC) to oversee the nuclear power industry and other civilian uses of nuclear energy. The NRC was independent of ERDA, which administered energy research and development, including nuclear power. The AEC's weapons program was incorporated into ERDA.

Glenn Seaborg (far left) as chairman of the Atomic Energy Commission, asked President Nixon (second from left) to present a special Atomic Pioneers Award to (center from left to right) Vannevar Bush, Gen. Leslie Groves, and James Conant for their service in running the Manhattan Project.

In 1977 ERDA and the energy programs from a number of other federal agencies (not including the National Science Foundation) were brought into the new cabinet-level Department of Energy (DOE). Major programs that were brought from other agencies into the new DOE included solar energy, energy efficiency, and fossil energy.

Although the broadened focus of this new Cabinet-level energy agency did not in principle undermine research strength from traditional AEC areas, heavy-element chemistry stagnated during the 1970s and 1980s as its Cold War justification began to wane, as nuclear energy suffered environmental stresses from the lack of a waste repository and from the nuclear accidents at Three Mile Island and Chernobyl, and as the cutting-edge excitement of new-element discovery required exotic and exhausting efforts to synthesize a few atoms of short-lived isotopes.

ERDA became part of DOE as a result of the Department of Energy Organization Act of 1977. As part of the formation of DOE, heavy-element chemistry and other chemical and material science research programs became part of the Office of Energy Research on October 1, 1977. The Heavy-Element Chemistry program was initially part of the Office of Nuclear Energy but was transferred without a change in focus to the Office of Basic Energy Sciences in 1983. Both offices were part of the DOE Office of Energy Research, which was renamed the Office of Science in 1998.

Elliot Pierce directed the Office of Chemical Sciences from 1973 through 1986. John Burnett was the program manager of the heavy-element chemistry program from 1969 through 1996. Pierce guided the program to separate and utilize the transplutonium isotopes that were generated in the HFIR reactor at Oak Ridge. These long-lived isotopes, especially berkelium-249 (half-life 320 +/-3 days), have been effectively utilized in chemical research and as targets for discovery and determination of properties of superheavy (transactinide) isotopes.

Pierce had the vision to commission and support DOE's sponsorship of a National Academy of Sciences workshop on transplutonium elements in February–March 1983. Gerhard Friedlander, an esteemed nuclear chemist, served as workshop chair and Henry Taube was session chair on inorganic chemistry. Friedlander and Taube represented scientific experts who were nonpartisan; they had neither a reputation in nor a vested interest in heavy-element chemistry. This workshop revitalized the study of transplutonium chemistry and physics in the US for the next two decades. Pierce guided the American Chemical Society Division of Nuclear Chemistry and Technology for years as division councilor, continuing today in the less formal role of division councilor emeritus. Even after retirement, Pierce continued to be active, authoring the influential 1998 report, *"The Education and Training of Isotope Experts,"* which was delivered to the subcommittee on energy and science of the Committee on Science of the US House of Representatives.

Events near the end of the Cold War era—the Chernobyl nuclear reactor accident in 1986, the fall of the Berlin Wall in 1989, and the breakup of the Soviet Union in the early 1990s—signaled a shift in actinide research from nuclear weapons production and nuclear reactor technology to nuclear stockpile stewardship and mitigation of the environmental effects of the Cold War nuclear legacy. The change in world vision and public policy led the Clinton administration in 1994 to eliminate reactor and reprocessing research and much other nuclear research and development from the DOE portfolio.

Global dialogues

Thanks to the Atoms for Peace initiative, which lifted secrecy of all nuclear literature, international actinide science meetings were initiated with the first International Conference on Plutonium in 1957 in Chicago, Illinois. This was followed by Plutonium 1960 in Grenoble, France, which centered on the properties of this most unusual metal; Plutonium 1965 in London, England, which expanded the scope to ceramic materials and their behavior under irradiation; Plutonium 1970 and Other Actinides in Santa Fe, New Mexico; Plutonium and Other Actinides and the Transplutonium Element Symposium in Baden-Baden, Germany in 1975; and the International Conference on the Electronic Structure of the Actinides in 1978 in Grenoble. The scope of these meetings was enhanced by the maturity of actinide research in the European Community and Japan, but somewhat inhibited by continuing Cold War ideological barriers. These barriers began to be lifted in the 1980s.

An international quadrennial series of heavy-element research conferences picked up where the earlier plutonium conferences left off; the first was Actinides 1981 in Asilomar, California. Subsequent conferences in the series included Actinides 1985 in Aix en Provence, France; Actinides 1989 in Tashkent, USSR; Actinides 1993 in Santa Fe; Actinides 1997 in Baden-Baden; Actinides 2001 in Hayama, Japan; Actinides 2005 in Manchester, United Kingdom; and Actinides 2009 in San Francisco, California. A number of heavy-element-related conferences that were initiated continue today. The Scientific Basis for Nuclear Waste Management symposia began in 1978 as part of Materials Research Society conference.

The International Conferences on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere—known as the Migration conferences—have been held biennially since 1987. They provide an international forum on research essential for understanding long-term nuclear waste disposal. The first Migration conference was held in Munich, Germany. Besides Germany, other venues have included the United States, Spain, France, Japan, Austria, Korea, and France. A series of conferences entitled Plutonium Futures—The Science was initiated by Los Alamos in 1997 to renew the tradition of open discussions of fundamental properties of plutonium and related elements. The vision and strong support of Los Alamos director Siegfried Hecker and associate director Paul Cunningham were key to establishing this conference series.

Actinide research today [2011]

The BES Heavy Element Chemistry program remains a key source of federal support in the United States for fundamental research on the chemistry of the actinides and their fission products. Within the Office of Science, Patricia Dehmer served as the director of BES from 1995 to 2007. Under her leadership, the BES budget more than doubled to $1.2 billion annually. Dehmer's DOE biography credits her with building "a world-leading portfolio of work in condensed matter and materials physics, chemistry, and biosciences. A five-year effort to relate fundamental research in these disciplines to real-world problems in energy—including problems in fossil energy and carbon dioxide sequestration, nuclear energy, renewable energy, energy efficiency, energy transmission and storage, and the mitigation of environmental impacts of energy use—facilitated greater integration of basic and applied research across DOE." During her tenure at BES, Dehmer was responsible for the planning, design, construction, and operational support of large research facilities, including the Spallation Neutron Source at Oak Ridge, built by a partnership of six DOE laboratories; the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory (formerly known as the Stanford Linear Accelerator Center); and five nanocenters.

DOE considers the five nanocenters to be the "premier user centers for interdisciplinary research at the nanoscale, serving as the basis for a national program that encompasses new science, new tools, and new computer capabilities." The centers are located at six national laboratories: Oak Ridge (the Center for Nanophase Materials Sciences), Lawrence Berkeley (the Molecular Foundry), Sandia and Los Alamos (the Center for Integrated Nanotechnologies), Brookhaven (the Center for Functional Nanomaterials), and Argonne (the Center for Nanoscale Materials). Dehmer, now deputy director for science programs in the DOE Office of Science, currently has oversight for the office's six science programs: basic energy sciences, biological and environmental research, fusion energy sciences, advanced scientific computing research, high-energy physics, and nuclear physics. The Office of Science supports research at some 300 colleges and universities nationwide, as well as at the DOE laboratories and private institutions.

In 2000, acting BES program manager Norman Edelstein initiated BES heavy-element chemistry contractor meetings. These meetings continue biennially as information-exchange forums in the spirit of the Gordon Research Conferences. Under Edelstein's guidance, the number of grants awarded to university actinide researchers increased dramatically. The grants' scope ranged from organoactinide chemistry to theoretical studies of actinide dioxides and metal surfaces. Collaborative research contracts were awarded to actinide researchers at six institutions under the Russian Academy of Sciences after proposals were solicited and peer reviewed. These research activities were carried out with the guidance and active collaboration of US actinide scientists at national laboratories and universities. Transport of actinides on colloids, aggregates, and nanoparticles was an innovative aspect of these binational collaborations carried out between 2001 and 2008.

New in 2009 for BES were Energy Frontier Research Centers and Single-Investigator and Small-Group Research projects. Awards under these initiatives led to a 40-percent increase in the heavy-element chemistry budget, from about $10 million annually to about $14 million annually. Paralleling the trend of many other research areas of physical science, theoretical advances in heavy-element chemistry now claim a partnership role with experimental advances. Advances in density functional theory have made it possible to model multi-atom systems that have significant relativistic and spin-orbit effects. Modeling of actinide atoms and ions requires theoretical treatment of these effects; such modeling is now successful for actinide metals, actinides on surfaces, actinides in gaseous species, and even in actinide ions that undergo oxidation-reduction reactions in aqueous solution.

Heavy-element theorists can suggest to experimentalists synthesis of new species and remeasurement of some data that may be incorrect and should be reconsidered. Experimentalists now partner with theoreticians by confirming the insights and quantitative results now achievable by theoretical methods as well as by measuring properties that calibrate theoretical calculations.

A final thought

"Science has its cathedrals, built by the efforts of a few architects and of many workers," says Coffey in Cathedrals of Science. While the "cathedral" of actinide science in the United States is no longer in a nascent stage, it is still developing and remains in need of the continued support of the government and its citizens. The role of the scientific leaders whose managerial vision fostered the growth of actinide science in the United States cannot be overemphasized and four "architects" of the US heavy-element chemistry program deserve another mention:

- Vannevar Bush, who led the National Defense Research Committee, the Uranium Committee, and the Office of Scientific Research and Development, and who guided the basic research tradition of peer-reviewed proposals in the National Science Foundation and the DOE Office of Science.
- Glenn T. Seaborg, for his leadership in transuranium element science at Berkeley, at the Metallurgical Laboratory, and as Atomic Energy Commission chairman, as well as for his visionary championing of basic research and science education.
- Elliot Pierce, for commissioning the 1983 workshop on transplutonium elements and for maintaining sponsorship of transplutonium element production, separation, and research in that decade.
- Patricia Dehmer, for initiating the Basic Research Needs Workshop for US Energy Security, which led to appreciation for the need for continued basic research in heavy-element science as well as funding enhancements in the first decade of the twenty-first century.

2020 Update

Since its beginnings, there have been a number of individuals from the international community who advanced the field of actinide science, engineering, research, and technology. Under their influence, this field grew from an obscure theoretical concept to one which impacts all aspects of human existence and future technological evolution. As more and more nation states are seeking energy independence and exploring options for reduced greenhouse gas emissions, nuclear power and the actinide materials which generate it are proliferating. The concern is that that proliferation left unmanaged can lead to a far greater threat to future global peace. International scientific involvement is a key means to help curb this threat.

ARQ First Quarter 2012:

"This article was contributed by Doug Kautz and David Gubernatis. Kautz works in Manufacturing Engineering Technology and has 30 years experience in manufacturing of weapons components. Gubernatis is a MET R&D engineer and has been at LANL 15 years."

ARQ FIRST QUARTER 2012

Swarfology: The Study of Turnings and Chips

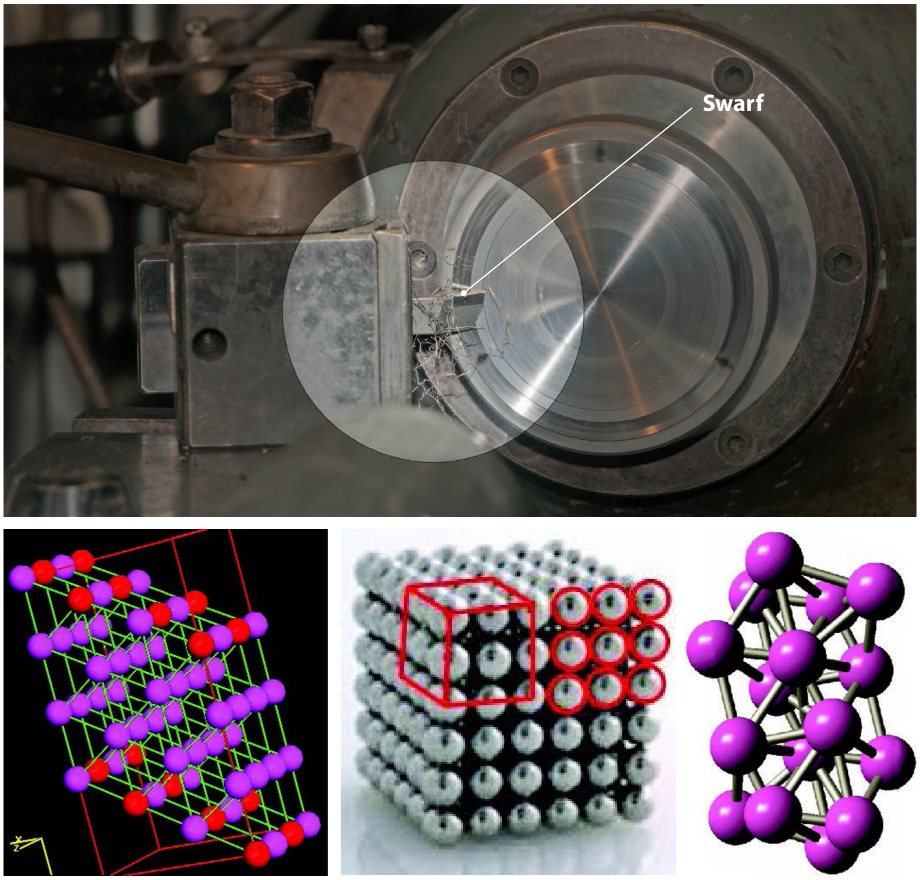
Doug Kautz, David Gubernatis

There are several terms for the material removed from stock during machining operations, including "turnings" and "chips." The general term to cover these waste materials is "swarf." In practice, when swarf does not break up into small manageable pieces, it is called a turning. When the material does break into smaller pieces, these pieces are called chips. Many parameters influence the type of swarf produced during machining, including machining parameters, tool insert design, and material properties. How well a material responds to machining depends on its mechanical and physical properties. Some brittle materials and alloys that are formulated for enhanced machinability will generally produce chips over a wide range of parameters and tool insert designs. Other very ductile materials (that deform under stress) are extremely difficult to machine without producing continuous turnings. Turnings may cause surface finish problems and safety issues during machining, therefore, adequate chip-breaking designs for tool inserts have been painstakingly developed by manufacturers. Tool insert manufacturers and end users have developed effective chip-forming inserts for most engineering materials.

Defense applications frequently use materials that are extremely brittle to ductile. Because these materials are not often machined in the industrial workplace, it is difficult to develop methods that work. Beryllium metal, with its hexagonal close-packed crystal structure, has excellent chip-formation qualities, but mechanically induced twinning (when a material mechanically deforms to form low-angle grain boundaries) causes its already low ductility to be reduced even further, increasing the likelihood of surface crack formation. Beryllium chips are readily recycled to produce new beryllium metal products, decreasing hazardous waste produced during processing. On the other end of the spectrum, delta-phase plutonium produces continuous turnings similar to other very soft face-centered cubic crystal structure materials such as aluminum and copper.

The pure plutonium alpha-phase material is more readily machinable because as it is machined it chips easily due to the brittle nature and high levels of defect structure in the metal machine stock. Plutonium is reactive with most tool insert materials, so machining feed rates must be kept fairly low to reduce tool wear and frictional heating. More common materials are also used for fabricated products needed in the defense industry; these include stainless steels, aluminum alloys, and titanium alloys. Austenitic stainless steel (made stable by being alloyed with nickel) readily adapts to the use of chip-breaking technology. It requires deep cuts during machining because surface phase transformations work-harden a thin layer on the surface of the material; other stainless steel alloys tend to machine-like high alloy carbon steels, which have been studied extensively by industry.

Aluminum alloys are readily machined and are compatible with chip-breaking tool inserts that have been designed to remove large amounts of material quickly and efficiently. An exception is the 1XXX series, commercially pure aluminum alloys.



Top: Machining process showing swarf.
Bottom, left: Beryllium structure, showing hexagonal close-packed crystal structure.
Bottom, middle: Aluminum face-centered cubic structure.
Bottom, right: Pure alpha-phase plutonium monoclinic structure.

These alloys can have problems with chip-breaking, but due to the deep cuts possible in this alloy series, problems are not as serious as those encountered with plutonium. Chip-breakers are designed to cause breakage at a certain depth of cut. If the cut is not deep enough the chip-breaking mechanism is not employed. In very thin cuts, it is difficult to find a tool with a chip-breaker to support the operation because the thin cutting edge will wear more quickly due to heat buildup. Most titanium alloys, aside from commercially pure grades, provide for excellent chip-making during machining, but these materials also are very abrasive to machine tool inserts, resulting in frequent stops to change inserts during machining. If dull tools are used with these alloys, smearing of the surface occurs that may cause embrittlement problems. Uncorrected defects could be passed to the customer, resulting in part failure during high-temperature applications.

Defense applications require the use of many nonstandard materials with properties that make fabrication difficult. LANL engineers have developed effective tooling and processes for these materials, minimizing waste and maximizing swarf recycling.

Top: Turning of a plutonium bar stock on a lathe. The rough plutonium bar is grayish due to oxidation of the surface.

Middle: Plutonium turnings where chip breaking has worked well. Note that the turnings are one-half-inch long and have broken into manageable pieces.

Bottom: Little chips of oxidized plutonium mixed with long turnings of plutonium. Chip breaking did not occur and resulted in the long turning. The long turnings pose a danger in glovebox operations because the turnings are sharp and whip around during machining. The whipping motion of the metal could potentially cause glove breaches and hand injuries.

ARQ FIRST QUARTER 2013

Space and the Atom LANL Powers Mars Curiosity Rover

Amanda Bean

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

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

Thermocouples are found in common, everyday items such as air conditioners or refrigerators, and the general principle is best described using the Seebeck effect (see box on p39). The quest for the perfect source of heat and power for deep-space probes is long and fascinating. A power source must meet stringent requirements to be of use for NASA missions; it must be impervious to cold, radiation, and other harsh effects of the space environment. It must operate continuously and require no maintenance because it cannot be repaired after launch into space. The RTG was developed by Mound Laboratories in Miamisburg, Ohio, in the late 1950s. The first RTG was launched in 1961 for use in a navigation satellite (Glenn Seaborg's speech quoted on the facing page at right celebrates that accomplishment). As NASA explains, more than 40 radioisotope power systems have been used over four decades on more than two dozen NASA spacecraft. The Apollo missions to the moon; the Pioneer, Voyager, Ulysses, Galileo, Cassini, and Pluto New Horizons missions to the outer solar system; and the Viking landers sent to Mars were all equipped with RTGs. "RTGs have never been the cause of a spacecraft accident, [though] they have been on board three space missions that did fail for other reasons," NASA says. "In all three cases, the RTGs performed as designed."

Inside the RTG is the actual radioactive heat source: the general purpose heat source (GPHS). The source of the heat is a pressed pellet of plutonium-238 oxide, PuO_2. The actual process of recycling the plutonium and producing the pellet happens within the ADPSM operations and engineering groups, NCO-5 and

ARQ First Quarter 2013:

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

ACTINIDE

Los Alamos National Laboratory

RESEARCH QUARTERLY

89 Ac

Issue 1
May 2013

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

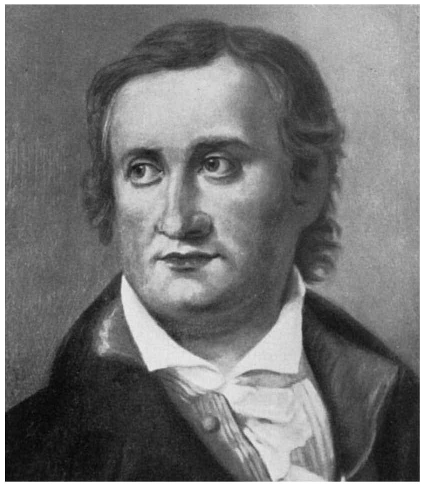
Cover story ARQ First Quarter 2013. Curiosity photograph courtesy NASA/JPL-Caltech. Artistic license was used with the view of space in the graphic.

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

– Glenn Seaborg, 1961, “Nuclear Power and Space,” a speech given as Chairman of the US Atomic Energy Commission, following the June launch of the TRANSIT IV-A, the first US atomic-powered satellite.

The Seebeck effect

This effect is the production of electricity through the use of temperature differences. A current loop is created when two metals respond to the temperature difference. First discovered in 1794 by Alessandro Volta, it is named after the physicist Thomas Johann Seebeck, who in 1821 independently rediscovered it. Seebeck observed the production of a magnetic field but did not recognize that an electric current was involved, so he called the phenomenon "thermomagnetic effect". Danish physicist Hans Christian Ørsted rectified the oversight and coined the term "thermoelectricity".



Thomas Johann Seebeck
1770-1831

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

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

MET-1, respectively. Once material has been identified to be used for the final pellet product, it is sent through the aqueous nitrate process to remove any impurities and uranium-238 that grows in as the Pu-238 undergoes radioactive decay. The resulting powder is likely to have differing particle characteristics based on the previous history of the starting material. Therefore, after the aqueous process, there is a progression to normalize the granules by grinding to a powder and then ball milling, cold pressing, and screening the powder to produce granules of a desired size range.

Once granules are of the desired size range and heated in an additional furnace treatment, they are loaded into a die and hot pressed. After the pellets have been pressed, they are sintered in flowing $H_2{}^{16}O$-saturated argon to reoxidize and reestablish stoichiometry from $PuO_{1.88}$ to $PuO_{2.00}$ and relieve mechanical stresses in the pellets to assist in transferring the pellet to the final cladding. The clad is then welded and decontaminated and ready for its final nondestructive testing and acceptance. For fiscal year 2013, 22 of the 28 heat sources to support potential future NASA missions have been manufactured. With the success of the landing of the Mars rover Curiosity, Los Alamos National Laboratory (LANL) is excited and optimistic about future missions to Mars and to other locations in the solar system.

Summary

These successes do not come without a lot of hard work. The Plutonium Facility at Los Alamos has supported the heat source program since the beginning of its operation in the late 1970s. There are significant investments being made to the Plutonium Facility in order to assure a reliable facility infrastructure. The NE-75, Space Power/Pu-238 project of the Nuclear Nonproliferation and Security Program, is investing in preventive maintenance to further sustain reliability of equipment. Some more recent investments have been the installation and method development of a DCArc instrument, which was installed in the Plutonium Facility and will be used for isotopic analysis. The ability to obtain this data inside the Plutonium Facility reduces the need to ship samples to CMR, Chemistry and Metallurgy Research, and also will greatly reduce the turnaround time for data. NE-75 also participates in a cost-sharing model with other equipment such as the installation of a plutonium assay/radiochemistry glovebox and equipment, which was sponsored by the NNSA Plutonium Sustainment Program, but will be a benefit to both programs. With continued planning of preventive maintenance, LANL is confident in its ability to continue to support the nation’s mission needs.

2020 Update

Supporting NASA space missions with radioisotope power systems is an operation that spans the DOE national laboratory complex. Oak Ridge National Laboratory generates Pu-238 oxide to NASA's specifications at the High Flux Isotope Reactor. This Pu-238 oxide is compressed into ceramic pellets, clad, and physically characterized for quality checks at Los Alamos National Laboratory. The clad fuels are then shipped to Idaho National Laboratory, where they are stored in a flight-ready state for future space missions. Targeted for launch in July 2020, the Perseverance Rover will utilize RTG technology in searching for human habitable conditions on Mars for future missions and for signs of past and present microbial life.

ARQ First Quarter 2015:

"This article was contributed by Albert Migliori, Director, and Franz J. Freibert, Deputy Director, Glenn T. Seaborg Institute for Transactinium Science, Los Alamos National Laboratory."

ARQ FIRST QUARTER 2015

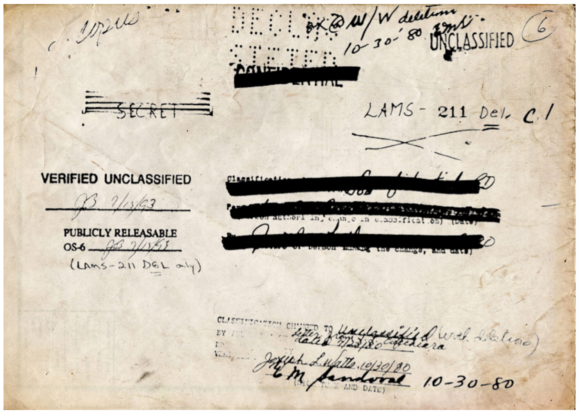
Reflections of Plutonium—In Search of Solutions to a Difficult Problem in Crystallography

Albert Migliori, Franz J. Freibert

The original research using X-ray diffraction reflections to determine the crystal structure of plutonium was shrouded by secrecy and classification at Site Y of the Manhattan Project, later to become Los Alamos Scientific Laboratory and then Los Alamos National Laboratory. The rush to make the first plutonium-fueled atomic bomb led to early misconceptions and errors regarding the stunning complexity of the five clearly-resolved phases of plutonium, the rarity of plutonium, and the difficulty of working with it. But these issues were resolved well before the structures of plutonium were revealed in peer-reviewed journals years after the work was completed. Eric Jette, a group leader in the Chemistry and Metallurgy Division, in a 1957 peer-reviewed paper with no references wrote, "The present author is merely acting as a reporter for the work represented in this summary. Since the beginning of 1944, at least forty individuals working in this laboratory have contributed to our knowledge of plutonium metal. Individual reports on the several properties of plutonium will be written by the persons actually concerned with the work today and it is hoped that adequate acknowledgement can be made there of the efforts of the earlier workers. Some time, however, may elapse before these articles can be published and therefore this summary is being presented."

For example, in January 1945, the wet purification process for plutonium (element 94, atomic weight 239, code-named "49") was tested for the first time at full scale, producing 160 grams of plutonium metal. Using resistivity and dilatometry, Frank Schnettler and his team reconfirmed that plutonium had five phases. Yet all this was classified until some years later when the crystal structures of plutonium in its various zero-pressure phases began to be published.

The creativity involved in solving the crystal structures of plutonium began when Willy (as he insisted on being called) Zachariasen hypothesized that a new series was starting, a series that included elements where active electrons were designated by the symmetry descriptor 5f. He gave a talk early in the Manhattan Project, after he had enough data to see some pattern emerging in the crystallographic studies of the new compounds we now call actinides. Willy called this the Thoride Series, because everything was happening after thorium, and he did this before Glenn T. Seaborg proposed the Actinide Series (see *Source of the Actinide Concept* by Glenn Seaborg, ARQ Second Quarter 1997, reproduced on p4 of this issue.). So, it may be that Willy discovered this correlation and series. Subsequently, Willy and Finley Ellinger, with hints from Frank Schnettler and others' work on physical properties, eked out the various crystal structures and later published them. These papers, dating from 1950 to 1963, are remarkable. Many are short with few or



OK @ W/W deletions 10-30-80

UNCLASSIFIED

(6)

[redacted]

~~SECRET~~

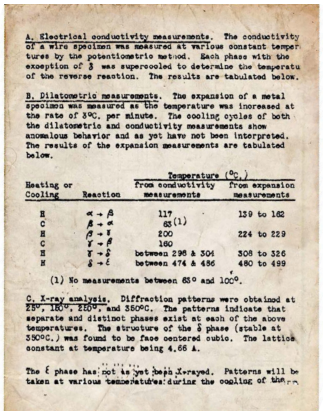
LAMS-211 Del. C.1

VERIFIED UNCLASSIFIED
JB 7/15/93

PUBLICLY RELEASABLE
OS-6 JB 7/15/93
(LAMS-211 DEL only)

[redacted]

CLASSIFICATION CHANGED TO Unclassified (with deletions)
BY letter from dated 7/23/80
Joseph L. Watts 10/30/80
E M Sandoval 10-30-80
(SIGNATURE AND DATE)



A. Electrical conductivity measurements. The conductivity of a wire specimen was measured at various constant temperatures by the potentiometric method. Each phase with the exception of δ was supercooled to determine the temperatu of the reverse reaction. The results are tabulated below.

B. Dilatometric measurements. The expansion of a metal specimen was measured as the temperature was increased at the rate of 3°C. per minute. The cooling cycles of both the dilatometric and conductivity measurements show anomalous behavior and as yet have not been interpreted. The results of the expansion measurements are tabulated below.

Heating or Cooling	Reaction	Temperature (°C.) from conductivity measurements	Temperature (°C.) from expansion measurements
H	$\alpha \rightarrow \beta$	117	139 to 162
C	$\beta \rightarrow \alpha$	63(1)	
H	$\beta \rightarrow \gamma$	200	224 to 229
C	$\gamma \rightarrow \beta$	160	
H	$\gamma \rightarrow \delta$	between 298 & 304	308 to 326
H	$\delta \rightarrow \varepsilon$	between 474 & 486	480 to 499

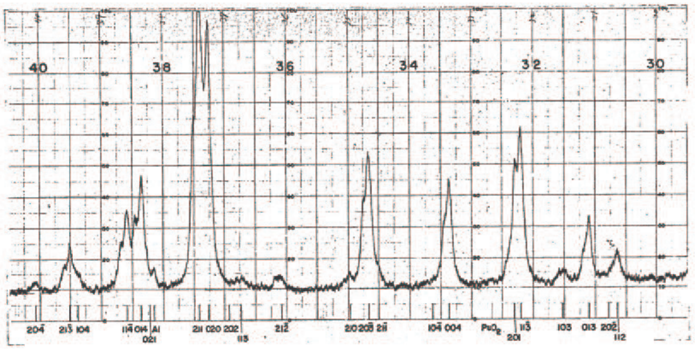
(1) No measurements between 63° and 100°.

C. X-ray analysis. Diffraction patterns were obtained at 25°, 150°, 250°, and 350°C. The patterns indicate that separate and distinct phases exist at each of the above temperatures. The structure of the δ phase (stable at 350°C.) was found to be face centered cubic. The lattice constant at temperature being 4.66 A.

The ε phase has not as yet been X-rayed. Patterns will be taken at various temperatures during the cooling of the

Far left: One of the early written accounts chronicling crystallographic studies of plutonium. Note the extent of secrecy given to reports of this kind. Such reports were not unclassified until the 80s.

Left: There were good reasons as to why researchers did not classify δ-prime plutonium as a separate phase when the first studies were set to paper. Taken from one such early report, this page demonstrates how erroneous conclusions were reached.

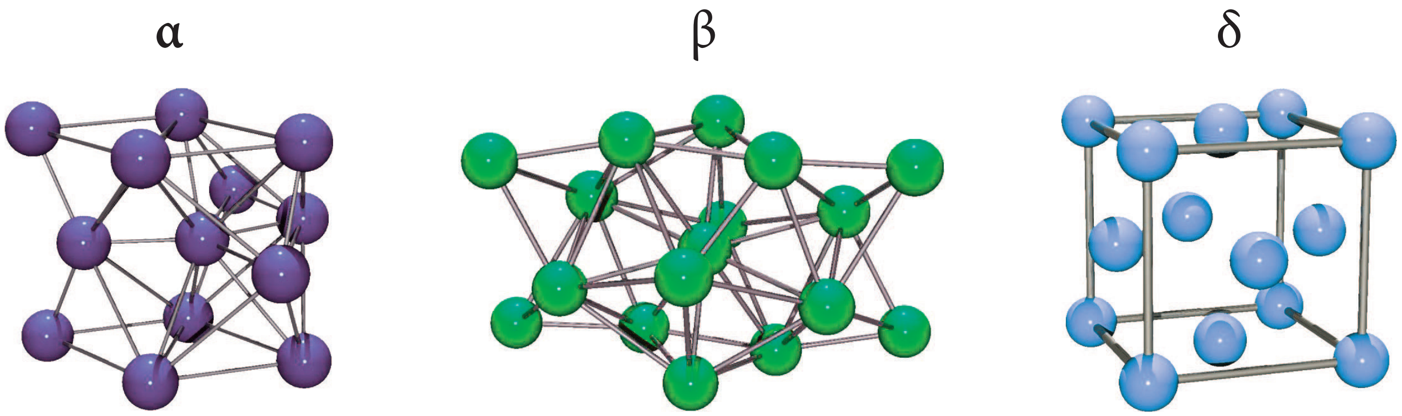


The raw X-ray reflections for α plutonium. Intensities were computed with a mechanical planimeter from graphs of this quality, as reported by Zachariasen et al., in "The Crystal Structure of Beta Plutonium Metal," in Acta Crystallographa in 1963.

no references. Some contain the entire paper's contents in the abstract. There were no computers when many of them were written. And there are only one or two authors on each paper. In terms of understanding plutonium and its electronic structure, these papers are revealing.

From basic thermodynamics, the plutonium crystal structure that exists near zero temperature is the only one not influenced by entropy and hence is controlled only by energy. For plutonium, the structure is completely bizarre, being monoclinic α phase with 16 atoms per unit cell, and having eight different distinct plutonium sites and some very short interatomic bonds. Zachariasen needed to reinvent some aspects of structure determination to solve this structure from the powder patterns because no single crystals could be produced. With these new tools, he says, "No novel principles are involved, no computational aids are required, and only the most elementary knowledge of lattice geometry is needed . . . one looks for recurrent values of differences."

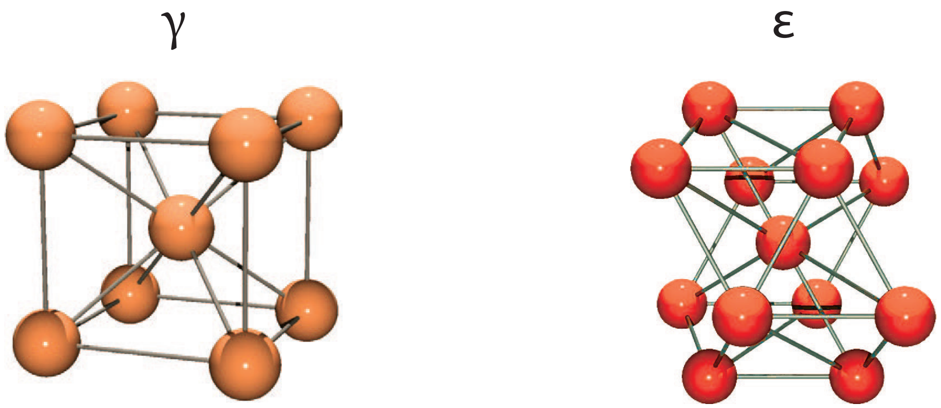
For an elemental metal, how can a monoclinic structure be the answer? In fact, for plutonium one should really ask, how can it not? With seven 5f electronic orbitals, each with a complex radial and spatial electron density distribution, it seems that plutonium can lower its energy by making four very short bonds from these orbitals in a way that reasonable electronic structure calculations can capture. With increasing temperature, β-phase plutonium forms as body-centered monoclinic crystals, now with 34 atoms per unit cell but "only" seven different sites. For both α and β phases, Zachariasen writes, "All attempts to prepare single crystals of beta plutonium large enough for X-ray diffraction studies have failed. Accordingly, the structure determination had to be deduced entirely from 'powder' diffraction patterns." And without a decent computer, too! "The intensities were measured by planimetering the area under the diffraction peaks."



Monoclinic
16 atoms/cell

Body-centered monoclinic
34 atoms/cell

Face-centered cubic
4 atoms/cell



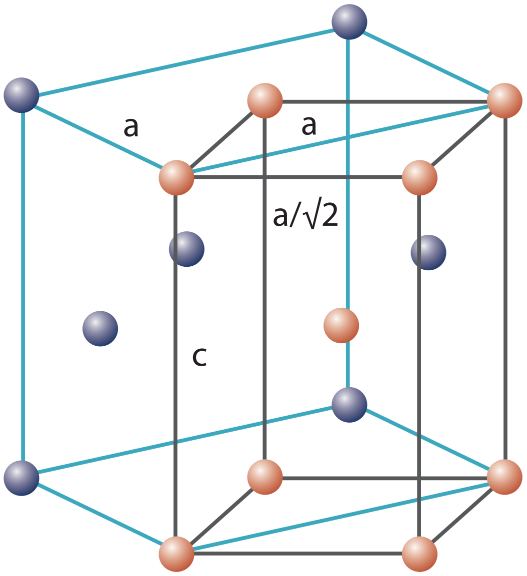
Body-centered cubic
4 atoms/cell

Body-centered cubic orthorhombic
8 atoms/cell

While work at Los Alamos was still heavily classified, Frank Schnettler and his team reconfirmed that plutonium had five phases. Shown here are modern models of the five easily distinguished crystal structures of plutonium. δ-prime, omitted, looks just like ε.

As plutonium is heated above the β phase, it becomes increasingly symmetric while remaining strange, advancing through a series of crystalline structures. These phases transition from the body-centered orthorhombic γ phase, to the face-centered cubic δ phase with a negative coefficient of thermal expansion (a close-packed structure and the lowest density of any phase of plutonium), and finally to the body-centered cubic ε phase with higher density than the colder phase just below it. Here, we dismiss the δ-prime phase as unimportant because a simple distortion (compression along a cubic axis) of δ plutonium produces δ-prime plutonium and then ε plutonium when the distortion equals $2^{1/2}$. The latent heat is negligible, and the error bars of the X-ray determination of δ-prime are the highest by an order of magnitude than for any phase of plutonium. Thus it is likely that the sluggishness of the δ-to-ε transition simply leaves a local strain field in which weakly distorted δ (which is what δ-prime looks like) remains until the transition is complete.

Jette describes some incredibly revealing gems about the phases above β. "It is to be specially noted that for no phase do both the coefficient of thermal expansion and the temperature coefficient of resistivity have the conventional sign. Thus, if the phase expands on heating, the resistance decreases." And, he further states,"Perhaps the most striking feature of the crystal structure data is that the δ phase, which has the

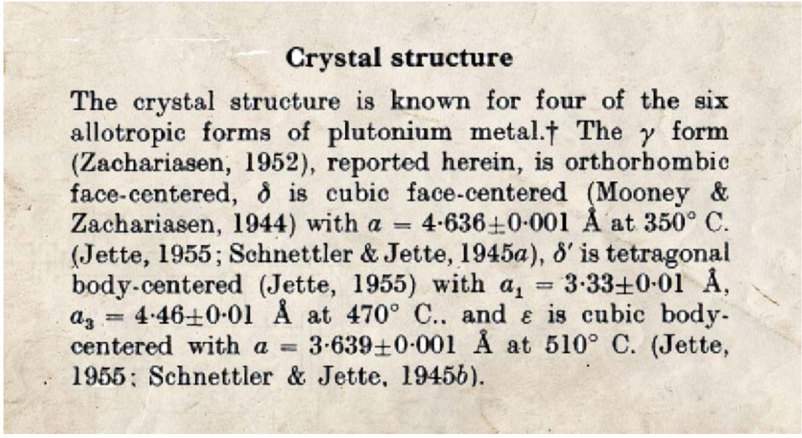


Paths of tetragonal states between two phases of a material, such as bcc and fcc, are called Bain paths. In this face-centered cubic (fcc) and body-centered tetragonal representation, compression along c takes δ plutonium (red-fcc) to ε plutonium (blue-bcc) when the compression of c/a equals 2½. The plutonium system is very soft to such distortion.

lowest density of any phase in the entire system, is the only phase with a close-packed structure. The increase in density in going from the face-centered cubic δ to the body-centered cubic ε is noteworthy."

The strangeness reaches a zenith with the work of Lawson et al. and Migliori et al. Lawson and co-workers used modern methods to measure the lattice parameters of gallium-stabilized δ plutonium with gallium concentrations such that the thermal expansion coefficients range from positive to negative. Lawson and his collaborators were able to fit the measurements quite nicely using a two-component (invar) model. Freibert and Migliori established that extrapolations of elastic moduli of delta plutonium containing gallium match the elastic moduli of δ plutonium without gallium at temperatures where both exist as δ plutonium. However, Migliori also established that from about 350 K to 800 K (where Lawson found that the thermal expansion, depending on gallium concentration, of δ plutonium was positive, zero, or negative), the adiabatic bulk modulus dropped about 10% on warming, about an order of magnitude greater than what aluminum would do, and independent of the sign of the thermal expansion.

This change in adiabatic bulk modulus on warming, combined with the strange resistivity results reported by Jette, is outside the ability of any ab initio electronic structure model to capture. Here's why: any electronic structure model using any form for electron orbitals places atoms in a crystal pattern, and then computes the total energy to find a minimum at some value of lattice parameter, based upon a very broad range of possible assumptions about potentials and orbitals. The adiabatic bulk modulus (the stiffness against hydrostatic compression) is determined by taking the final solution and simply computing the ratio of the change in energy to a change in volume (or lattice parameter), keeping all electron occupation numbers fixed, which is an easy thing to do. Temperature does not come into such a calculation. Thus we must ask, "How can the bulk modulus change by the same 10% when the volume increases, decreases, or does not change at all?"



Crystal structure

The crystal structure is known for four of the six allotropic forms of plutonium metal.† The γ form (Zachariasen, 1952), reported herein, is orthorhombic face-centered, δ is cubic face-centered (Mooney & Zachariasen, 1944) with $a = 4{\cdot}636 \pm 0{\cdot}001$ Å at 350° C. (Jette, 1955; Schnettler & Jette, 1945*a*), δ' is tetragonal body-centered (Jette, 1955) with $a_1 = 3{\cdot}33 \pm 0{\cdot}01$ Å, $a_3 = 4{\cdot}46 \pm 0{\cdot}01$ Å at 470° C., and ε is cubic body-centered with $a = 3{\cdot}639 \pm 0{\cdot}001$ Å at 510° C. (Jette, 1955; Schnettler & Jette, 1945*b*).

Paragraph scanned from Zachariasen and Ellinger, "The Crystal Structure and Thermal Expansion of γ-Plutonium," 1955. The error in the determination of the crystal structure of δ-prime plutonium is an order of magnitude greater than for any other phase.

William H. Zachariasen. See ARQ Second Quarter 2004 for another article on Zachariasen's work: *"Sixty years of structural determinations of the 5f elements . . . or, why are the actinides so named?"*

Summary

The inescapable conclusion is that volume is unimportant in understanding δ plutonium, the most important metallic form for our mission, and that simply knowing the structures and stiffnesses raises deep fundamental science questions about plutonium that may be at the cutting edge of correlated-electron physics. If we consider together the monoclinic phases, the strange effect of δ plutonium being in a close-packed structure but with the lowest density of any form of plutonium, and the odd behavior of the bulk modulus with temperature and volume changes, it is clear that very much more complex physics is required before we have even a minimal understanding of plutonium.

Acknowledgements

This work was supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Basic Energy Sciences, under Award #DE-SC0001089.

2020 Update

Crystallography remains the key structural property determination method used in chemistry, physics, materials science, biology, geology, and other sciences. The plutonium crystallography of W.H. Zachariasen remains the standard for comparison of other crystal structure techniques and elucidation of ab initio electronic structure and atomic bonding determination. Based solely on this work, Zachariasen recognized the correlation between structure and electronic behavior as plutonium transitions from uranium-like bonding of the α-phase to americium-like localized of the δ-phase. The essence of this correlation remains an open scientific question today.

Actinide Research Quarterly is published by Los Alamos National Laboratory and is a publication of the Glenn T. Seaborg Institute for Transactinium Science, a part of the National Security Education Center. ARQ (est. 1994) highlights research 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.

LA-UR-20-23869

Address correspondence to:
Actinide Research Quarterly
c/o Editor
Mail Stop T-001
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

National Security Education Center
David L. Clark, Director

G. T. Seaborg Institute for Transactinium Science
Science Advisors
Franz Freibert, Director
Ping Yang, Deputy Director

Editor
Owen Summerscales

Contributing editors
Susan Ramsay

Designers/Illustrators
Don Montoya
Owen Summerscales

Circulation Manager
Susan Ramsay

Los Alamos National Laboratory is operated by Triad National Security, LLC, for the National Nuclear Security Administration of US Department of Energy (Contract No. 89233218CNA000001).

This publication was prepared as an account of work sponsored by an agency of the U.S. Government. Neither Triad National Security, LLC, the U.S. Government nor any agency thereof, nor any of their employees make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by Triad National Security, LLC, the U.S. Government, or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of Triad National Security, LLC, the U.S. Government, or any agency thereof. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Los Alamos
NATIONAL LABORATORY
EST.1943

NNSA