The Actinide Research Quarterly

Los Alamos National Laboratory

Nuclear Materials Research and Technology

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In This Issue

Plutonium Conference Illuminates Aspects of Unique Element

The second international "Plutonium Futures—The Science" conference opened Sunday afternoon, July 9, at La Fonda, on the historic Santa Fe plaza. Sponsored by the Laboratory in cooperation with the American Nuclear Society, the three-and-a-half-day conference, plus tutorial, drew 410 participants from 15 countries and included some 50 post-doctoral researchers and graduate and undergraduate students, not including those from the Laboratory. Attendance for many of these students was sponsored by the conference.

The conference provided those in attendance with an opportunity to participate in an assessment of the current understanding of plutonium and actinide sciences and to focus on the science needed to solve important national and international issues associated with plutonium. It placed an emphasis on involving students who will carry on the task of solving nuclear issues into the next century. The conference pursued the science of plutonium with noted plenary speakers discussing policy and management issues, followed by 35 selected oral presentations given by speakers from a dozen countries and 140 posters addressing topics in materials science and nuclear fuels, condensed matter physics,

PLUTONIUM FUTURES —THE SCIENCE

Plutonium Conference Illuminates Aspects of Unique Element *(continued)*

actinides and processing, actinides in the environment, and actinides and transuranic wastes.

In Sunday's preconference tutorial session, David Clark, head of the Glenn T. Seaborg Institute for Transactinium Science at Los Alamos, voiced a theme woven throughout the conference, "Plutonium is absolutely unique among all of the elements. After some 50 years of research into the characteristics of Plutonium, something as simple as the number of phases the element can take and the phase diagram of Pu-Ga alloy are still undetermined." Other speakers in the overflow tutorial session gave the history of the discovery and studies of plutonium, Pu surface science, and studies of Pu oxides.

Plenary speakers on the opening day of the conference highlighted both scientific and international policy discussions of plutonium. Darleane Hoffman, UC Berkeley, reprised the talk she gave as a recipient of the coveted Priestly Medal, highest award of the American Chemical Society for lifetime achievement, in April this year. She talked about the continuing search for super-heavy elements.

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Nikolai Ponomarev-Stepnoi of the Russian Kurchatov Institute showed a video with English narration on past, present, and future uses of plutonium in Russia. His vision of the future is "clear, cloudless skies without any greenhouse effects" through the use of advanced, nuclear-fueled thermal reactors for power generation.

Thomas Cochran of the Natural Resources Defense Council says his vision is for "complete disarmament under strict and effective international controls" with specific suggestions for bilateral efforts to do so. He believes such efforts should result in a complete ban on weapons-usable materials, moving them into unclassified forms for long-term storage. Breaking from his fellow environmentalists, he does favor radioactive sources for use in space.

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Leo Brewer, UC Berkeley professor (Emeritus), challenges scientists to be innovative and to be willing to follow in whatever direction their research takes them. Using himself as an example, he says, "My ideas are rejected, then ten years later my ideas are

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confirmed and I get an award!" In another theme that echoed throughout the conference, Brewer challenged the audience to educate the public on radioactivity. "Use the example of potassium," he urged. "Tell them if they didn't get their potassium, they would die."

Vladimir Onoufriev of the International Atomic Energy Agency gave his vision for nuclear power of the future. "In the long term," he said, "we will see fast reactors using technologies specifically designed for MOX (mixed-oxide) fuels." However, he feels that if plutonium fuels do not become commercially attractive to utilities, plutonium and other actinides will still be reprocessed in international fuel-cycle centers for future needs.

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In any case, he predicts that advanced processes will make nuclear reactors low-cost and environmentally safe.

Former Lab Director Siegfried Hecker returned to the question of why plutonium is such an unusual metal. "It is the f electrons, and specific aspects of the f electrons that make plutonium so peculiar from a metallurgist's point of view," he stated. He echoed the tutorial session as he talked about plutonium's thermal instability, pressure instability, and unexpected alloying behavior. "Some see plutonium as the 'scourge of mankind,'" he concluded, "Others see it as the savior of mankind. But what it *is* is the most fascinating element we know of."

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Plutonium Conference Illuminates Aspects of Unique Element *(continued)*

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A spirited exchange of views on these topics continued in the evening panel discussion. There was a broad consensus on the panel that plutonium separated from weapons should be rapidly moved toward the spent fuel standard (SFS), where reuse, especially clandestine reuse, is difficult. The active debate centered on the means of achieving the SFS and the role of nuclear power, especially plutonium, in meeting future global energy needs. Finally, political and technical statements were braided together by the panelists in answer to audience questions. Those panelists who see nuclear power generation in the future avowed that science and technology will provide technical solutions to the political questions.

The conference poster session provided a surprisingly large and diverse collection of papers from many countries. Awards were given to the ten best posters. The articles following in this issue of Actinide Research Quarterly are based on two of these posters. The award-winning posters may be seen on the conference Web site at http://www.lanl.gov/pu2000.html .

Financial support for the conference was provided by the Associate Laboratory Directorate for Weapons Programs and the Associate Laboratory Directorate for Threat Reduction. The Office of Basic Energy Sciences/US Department of Energy sponsored student attendance at the conference. Plutonium-related exhibits were provided by Westinghouse Savannah River Company, Argonne National Laboratory, Lovelace Respiratory Research Institute, and Los Alamos National Laboratory.

Conference proceedings were distributed to all participants and are available from the American Institute of Physics (AIP Conference Proceedings 532). Participants also received a preview of the upcoming *Los Alamos Science* issue "Challenges in Plutonium Science," (Number 26, 2000) on CD. Hard copies and CDs of the entire issue will be available by mid-October. People are welcome to request copies (see http://www.lanl.gov/worldview/science/lascience/). The conference Web site including photos and the final conference program will be maintained until the next conference, tentatively scheduled for summer 2003. Comments and suggestions for that conference are welcome.

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PLUTONIUM FUTURES —THE SCIENCE

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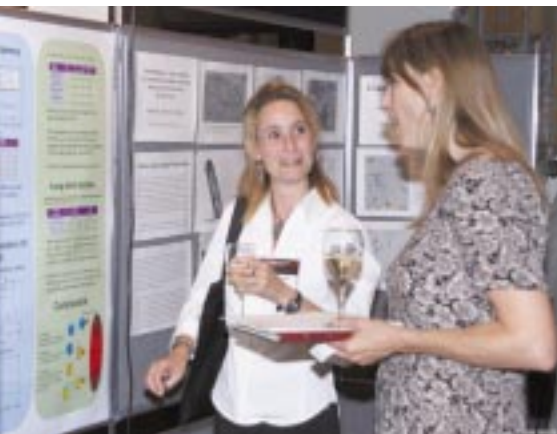*C688-1605.tif*

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Conference Banquet Speaker
Opposes Nuclear Fuel Reprocessing

The following is a summary of the talk "Plutonium Nonproliferation and Nuclear Power," by **John Holdren**, Teresa and John Heinz Professor of Environmental Policy, John F. Kennedy School of Government, Harvard.

Options for Disposition of "Excess" Weapons Pu

"The worldwide supply of weapons plutonium is about 250 tons, including that declared 'excess,'" declared John Holdren, banquet speaker for the second international "Plutonium Futures—The Science" conference. He continued, "Reactor plutonium supplies amount to about 1,120 tons. The options for disposition of these materials are to store them in different forms, burn them in existing reactors, save them for advanced reactors of the future, or immobilize them for disposal in waste repositories. There may be other options as well."

Holdren described how a committee of the National Academy of Sciences evaluated the options for weapons plutonium. Holdren was a member of this committee. The committee report was published in two volumes in 1994 and 1995 and concluded that "excess" plutonium poses a danger to the US and the world. "Well-guarded storage is not sufficient," Holdren added; "appropriate barriers are needed as well. The material must be made as difficult as reactor plutonium to reuse; that is, it needs to meet the spent fuel standard (SFS)." The committee also concluded that the difficult disposition decisions need to be made now, before other nuclear energy issues are solved.

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The two least problematical disposition methods to use in meeting the SFS, the committee pointed out, are to immobilize the materials in glass logs or to use them as MOX (mixed-oxide) fuels, once-through in reactors. The committee recommended that this option be pursued in parallel by both U.S. and Russia in cooperation. Holdren noted that a U.S./Russian commission came to the same conclusion, but with four nonproliferation conditions: a joint agreement is needed, international funding is needed, the material should be protected as reprocessed plutonium, and we should not delay.

Where Are We Going?

Holdren said the energy supply message is this: at the end of the twentieth century, the world is still dependent on fossil fuels in spite of the work done on renewable energy sources. "Business-as-usual" can be defined as the same rate of population growth and economic growth, the same efficiency of energy sources, and the same percentage of carbon-based fuels. Under business-as-usual, the amount of CO_2 in the environment will triple.

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Holdren stated that the world is *not* running out of energy. "The essence of the energy problem," he explained, "is that the world is running out of cheap oil, the environment needed to absorb the impacts of business-as-usual, and the tolerance for inequity of who has/doesn't have energy and who is/is not producing waste. The world is also running out of money for better options, the time for a smooth transition to non-carbon-based forms of energy, and the leadership to do what is required."

Environmental issues surrounding the continued use of carbon-based energy are the most intractable, Holdren noted. The most dangerous of these is global climate change, which is involved in 80% of present energy production. Developing countries are becoming the largest part of the problem.

As a consequence of business-as-usual, Holdren predicted, the earth will become warmer, as much as 5% warmer. Sea levels will rise, displacing people all over the world who live in coastal areas. There may be some unpleasant surprises as well: disease, storms, shifts in ocean currents, and more. If the world goes beyond double the preindustrial concentrations of air pollutants, these consequences may be expected. "With business-as-usual," Holdren warned, "we will triple these concentrations or more.

Holdren expressed the need for renewable, non-carbon-emitting sources and solutions to the worldwide energy generation needs, and said nuclear fission or fusion sources can help fill these needs. "Capturing emissions from current sources will help as well," he added.

Can the Contribution of Nuclear Power Be Expanded?

Holdren listed the remaining obstacles to the expansion of nuclear energy: reactor safety, waste management that is acceptable to the public, and minimized linkage to nuclear weapons. "The latter is the most important," he said. "While many include economics as an obstacle," he predicted, "in the long term fossil fuels will be more expensive, equal to the costs of nuclear generation. So economics is really not an issue."

Holdren calculates that if nuclear power were to go from the present one-sixth of total energy production to a one-third share, nuclear plants would have to be ten times more numerous than they now are. But he predicts that by 2050 fission power may be phased/phasing out. He suggested that

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tion and high recycling such as advanced heavy metal reactors (AHMRs).

"Waste management complexities interact with other complexities such as threats," Holdren added. Threats he listed include the diversion of materials from power to weapons, theft of materials, and a loss of confidence in the prevention of diversion or theft.

"In the short term, 10 years or so, the materials that pose the threats are separated military plutonium, civilian plutonium, and highly enriched uranium," Holdren enumerated. "These should be put away in SFS forms. Reprocessing and recycling nuclear materials at this time make these threats more credible, make proliferation worse, and are more expensive than the once-through or AHMR options."

Holdren concluded, "For the medium-long- and unimaginable-long terms it is premature to assume that we can reprocess or transmute nuclear materials, but research should continue. If we want to maximize our chances of providing a larger percentage of power generation with nuclear fuel, we need to make it safer, more economical, and more acceptable. Reprocessing will not accomplish these goals."

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options that may be viable in the future include "once-through" nuclear fuel, which yields high power generation and low recycling, or some method that yields high genera-

Editorial
Plutonium Science Challenges Future Researchers

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This editorial was provided by **S. S. Hecker**, senior fellow at the Laboratory. Illustrations courtesy of *Los Alamos Science* magazine.

The International "Plutonium Futures: The Science" Conference in Santa Fe in early July was a convincing testament to the resurgence of interest in plutonium science. More than 400 attendees from 15 countries gathered to discuss advances and challenges in plutonium chemistry and materials science. The technological challenges stem from the applications of plutonium—principally stockpile stewardship and nuclear power, and from dealing with the problems left behind by those applications—environmental concerns, waste disposal issues, and potential proliferation concerns. The scientific challenges stem from the fact that plutonium is the most complex element in the periodic table.

Plutonium is of interest because of the extraordinary nuclear properties of the isotope plutonium-239. Extracting the energy of its nucleus provides a "factor of millions" advantage in energy production or explosive power. However, electrons determine its chemical, physical, and mechanical properties and its engineering behavior. In the metal, it takes little provocation to change its density by as much as 25 percent. It can be as brittle as glass or as malleable as aluminum; it expands when it solidifies—much like water freezing to ice; its shiny, silvery, freshly machined surface will tarnish in minutes, producing nearly every color in the rainbow. It is highly reactive and a very strong reducing agent when in solution, readily forming compounds and complexes during chemical processes or in the environment. It transmutes itself by radioactive decay, causing damage to its crystalline lattice and leaving behind helium, americium, uranium, and other impurities. It also damages all materials or solutions in contact, making it difficult to store and difficult to predict its transport. No wonder its principal applications are limited to those for which the "factor of millions" is crucial.

We have never fully understood the fundamental reasons for the unusual properties of plutonium. We have learned just enough about its chemical behavior to allow us to separate it from the reactor products and purify and recover it from scrap, and enough about its metallurgical behavior to shape it and engineer it for its applications. The early quest for fundamental understanding slowed down considerably in the 1980s and early 1990s, but now interest has been revived for two principal reasons. First, the era of no nuclear testing ushered in by the end of the cold war places a premium on understanding plutonium better because we can no longer do the proof tests that allowed us to bridge the gap between our understanding of physics and actual weapon function. Second, we must now find more efficient and cost-effective methods to deal with the environmental problems created during the cold war and to make certain that we do not create additional problems in the future. In addition we must provide protection for fissile materials and cost-effective disposition of plutonium declared excess to the nuclear weapons programs. Thus, we must resolve fundamental questions about the physics, chemistry, and metallurgy of plutonium.

Much of the current work in the actinides was reviewed in Santa Fe. The single most unusual characteristic of plutonium is its instability. In the metal, it is extremely sensitive to the slightest changes in temperature, pressure, or chemistry. Small changes, in turn, produce very large changes in physical and mechanical properties. In solution, changes in oxidation state, which occur readily through small changes in solution chemistry or even through radiolysis, lead to a variety of molecular complexes, each with a characteristic solubility and chemical reactivity. Recent electronic
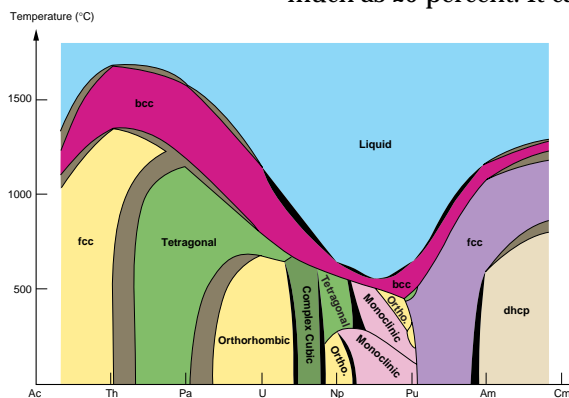

Figure 1. Connected binary-phase diagram (temperature vs. composition) of the actinides. Such diagrams demonstrate the transition from typical metallic behavior at thorium to the enormous complexity at plutonium and back to typical metallic behavior past americium. With little provocation plutonium will change its density by as much as 25 percent. It can be as brittle as glass or as malleable as aluminum; it expands when it solidifies. Its unusual behavior is just one of the challenges of understanding plutonium.

Figure 2. The color of plutonium oxidation states. Each oxidation state, ranging from Pu(III) to Pu(VII), has a characteristic color in solution. Plutonium will often change oxidation states in solution, making its interaction with the natural environment inordinately complex.

structure calculations provide valuable insight to demonstrate how the unusual properties of plutonium result from the systematic variation in the bonding of the $5f$ electrons across the actinide series. By examining the trends across the series, we find that the peculiarities of plutonium are not a single anomaly but the culmination of a systematic trend of bonding behavior of the $5f$ electrons. Plutonium sits right at the knife-edge in the transition between bonding or chemically active $5f$ electrons and localized or chemically inert $5f$ electrons.

While the science of plutonium is thus complex and exciting to study of itself, we must redouble our efforts to bring fundamental knowledge to bear on the demanding set of applications we face this century. For example, to certify nuclear weapons without testing we must develop a better understanding of aging effects, particularly the effect of self-irradiation damage on plutonium's already notorious instability. Furthermore, although plutonium is a man-made element created an atom at a time in reactors, the world now has more than 200 tonnes of plutonium in its military stockpiles and more than 1000 tonnes (800 tonnes are contained in spent-fuel elements) in civilian inventories. Its protection from unauthorized use, its potential utilization as reactor fuel, or its geologic disposition represents not only a great scientific challenge, but also a national security imperative.

We also recognize that during the cold war significant quantities of plutonium and other radioactive materials were released into the environment. In addition, civilian nuclear power programs continue to create nuclear waste waiting for an acceptable method of disposal. These problems represent one of the most challenging applications of modern chemistry because of the inherent complexity of plutonium and the corresponding complexity of the natural environment.

To enhance our understanding of the fundamental behavior of plutonium and to apply this knowledge to solving these challenging problems, we must attract the next generation of scientists and engage the international scientific community. The Plutonium Futures Conference took an important step in these directions. Also, as Dave Clark pointed out in a previous editorial, we must rekindle the educational programs in transactinium science. To attract the next generation of researchers and the academic community, we must continue to instill a spirit of scientific excitement that was so evident in Santa Fe.

The greatest challenge, however, will be to turn around the crisis of confidence that has developed in the operation of the nation's plutonium facilities during the past decade. The inordinate difficulty in accomplishing experimental plutonium work today, which underlies this crisis, is having a chilling effect on the ability to recruit and retain the best and the brightest. Our ability to operate nuclear facilities safely and successfully is of utmost importance in regaining public confidence and attracting the next generation of plutonium scientists.

Figure 3. Pourbaix diagram for plutonium: another demonstration of the complexity of plutonium in the environment. This Eh vs. pH diagram is calculated for plutonium in water containing hydroxide, carbonate, and fluoride ions. The red dots are triple points, where plutonium can exist in three different oxidation states. The range of Eh/pH values found in natural waters is bounded by the solid black outline. Dashed lines define the area of water stability.
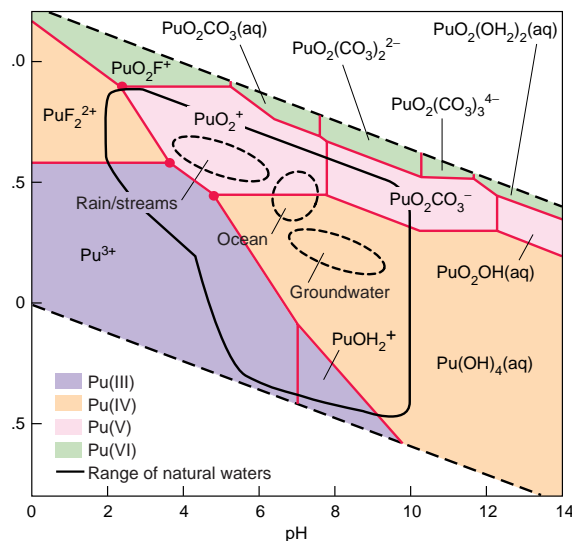
Speaker Urges: Eliminate Nuclear Weapons and Nuclear Fuel Reprocessing

This is a summary. The complete text may be found on the Web at http://www.lanl.gov/pu2000.html

Beyond trace amounts in uranium ore deposits, plutonium is man-made; its existence and quantities are determined by its production and utilization since the 1940s. Plutonium has two major applications—as a nuclear explosive material and as a nuclear reactor fuel—and one minor application where the isotope ^{238}Pu is highly concentrated as a source material for radioisotope thermoelectric generators and heater units.

Today eight countries possess nuclear weapons—the United States, Russia, the United Kingdom, France, China, Israel, India and Pakistan. The first five have signed the Nuclear Nonproliferation Treaty (NNPT). The parties have an obligation under Article VI of the NNPT:

"to pursue negotiations in good faith on effective measures relating to cessation of the nuclear arms race at an early date and to nuclear disarmament, and on a treaty on general and complete disarmament under strict and effective international controls"

To meet this obligation they must undertake (1) political steps designed to reduce incentives to acquire and accumulate nuclear weapons and threaten their use, and (2) technical steps to eliminate existing arsenals and increase the time it takes to reconstitute them or acquire new ones. With regard to the technical measures, it is important to recognize that our NNPT obligations are not limited to the elimination of nuclear warheads themselves. If a nation disassembles an arsenal of nuclear warheads and stores the critical components, the effect is only to marginally increase the time it takes to reassemble and use them. A more useful parameter for measuring progress in achieving nuclear disarmament is the availability of deliverable warheads over time.

Thus, the parties must reduce the number of nuclear warheads on launch-ready alert, on generated alert, in the active stockpile, in the inactive stockpile, and awaiting dismantlement. They must reduce the stockpile of weapons-usable fissionable materials in weapon component form (e.g., pits), in strategic reserves, and in separated forms.

The lack of progress made by the U.S. and Russia in achieving meaningful reductions in most of these categories is evidence that neither country is making a good-faith effort to meet its NNPT obligation under Article VI.

To meet its treaty obligation, the U.S. should take the following steps immediately and unilaterally:

1. **Stop specifically targeting Russia and other countries with nuclear weapons.** Under new guidance the U.S. should not target any country specifically but create the capability to quickly construct contingency war plans if needed.
2. **Take all U.S. land-based ICBMs off alert.**
3. **Ratify the Comprehensive Test Ban Treaty.**
4. **Redirect and scale back the Stockpile Stewardship and Management Program to focus on acquiring the capability to remanufacture existing, well tested designs to original specifications, as required.** The stewardship program should be scaled back and limited to finding ways to maintain a set of well tested nuclear designs, without the emphasis on providing the capability to develop and certify new nuclear weapons without testing.
5. **Permanently close the Nevada Test Site.** Negotiate with Russia the joint permanent closure of NTS and Novaya Zemlya. This would have the added benefit of making the Comprehensive Test Ban Treaty easier to verify and consequently easier to ratify.

In addition, the U.S. should seek the following on a bilateral or multilateral basis:
6. **Much deeper reductions in U.S. and Russian strategic arsenals.**

7. **The elimination of all non-strategic nuclear warheads, all reserve warheads and all strategic reserves of fissile materials.**

8. **Public declarations of all nuclear weapon and weapon-usable fissile material stockpiles and production histories, and cooperative verification measures to confirm data included in these declarations and data exchanges.**

9. **More informal transparency measures. (demonstrate progress and fairness in on going arms reduction processes, build confidence that they are significant and unlikely to be reversed, reduce uncertainties in estimates of weapons and weapons materials).** New security measures proposed or recently imposed further hamper this effort.

10. **Verified dismantlement of warheads and monitored interim storage of their fissile material components.**

11. **Increased security and safe disposition of existing stocks of weapon-usable materials.** The effort to place under International Atomic Energy Agency safe guards fissile material inventories that have been declared to be in excess of national security needs by Russia and the U.S. is moving ahead so slowly that the DOE lab-to-lab program must be counted as a failure.

12. **Verified storage and disposition of highly enriched uranium (HEU) and plutonium declared to be *in excess of* national security needs.** The program to assist Russia in disposing of its excess plutonium is unlikely to be successful because its mission is to assist Russia in converting excess plutonium into MOX to be burned in existing reactors. Russia has no MOX fabrication facility and cannot afford one, and no country has indicated any willingness to pay. The Russian plutonium disposition effort should be refocused on converting plutonium pits to unclassified shapes and placing the effort under bilateral and ultimately international safeguards.

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Thomas Cochran is associated with the Natural Resources Defense Council, Inc.

13. **Assist in downsizing Russia's nuclear weapons complex and provide alternative employment opportunities for workers in Russia's nuclear weapon complex.** A potential source of new additional revenues for several of these initiatives is the NonProliferation Trust, Inc. (NPT, Inc.) proposal, with which I am involved. This nongovernment initiative has the potential to raise $15 billion in revenues, of which over $11.5 billion will be allocated to a variety of worthy projects in Russia. The revenues would be raised providing spent fuel management services in Russian for 10,000 tonnes of foreign (non-Russian and non-U.S.) spent fuel. Western companies would build and operate in Russia an interim, dry-cask spent fuel storage facility licensed by

Speaker Urges: Eliminate Nuclear Weapons and Nuclear Fuel Reprocessing *(continued)*

GAN, the Russian licensing authority, that would meet the technical licensing criteria of the Nuclear Regulatory Commission.

Under the current NNPT proposal plan $2.3 billion of the revenues is allocated for the construction of a geologic repository for the foreign spent fuel in addition to Russian spent fuel and high-level radioactive waste. An additional $1.5 billion is allocated to fissile material security, $2 billion for alternative employment opportunities for workers in the Russian nuclear weapons complex, $3 billion for environmental cleanup, $0.5 billion for regional economic development, and $2.25 billion for humanitarian causes in Russia.

In the late 1960s the Atomic Energy Commission was predicting that increased use of nuclear power would lead to reductions in power plant costs and scarcity and increased costs of uranium, thus making plutonium recycling and fast breeder reactors economical. These claims have proven to be false. Nevertheless, many countries adopted the closed fuel cycle—plutonium separation and recycling—in preference to direct disposal of spent fuel. As a consequence global inventories of weapon-usable plutonium in civil stockpiles now exceed plutonium inventories in military programs, and the civil stockpiles continue to grow largely as a consequence of commercial reprocessing contracts made years ago.

Today it is abundantly clear that fast breeder reactors and plutonium recycling in thermal reactors is uneconomical and will remain so for the foreseeable future. The commercial use of plutonium in most countries is on the decline.

The concept of accelerator transmutation of waste (ATW) has been promoted as a means of reducing the long-term risks associated with geological disposal of high-level radioactive waste. A recent DOE sponsored "roadmap" of the ATW concept indicates that this technology will be prohibitively expen-

sive. More importantly, no case has been made to date that (1) the potential lives saved by reducing the transuranic and other isotopes going into a geologic repository will exceed the potential lives lost resulting from the implementation of an ATW program, (2) the cost of implementing an ATW program is worth the benefits, (3) greater benefits cannot be achieved at less cost by selecting an alternative repository site and technology, (4) the nonproliferation benefits of an ATW program are positive, or (5) that an ATW program can be implemented by private industry.

So long as the global norm permits nations to separate and stockpile large inventories of weapon-useable fissile materials ostensibly for peaceful purposes, there is little hope that the nuclear weapons states will be willing to move to small nuclear weapon stockpiles. Since plutonium recycling is uneconomical and unnecessary for energy independence or waste management, the preferred course from a nonproliferation prospective is a complete global ban on commercial use of weapon-usable fissile material.

The DOE has supplied 44 radioisotope thermoelectric generators (RTGs), each containing kilogram quantities of ^{238}Pu, and ^{240}Pu radioisotope heater units (RHUs), each containing grain quantities of ^{238}Pu, on 26 space missions since 1961. Unless and until a more benign reliable energy source can be found, it will be necessary to continue to use ^{238}Pu sources for some deep space missions.

We have an obligation to the international community to eliminate nuclear weapons and convert existing stocks of separated plutonium into a form that is no more attractive as a source of weapon material than spent nuclear reactor fuel as a source of plutonium for weapons. There is no economic, environmental, or nonproliferation utility in separating additional plutonium from spent fuel, at least not in the foreseeable future. ^{238}Pu has limited utility in small quantities for deep space missions. In sum, plutonium has a long half-life, but except for deep space missions, it has no future.

Researchers Address the Interrelationship of Hydrolysis and Pressure in Stored Pu

The U.S. Department of Energy/Environmental Management (DOE/EM) is responsible for the management and long-term disposition of a variety of materials located at Rocky Flats Environmental Technology Site, Hanford, Savannah River, and other DOE sites. The new plutonium storage standard, set to replace DOE 3013, requires thermal stabilization of the materials before they are packaged for storage. The Pu content of those materials can vary from ~86 weight percent, (essentially pure PuO_2), down to ~30 weight percent. With such a range of compositions, plutonium dioxide can be in contact with a variety of other materials. Typically, these "impurites" include alkali metal chlorides, MgO, $MgCl_2$, $CaCl_2$, Fe_2O_3, and other materials that are not well characterized. In addition, these solid mixtures are in contact with the gas phase under which the materials were packaged; the moisture content may not be known or well controlled. The new plutonium stabilization standard does not set acceptable glove box moisture levels nor does it prescribe the time duration between calcination and packaging.

The 3013 standard contains an equation that predicts the total pressure buildup in the can over the anticipated storage time of fifty years. This equation was meant to model a worst-case scenario to insure pressures would not exceed the strength of the container at the end of 50 years. As a result, concerns about pressure generation in the storage cans, both absolute values and rates, have been raised with regard to rupture and dispersal of nuclear materials. Similar issues have been raised about the transportation of these materials around the complex.

The technical basis for the pressure equation given in the 3013 standard has not been fully established. The pressure equation contains two major assumptions, (1) that hydrogen and oxygen generated from radiolysis of organic materials do not react to form water and (2) that the oxygen generated by radiolysis reacts with the oxide material and does not contribute to the pressure in the container. With regard to the first assumption, if the formation of water from hydrogen and oxygen is significant, then the calculated pressures would be dramatically reduced. The formation of water is thermodynamically favored (more stable) over the splitting of water into hydrogen and oxygen. In addition, the corporate knowledge from shelf-life programs around the complex is that most containers do not show signs of extreme pressurization.

In order to provide a stronger technical basis for the standard, we measured the recombination rates of hydrogen/oxygen mixtures in contact with pure and impure plutonium oxides. The goal of these experiments was to determine whether the rate of recombination is faster than the rate of water radiolysis under controlled conditions. We used a calibrated pressure-volume-temperature apparatus to measure the recombination rates, in a fixed volume, as a gas mixture was brought into contact with oxide powders whose temperatures ranged from 50°C to 300°C.

This article was contributed by **Luis Morales,** NMT-16.

Figure 1. To provide a stronger technical basis for the new DOE plutonium stabilization standard for storage, NMT-16 researchers measured recombination rates of hydrogen/ oxygen mixtures in contact with pure and impure plutonium oxides.

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Researchers Address the Interrelationship of Hydrolysis and Pressure in Stored Pu *(continued)*

These conditions were selected in order to bracket the temperature conditions expected in a typical storage can. The gas mixture used in these studies was composed of 2% hydrogen, 19% oxygen, and 79% nitrogen. This 2% H_2/air mixture encompasses scenarios in which actual storage cans were sealed in air, and over time various amounts of hydrogen are formed. This gas composition is below the explosion limit.

The recombination of hydrogen and oxygen has been studied over the 50°C–250°C temperature range in a 2% H_2/air mixture. We obtained pressure-time curves and mass spectrometric results for pure and impure plutonium oxides exposed to the gas mixture. The pure oxide was obtained from oxidation of alpha metal. The impure oxide was obtained through the Defense Nuclear Facilities Safety Board 94-1 R&D program's Materials Identification and Surveillance project and selected for its low plutonium content, 29 weight percent, and its high chloride content. Analysis by x-ray powder diffraction shows that the impure oxide is a mixture of plutonium dioxide, sodium chloride and potassium chloride. (These materials contain galium in amounts undetectable by x-ray diffraction.)

The measured kinetic data, which consist of monitoring the total system pressure as a function of time, were collected for the pure and impure oxide samples. These kinetic data show that the rate of the pressure drop at 100°C, 200°C, and 300°C for the pure oxide are equal based on the initial slopes of the pressure-time curves. Only the data collected at 50°C show deviation from this behavior. The data for the 100°C run for the pure oxide clearly show a sharp break in the slope approximately 100 minutes into the experiment. The pressure-time curves for the impure oxide experiments yield rates that are lower than those for the pure oxide counterparts.

Surface effects were investigated. The pure oxide, without any pretreatment, was allowed to react with the starting gas mixture. When that phase of the experiment was complete, that same sample was then baked at 350°C under dynamic vacuum for 24 hours and then allowed to react with the starting gas mixture again. Treating the sample by heating under vacuum increased the initial slope of the pressure-time curve by approximately a factor of four. Long-term experiments were also conducted on the pure oxide. After an initial, rapid pressure drop, the total pressure over the pure oxide sample remains constant out to 20 days.

In each experiment, the total pressure decreased rapidly after the reactants were combined. The mass spectrometric results show an overall depletion of stoichiometric amounts of hydrogen and oxygen. The mass balances for the mass spectrometric results are in excellent agreement with the assertion that hydrogen and oxygen recombine quickly to form water. The kinetic results indicate that the surface of the plutonium oxide powder plays a role in the recombination of hydrogen and oxygen. The data collected at 200°C before and after the thermal/vacuum treatment show a marked difference in the pressure-time curves and therefore in the rate of recombination. This difference is a clear indication of surface effects. In addition, the abrupt change in the slope of the pressure-time curve and therefore the rates of recombination at 100°C suggest that the surface of the oxide plays a role in the recombination of hydrogen and oxygen. For those data the slope, and hence the rate, of the pressure-time curve changes abruptly within 100 minutes. In contrast, the data collected at 200°C and 300°C show a smooth decrease in the pressure with time out to approximately 800 minutes when essentially all the hydrogen had been depleted.

Above 100°C, the reaction is second-order overall. At and below 100°C, the process may be third- or fourth-order. It is important to note that the change in the reaction order across the 100°C temperature boundary is significant. The results of the long-term experiments indicate that steady-state gas compositions are reached, suggesting that the rates of recombination and water radiolysis become equal under these experimental conditions.

These data show that when this gas mixture is exposed to pure plutonium oxide heated above 100°C, the recombination rate is dramatically faster than the radiolysis of water initially. Above 100°C enough thermal energy is provided to remove water or hydroxide and to maintain a larger fraction of the active sites available for catalysis. Below 100°C, the recombination rate seems to be governed by the number of available sites and the rate at which they are filled. These observations are more consistent with a chemical reaction of H_2 and O_2 at catalytic sites on the plutonium oxide, as opposed to radiolytic formation of radicals in the gas phase. One would expect the latter process to be temperature-independent and surface-insensitive. Presently, we do not know to what extent the alpha radiation may initiate or enhance the surface reaction. To resolve this issue, further work is needed in which the isotopic composition of the oxide and hence the flux of alpha particles is changed (^{239}Pu vs. ^{242}Pu).

The results of the long-term experiments suggest that an equilibrium gas composition is reached, indicating that the rates of recombination and water radiolysis become equal. Based on these preliminary results, extreme pressurization of sealed containers as a result of the radiolysis of water adsorbed on the oxide is not likely. Surface-catalyzed hydrogen/oxygen recombination is a primary process responsible for pressure reduction and/or hydrogen removal from the system. The kinetic data collected thus far indicate this interplay between surface-catalyzed recombination and water radiolysis. The rate of recombination serves to limit the potential pressure in the container from water radiolysis.

Figure 2. Simulating conditions of stored plutonium, researchers obtained pressure-time curves and mass spectrometric results for pure and impure plutonium oxides over the 50°C–250°C temperature range in a 2% H_2/air mixture.

C217-1

Interactions of Pu with Desferrioxamine Siderophores Can Affect Bioavailability and Mobility

This article was provided by **C. E. Ruggiero, M. P. Neu, J. H. Matonic**, and **S. D. Reilly** (Group CST-18).

Plutonium is thought to exist mostly as very low-soluble and/or strongly sorbed plutonium(IV) hydroxide and oxide species in the environment and therefore has low risk of becoming mobile or bioavailable. However, compounds that solubilize plutonium or change the oxidation state can significantly increase its bioavailabilty and mobility. We are examining the fundamental inorganic chemistry of actinides with microbial siderophores in order to understand how they could affect actinide biogeochemisty. Siderophores are low-molecular-weight, strong, metal-chelating agents produced by most microbes to bind and deliver iron into microbial cells via active transport systems.

We have focused on the tri-hydroxamate siderophores desferrioxamine B and E (DFB and DFE, or generically, DFO) because they are well studied and are readily available (Figure 1). Hydroxamate siderophores have been estimated to be present at 0.1-0.01 μM concentrations in soils. The equilibrium constant for the Pu(IV)-DFB complex formation reaction has been estimated to be $10^{30.8}$. This is higher than many organic chelators.
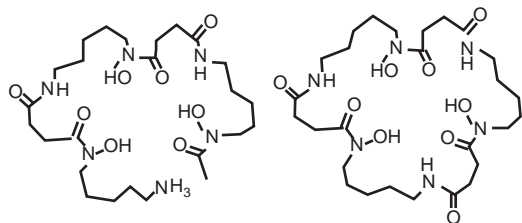
Figure 1: The desferrioxamine siderophores DFB (left) and DFE (right).

We have examined the redox chemistry of plutonium with DFO and have investigated the ability of DFO to solubilize $Pu(OH)_4$ solid. We have found that the Pu(IV)-DFO complex is a thermodynamic sink: no matter what oxidation state of Pu is present initially (III, IV, V, or VI), desferrioxamines eventually cause the Pu(IV)-DFO complex to form.

When DFO is added to a Pu(III) solution, the Pu(III) is oxidized quickly to form Pu(IV)-DFO. We have isolated single crystals from this reaction. X-ray analysis reveals the product to be $Al(H_2O)_6[Pu(DFE)(H_2O)_3]_2(CF_3SO_3)_5 \cdot 14H_2O$, the first plutonium-siderophore complex to be structurally characterized. The asymmetric unit contains the $Pu(DFE)(H_2O)_3^+$ cation (Figure 2), a hexaaquoaluminum(III), four trifluoromethanesulfonates, and seven waters.

The nine-coordinate Pu atom is bound by DFE in approximately one hemisphere and by three waters in the other. The polytopal geometry of the Pu coordination sphere is slightly distorted, tricapped, trigonal, and prismatic. This is the first discrete molecule containing a nine-coordinate Pu(IV) ion. The Fe(III)-DFE complex and the DFE ligand (without metal) have also been structurally characterized (Figure 2).

When a solution of DFO is added to a solution of Pu(VI) at pH = 2 in an equal molar ratio, the Pu(VI) is instantly reduced to Pu(V). The reduction occurs as rapidly as could be detected even at concentrations as low as 40 mM Pu. Stoichiometric titration of Pu(VI) into a DFO solution showed that up to twelve molar equivalents of Pu(VI) could be rapidly reduced to Pu(V) per DFO, corresponding to four reducing equivalents per hydroxamate of the DFO molecule. The Pu(V) solution that initially forms slowly reduces to form the Pu(IV)-DFO complex.

The rates of both the initial reduction of Pu(VI) to Pu(V) and the subsequent reduction of Pu(V) to Pu(IV) depend on pH. If the reaction is performed at pH 1 to 5.5, the reduction of Pu(VI) to Pu(V) is instant, but the subsequent reduction of the Pu(V) to Pu(IV)-DFO is significantly slower, taking months to fully reduce. However, if the pH is raised above 5.5 after the initial reduction reaction, the Pu(V) is instantly and irreversibly reduced to Pu(IV), and the amount of Pu(IV) formed is proportional to the pH. If the reaction is started above pH=6, the Pu(VI) is instantly and irreversibly reduced directly to Pu(IV)-DFO.

The rates of the reduction steps also depend on the ratio of DFO to Pu. At ratios from one molar equivalent DFB reacting with one molar equivalent plutonium (1 DFB : 1 Pu) to 1 DFB : 4 Pu, the reduction of Pu(VI) to Pu(V) is instant. At ratios from 1 DFB : 6 Pu to 1 DFB : 12 Pu, the rate of reduction is slower, but still very rapid (< 1 hour). For the reaction at a ratio of 1 DFB: 12 Pu, up to 20% Pu(VI) is still present after 10 minutes, allowing spectroscopic observation of a probable Pu(VI)-DFB species that must form as a first step in the reduction process.

The rate of secondary reduction of the Pu(V) to Pu(IV) is also faster at higher DFB-to-Pu ratios. The presence of excess DFB acts as a thermodynamic driving force for the formation of a stable, soluble Pu(IV)-DFB species. In the reaction performed at a ratio of 1 DFB : 12 Pu, where the DFB is completely oxidized, only Pu(V) is detected in solution, but a precipitate slowly forms. Presumably, any Pu(IV) that forms as a result of the disproportionation of Pu(V) slowly precipitates out of solution as the hydroxide.

Surprisingly, the Pu(IV)-DFO complex is still reactive. When Pu(VI) is added to a solution of the Pu(IV)-DFB or -DFE complex at pH = 2 or pH = 9, the Pu(VI) is rapidly reduced, despite the fact the DFO is already complexed to Pu(IV). The reaction is slower than the reaction without Pu(IV) initially present. Variable temperature NMR (nuclear magnetic resonance) indicates that the Pu(IV)-DFO complexes are highly fluxional and may undergo ligand exchange with free DFO, which would allow for DFO interaction with and reduction of the Pu(VI).

Despite the fact that the Pu(IV)-DFB complex has an exceptionally large equilibrium constant for its formation, the desferrioxamine siderophores are poor at solubilizing solid Pu(OH)$_4$. Pu(IV) hydroxide is slowly solubilized by chelates such as EDTA, citrate, and tiron. We have measured rates of approximately 1.13 mM, 0.16 mm, and 0.10 mm per day reaching 310 mM, 41 mM, and 27 mM, respectively, after 253 days. However, the

siderophores DFE and DFB are 50 to 500 times slower than EDTA with rates of 0.02 (DFE) and 0.002 mM/day (DFB), although they are faster than controls without a chelator present. These results are unexpected given that the thermodynamic equilibrium constants for the formation of the Pu(IV) tiron, citrate, and
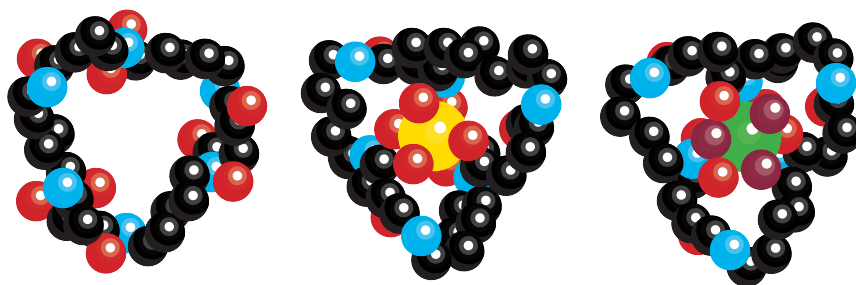
EDTA complexes are lower than for the formation of Pu(IV)-DFO complex. In fact, EDTA solubilization of Pu(OH)$_4$ was 10 times slower after the plutonium is pretreated with DFB (0.11 mm per day). These surprising results suggest that the desferrioxamine siderophores are actually passivating the surface of the Pu(OH)$_4$ and thereby inhibiting solubilization.

We have shown that siderophores and potentially other naturally produced chelators could play a major role in the environmental behavior of plutonium. (Figure 3.) The basic chemistry is becoming clearer: siderophores have high formation constants for Pu(IV), which could keep Pu(IV) species solubilized and mobile. Their higher formation constants indicate that siderophores can "steal" plutonium from other chelators, such as EDTA and NTA, present with plutonium wastes. Hydroxamate siderophores have a large reducing capacity for Pu(VI) and Pu(V), leading to the formation of Pu(IV) siderophore complexes. Siderophores can very slowly solubilize Pu solids, but they could also interfere with solubilization of Pu solids by other chelators.

Figure 2: Metal-free DFE (left), Fe(III)-DFE Complex (middle), and Pu(IV)-DFE Complex (right). Oxygen atoms are shown in red, oxygen atoms of water molecules are maroon, nitrogen atoms are blue, carbon atoms are black, the Fe(III) atom is yellow, and the Pu(IV) atom is green.

Interactions of Pu with Desferrioxamine Siderophores Can Affect Bioavailability and Mobility *(continued)*

We are now beginning to address more complex questions regarding Pu biogeochemistry: Can bacteria bioaccumulate plutonium by actively transporting siderophore-Pu complexes? (we think so), by surface absorption of Pu onto the bacteria capsule (we know so), or by unchelated passive diffusion? Will bacteria that accumulate plutonium increase the mobility of plutonium (biocolloid formation) or decrease it (biofilm formation)?

Can siderophores or other microbial chelators solubilize other forms of Pu in the environment, such as Pu absorbed on mineral, bound by humate, or precipitated by bacteria redox processes? What kinds of ternary complexes can form in the presence of siderophores and other microbial chelators, and will they lead to an increase or decrease in mobility of plutonium? How will local environmental changes caused by bacteria effect plutonium speciation? These processes could play critical roles in plutonium biogeochemistry, which has only begun to be investigated. Understanding how bacteria effect plutonium environmental chemistry is crucial for both the safe long-term storage of plutonium wastes and for proposed bioremediation strategies of plutonium and the organic wastes often present with plutonium.

Figure 3. Microbial interactions with actinides in the environment. All processes could increase or decrease solubility and/or mobility depending on specific bacteria and numerous environmental and chemical factors. Key: â = ⊃ *microbially produced chelator (e.g., siderophores, organic acids, sloughed exopolymer.* ⊏ *= anthropogenic chelator often present with Pu Contamination. An = actinide species. Æ = reaction involving microbially produced chelators. Æ = reaction does not directly involve microbially produced chelators. 4 = reaction can occur with and without microbially produced chelators.*
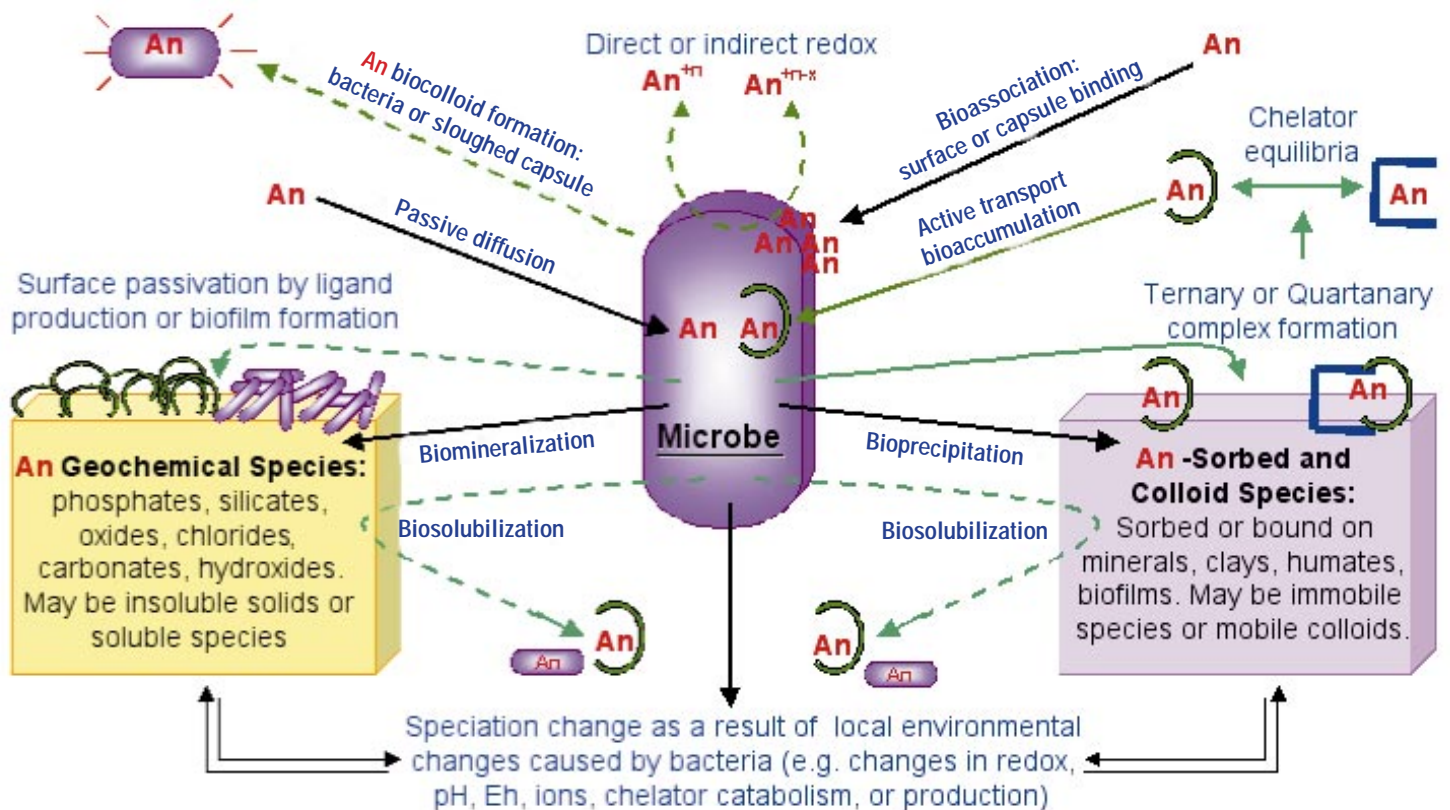
Publications and Invited Talks
(January 2000–July 2000)

Danis, J. A., H. T. Hawkins, B. L. Scott, W. H. Runde, B. E. Scheetz and B. W. Eichhorn, "X-ray Structure Determination of Two Related Uranyl Phosphate Crown Ether Compounds" *Polyhedron*, in press.

Jacobsen, S. D., J. R. Smyth, R. J. Swope, and R. I. Sheldon, "Two Proton Positions in the Very Strong Hydrogen Bond of Serandite, $NaMn_2[Si_3O_8(OH)]$," *American Mineralogist*, **85** 745-752 (2000).

Park, J. J., "Creep Behavior of W-4Re-0.32HfC and Its Comparison with Some Creep Models," *International Journal of Refractory Metals and Hard Materials* **17** 331-337 (December 1999).

Park, J. J., D. P. Butt, and C. A. Beard, "Review of Liquid Metal Corrosion Issues for Potential Containment Materials for Liquid Lead and Lead-Bismuth Eutectic Spallation Targets as a Neutron Source," *Nuclear Engineering and Design* **196** 315-325 (April 2000).

Pillay, G., S. R. Billingsley, and J. J. Balkey, "Electrochemical Treatment and Minimization of Defense-Related Wastes," Keynote Address, in *Environmental Aspects of Electrochemical Technology: Proceedings of the International Symposium*, E. J. Rudd and C. W. Walton, eds., 99-39, The Electrochemical Society, Inc., Pennington, NJ (2000) (also published in *Federal Facilities Environmental Journal* **11**, No. 2, Summer 2000, pp. 115-127).

Sheldon, R. I., T. Hartmann, K. E. Sickafus, A. Ibarra, B. L. Scott, D. N. Argyriou, A. C. Larson, and R. B. Von Dreele, "Cation Disorder and Vacancy Distribution in Non-stoichiometric Magnesium Aluminate Spinel," *J. Am Ceram. Soc.* **82**(12), 3293-3298 (1999).

Sickafus, K. E., J. M. Wills, S. Chen, J. H. Terry, T. Hartmann, and R. I. Sheldon, "Development of a Fundamental Understanding of Chemical Bonding and Electronic Structure in Spinel Compounds," Los Alamos National Laboratory report LA-UR-99-2731, Los Alamos, NM (1999).

NewsMakers

■ **Gary H. Rinehart** (NMT-9) is the winner of the American Nuclear Society's Mishima Award this year. The Mishima Award was established in 1991 to honor Dr. Mishima Yoshitsugu, Professor Emeritus of the University of Tokyo, to recognize an individual for his/her outstanding contributions in research and development work on nuclear fuels and materials. Reinhart is recognized for his sustained contributions to the development, production, testing and decommissioning of ^{238}Pu heat sources for medical, space and terrestrial applications.

■ **D. Kirk Veirs** (NMT-11) is one out of eight individuals honored as part of the 2000 Career Development Mentor Awards. The award recognizes and applauds exemplary mentoring at the Laboratory.

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