To Mars and Beyond
Los Alamos expertise in plutonium-238 heat-source production will play an important role in a new NASA initiative

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A hot-pressed fuel pellet of plutonium oxide glows red before the surface has cooled. Fuel pellets like this are made at TA-55 out of purified scrap from disassembled heat sources. The pellets, about 27.5 millimeters in diameter and 27.5 millimeters in length, will be encapsulated to form fueled clads to be used in radioisotopic thermo-electric generators for NASA missions. The image running across the bottom of the cover shows the microstructure of a conforming weld of a nonimpacted fueled clad. To study a sample with metallography, researchers polish a sample to a mirror finish, treat the surface to reveal the grains or microstructure, and then examine the structure under the microscope. If the weld is nonconforming, it is analyzed further and the information used to adjust welding parameters. The complete story is on pages 1-4.
NASA has announced a new research program that will propel deep-space exploration through the coming decades. Plutonium-238 and Los Alamos will play an important role in the initiative, which will rely on radioisotope heat sources fabricated at Los Alamos to supply power and heat for missions to Mars and beyond.

NASA said the initiative will enable sophisticated mobile laboratories to travel over the surface of Mars, drilling deep underground at promising sites where signs of life can be sought, and conduct a large variety of other experiments day and night, around the clock.

Radioisotope Thermoelectric Generators (RTGs) fueled by plutonium-238 have been used to provide electrical power for spacecraft since 1961. In addition, low-power Light Weight Radioisotope Heater Units (LWRHUs) have been used to maintain spacecraft equipment within their normal operating temperatures. These RTGs and LWRHUs are in two dozen spacecraft, including Pioneer, Voyager, Galileo, Cassini, and Mars Pathfinder. (For more information on the historical perspective on plutonium-238 heat sources, see ARQ, 1st Quarter, 2001.)

Los Alamos has the only plutonium-238 scrap recovery, fuel processing, and analysis capabilities in the United States. Until the late 1980s, plutonium-238 was produced and purified in reactors at Savannah River. Those reactors have been shut down, so the aqueous scrap recovery process of heat-source materials is now performed at Los Alamos’ Plutonium Facility at TA-55. For the next two decades, it is estimated that Los Alamos will produce two to eight kilograms of plutonium-238 fuel per year to meet the needs of NASA’s space applications.

Currently, the aqueous scrap recovery process is being done in a bench-scale operation. A full-scale aqueous scrap recovery glove-box line is expected to become operational later this year. The Plutonium-238 Science and Engineering Group (NMT-9) oversees the plutonium-238 recovery and heat-source fabrication operation.

To make a general-purpose heat source (GPHS) unit or LWRHU, researchers at TA-55 recover plutonium-238 fuel from old, disassembled heat sources. The scrap is purified to remove decay products (mainly uranium-234) and other impurities from the plutonium dioxide. The resulting purified oxides are formed into fuel pellets and encapsulated to form fueled clads.

Before these fueled clads can be used in GPHSs or LWRHUs, a set of chemical and physical parameters must be met during purification and fabrication steps. Los Alamos has full capabilities to determine these parameters for heat-source production and provide analysis for safety impact testing. These capabilities include chemical analyses, neutron emission-rate measurements, particle size determination, calorimetric measurements, helium leak tests, metallography and ceramography, ultrasonic weld examinations, and radiography.
The full-scale aqueous scrap recovery operation will also include gamma-based measurement equipment (a plutonium process monitoring—or PPM—system) and a solution in-line alpha counter (SILAC). These technologies will be used to monitor the ion-exchange process and alpha concentration of solutions inside the glove-box line.

**Chemical analysis capabilities**

Researchers need chemical data on plutonium-238 samples (feed oxides, purified oxides, granular plutonium-238, and process solutions) to establish the necessary baseline parameters and measurements for process control, material control and accountability, waste disposal, and product certification. To acquire the data, members of the Actinide Analytical Chemistry Group (C-AAC) perform chemical analyses at laboratories located in the Chemistry Materials and Research (CMR) Building.

The chemical analysis begins by dissolving plutonium material in concentrated hydrochloric and hydrofluoric acids using the sealed-reflux procedure. The sealed-reflux dissolution method allows researchers to dissolve high-fired fuel at a temperature of 150 to 200 degrees Celsius and a pressure of 50 to 115 pounds per square inch. Spectroscopy is used to determine the purity of the resulting plutonium oxide. If the expected plutonium content is low (one microgram per gram or less), gross alpha counting is used to calculate the plutonium-238 content.

Analyses of actinide impurities, including uranium-234, americium-241, neptunium-237, and plutonium-236, are performed by radiochemical methods (gross alpha and gamma counting, gamma and alpha spectroscopy, and radionuclide separations). The plutonium isotopic composition is determined by thermoionization mass spectrometry. Direct-current arc and inductively coupled plasma mass spectrometry techniques are used to determine nonactinide cationic and anionic impurities.

Because of material-at-risk issues at the CMR Building, Los Alamos has begun consolidating plutonium-238 operations. The majority of the plutonium-238 chemical analysis capabilities will be moved into the TA-55 Plutonium Facility within the next several years.

**Physical measurement capabilities**

Spontaneous fission of plutonium-238 produces approximately 2,220 neutrons per second per gram. Energetic alpha particles react with light isotopes, producing even higher neutron emission rates. To reduce the neutron emission rate, researchers treat the purified oxide with oxygen-16 exchange to reduce oxygen-17 and -18 in the products. Researchers then measure the neutron emission rate of the oxide using a thermal neutron counter.
After a fuel pellet is hot-pressed, it is encapsulated in an iridium alloy container and subjected to ultrasonic immersion testing to examine the integrity of the weld. These images show the test results of conforming (top) and nonconforming (middle) welds of fueled clads. The green area in the nonconforming weld’s data indicates a possible defect. The bottom table shows the magnitude of the signal reflected in the test. The black line is the trace of the magnitude illustrated by color in the middle image, and the blue line is the trace of the magnitude in the top image. If a fueled clad has ultrasonic reflectors in excess of a set level, it is inspected with radiography to determine whether the heat source is acceptable for flight use.

Calorimetry is used to determine the power output of heat-producing materials. Plutonium-238 has a half-life of 87.74 years and a power output of 0.567 watts per gram. Several types of calorimeters are used at TA-55 to measure low-wattage (up to five watts) and high-wattage (up to 200 watts) fuel. A typical GPHS fueled clad contains approximately 150 grams of plutonium-238 oxide and has 61 to 62 watts of power.

An LWRHU contains 2.67 grams of plutonium-238 oxide and has a nominal heat output of one watt. Calorimetric measurements are also used to perform material accountability measurements of plutonium-238.

A plutonium-238 GPHS fuel pellet is hot-pressed and encapsulated in an iridium alloy container with a weld shield. Each iridium clad contains a sintered iridium powder frit vent designed to release the helium generated by the alpha particle decay of the fuel. Ultrasonic immersion testing is performed to examine the weld integrity of the plutonium-fueled clad. If a fueled clad has ultrasonic reflectors in excess of the reject specification level, it is inspected with radiography. This additional engineering data determines whether the heat source is accepted or rejected for flight use.

Heat sources must be designed and constructed to survive impact. NMT-9 can determine the particle-size distribution of fines—small particles that are broken off from the fuel pellet during the impact test—recovered from impact tests that are less than 100 microns in diameter. Impact tests on plutonium-238 and simulant fueled clads are conducted to determine the response to probable launch accident scenarios of bare fueled clads and of GPHS modules with up to four clads each.

Particle-size analysis is also used to verify the particle size of milled oxides before dissolution. NMT-9 has equipment that can measure particles ranging in size from 0.5 to 600 microns.
Researchers use metallographic and ceramographic examinations on components recovered from impact tests. The microstructure of the clad material, girth welds, and samples of fuel pellets are also examined. A metallograph with a magnification range up to 500 times actual size is interfaced to the glovebox line through a unique hood extension.

**In-line process monitoring capabilities**

In the full-scale plutonium-238 aqueous recovery operation, a PPM system will be used to monitor americium, uranium, and plutonium gamma rays during the ion-exchange process. This PPM system will provide real-time elution profiles of actinide impurities that will help in reducing solution waste volume and will provide a monitoring tool during washing and elution steps.

In addition, a SILAC will be used for monitoring the alpha activity in hydroxide filtrate in the full-scale residue polishing operations. By knowing the approximate alpha concentration, an operator can adjust the operating parameters of the ultrafiltration process to maximize the removal of plutonium and uranium from the residue solutions before discharging them into the Laboratory’s Liquid Waste Treatment Facility.

To help meet its goals, NASA is depending on Los Alamos and the Plutonium Facility’s unique capabilities to process and fabricate plutonium-238 into heat sources. Several Mars and deep-space exploration programs that require plutonium-238 heat sources are currently ongoing or under development. For example, the twin Mars Exploration Rovers that are being prepared for launch in the summer of 2003 are expected to carry several plutonium-238 LWRHUs on board.

Support for the Laboratory’s heat source work is provided by DOE’s Office of Space and Defense Power Systems.
DURING the last few months there have been a number of important policy decisions made that will have a direct impact on research programs related to the fate of plutonium and other actinides.

This past November, President George W. Bush proposed to reduce the number of deployed U.S. warheads from 6,000 to between 1,700 and 2,200 by 2012. Russian President Vladimir Putin responded with a pledge to reduce the Russian nuclear arsenal to 1,500 warheads.

The Department of Energy (DOE) subsequently announced that it will move forward with a plan to convert approximately 34 metric tons of “excess” weapons plutonium into a mixed oxide (MOX) fuel to be “burned” in commercial reactors.

An earlier parallel program to immobilize a part of this plutonium—the so-called “scrap plutonium”—into a durable solid for storage and direct disposal has been abandoned. The parallel strategies were based on the concept of the “spent fuel standard” that envisioned the fissile material as being protected by highly radioactive fission products.

President Bush has recommended the Yucca Mountain site in Nevada for the geologic disposal of used nuclear fuel from nuclear power plants and high-level waste from defense programs. The MOX fuel, after a once-through cycle of burn-up, is destined for disposal in the Yucca Mountain repository.

Each of these policy decisions is controversial, and each is linked to the other through a complex chain of legal, regulatory, and political decisions. The failure of any single part of the policy chain will have a profound effect on the success or failure of the other policy decisions.

**Issues affecting policy formation**

As an individual researcher, I have become increasingly concerned at the minimal role science plays in arriving at these decisions, and even more concerned that these decisions remain disconnected from one another. In this short piece, I cannot argue the merits or deficiencies of the individual policy decisions or describe their connections. I can, however, raise some simple issues that should be addressed in the formulation of these policies.

“Burning” the weapons-grade plutonium will not reduce, to any major extent, the inventory of plutonium. U.S. vulnerability to terrorist attack using diverted materials is not much reduced by the new policy. Although the isotopic vector of the plutonium will have been modified, the spent MOX fuel is still a potential source of weapons-usable material.

Protecting fissile material, either in the spent nuclear fuel or in a high-level nuclear waste glass, is only a short-term solution, as this strategy essentially protects a fissile nuclide with a half-life of 24,100 years with the high activity of fission products whose half-lives are on the order of 30 years.

Finally, MOX fuel, mainly UO$_2$, is not stable under the oxidizing conditions that will prevail at Yucca Mountain. In presence of moisture and air, one can expect rapid alteration of the spent fuel and the formation of mobile UO$_{2^{+}}$ complexes. This spent MOX fuel increases the overall inventory of long-lived fissile material, and this may have an impact on the long-term safety of the repository.

**Science vs politics**

As researchers, should we be concerned with these policy decisions? We could, perhaps, leave such considerations to higher-level government officials, but as Thomas Jefferson said, “Science is my passion; politics my duty.”

Because of changes in policy, research programs will begin and end abruptly.

**Guest Editorial**

"We should not expect that the same level of understanding that caused the problem will be sufficient to solve the problem.”

Albert Einstein

Rodney C. Ewing

This editorial was contributed by Rodney C. Ewing of the University of Michigan, departments of Nuclear Engineering and Radiological Sciences, Materials Science and Engineering, and Geological Sciences.

The opinions in this editorial are the author’s. They do not necessarily represent the opinions of Los Alamos National Laboratory, the University of California, the Department of Energy, or the U.S. government.
New programs will be focused on supporting the present policy decision. Effort and expertise are lost with each change. Costs escalate as programs are redirected. Less time than money is usually available to develop supporting data, models, and a scientific rationale for a new policy.

I understand that change is necessary, as every new policy has specific scientific and technical needs, but these changes drive the science—rather than having science inform the policy.

I want to argue that, while abrupt changes may be the fate of applied research programs, this should not be the fate of basic research. A policy decision does not settle the fundamental scientific issues.

In fact, in my experience, there is little evidence that the fundamental limitations outlined by science are used to constrain the conceptual framework of the policy. Cost, schedule, and politics are more likely to be the drivers of policy than the underlying science. With faith and funding, every technical problem is presumed to have a solution.

However, most policy decisions in the nuclear domain have proven to be high risk, the cost is high, and failure propagates throughout the system. The high cost and extended delays in the construction and operation of the Defense Waste Processing Facility at Savannah River have impacted the efforts to build a similar vitrification facility at Hanford.

A recent directive from the Assistant Secretary for Environmental Management now promotes a goal of eliminating the need to vitrify at least 75 percent of the waste presently destined for vitrification.

The original decision to vitrify waste at Savannah River coincided with the decision to eliminate basic research on alternative waste forms. The decision to look at alternatives to vitrification at Hanford will now require considerable effort and research on alternative waste forms. With each swing of the pendulum, the cost increases.

In studies of the radiation-resistance of compositions in the Gd$_2$($Zr$$_{1-x}Ti_x$)$_2$O$_7$ binary, we discovered that ion beam irradiations could be used to create a buried layer of disordered fluorite-type structure in a matrix of pyrochlore. The disordered structure forms at the peak of the damage profile and has an ionic conductivity of two to three orders of magnitude greater than the surrounding insulating matrix. Thus, research on a potential plutonium-bearing waste form has also created a new avenue for the design and fabrication of nanoscale mixed ionic-electronic conductors in the pyrochlore oxides. This has important applications in the development of solid oxide fuel cells and sensors. (Physical Review Letters, 87, 2001).
Basic research should provide alternatives to policy

Every policy decision should anticipate failure and explicitly develop alternatives. As a small example, I cite our own work on radiation effects in phases that can incorporate actinides.

Until recently, the U.S. strategy included the development of a titanate pyrochlore for the immobilization of the “scrap” plutonium (to be surrounded by a high-level waste glass in a canister, the “can-in-can” concept).

Although durable, the titanate pyrochlore is highly susceptible to alpha-decay damage, becoming fully amorphous in hundreds of years. However, through a basic research program funded by Basic Energy Sciences, our research group discovered that the closely related zirconate pyrochlore is resistant to radiation damage, remaining crystalline for millions of years.

From a scientific perspective, this phenomenon is of fundamental interest and is the subject of exciting research at Los Alamos and Pacific Northwest National Laboratory in Washington, as well as in France, England, and Russia. From a policy perspective, the discovery is irrelevant, as immobilization of plutonium in ceramics is not the present strategy.

Still, this discovery provides an alternative to the present policy.

The discovery of a new class of radiation-resistant solids opens the door to research on a new class of materials that may have many applications to the materials problems throughout the DOE complex. As is often the case, there have already been important spinoffs from studies of the radiation damage effects in these materials because the ionic conductivity of Gd\(_2\)(Zr\(_x\)Ti\(_{1-x}\))\(_2\)O\(_7\) can be greatly increased by disordering the structure to a simpler fluorite structure. Ion-beam irradiations have been used to manipulate the conductivity of these solids at the nanoscale.

The structure of funding within DOE often places a high priority on research and engineering programs that support present policies. However, the risk of failure could be lowered if there were a conscious effort to fund basic research programs that provide future alternatives to today’s policy.
Three years ago the Waste Isolation Pilot Plant (WIPP) in southeastern New Mexico accepted its first shipment of low-level transuranic waste. Since then, almost 18,000 drums of waste have been delivered to the site, and a milestone was reached in January when the site accepted its 500th shipment. During the next 35 years, about 37,000 shipments are expected to be delivered to the site.

WIPP is the nation’s first permanent, deep geological disposal facility for low-level waste generated by the nuclear weapons program. Regulations do not allow WIPP to accept commercial or high-level radioactive waste. President George W. Bush has endorsed a high-level waste repository at Yucca Mountain in Nevada. Congress is expected to take up that debate later this year.

WIPP required years of scientific research, regulatory struggles, and input from the public before it began operations in March 1999. The idea for a WIPP dates back to the 1950s, when the National Academy of Sciences launched a search for a geological formation stable enough to contain wastes for thousands of years. In 1955, after extensive study, salt deposits were recommended as a promising medium for the disposal of radioactive waste.

Salt is a good candidate for nuclear waste disposal for several reasons. Most salt deposits are found in stable geological areas where there is very little earthquake activity. Salt deposits are found in areas where there is no flowing fresh water—if water were present, it would have dissolved the salt beds. Salt also is relatively easy to mine. And, because rock salt heals its own fractures, the salt formations will slowly move in to fill mined areas and seal the waste from the environment. The salt rock also provides shielding from radioactivity similar to that of concrete.

The Atomic Energy Commission (AEC), the forerunner to the Department of Energy (DOE), originally selected a salt mine near Lyons, Kansas, for WIPP, but it turned out to be unacceptable. Several years later, a site near Carlsbad, N.M., was chosen. Congress authorized WIPP in 1979, and the DOE constructed the facility during the 1980s.
The salt formations at WIPP were formed about 225 million years ago during the evaporation of an ancient ocean. These geologic formations at WIPP are about 2,000 feet thick, beginning 850 feet below the surface.

Waste destined for WIPP consists mainly of equipment, clothing, and other debris that has been contaminated with small amounts of plutonium and other transuranics. The waste, which has been accumulating since the Manhattan Project, is currently stored at almost two dozen sites around the United States.

Ninety-seven percent of the waste comes from just five sites: Los Alamos, Rocky Flats Environmental Technology Site in Colorado, Idaho National Engineering and Environmental Laboratory, Hanford Site in Washington, and Savannah River Site in South Carolina.

Federal and State regulations require that waste be characterized before it is shipped to WIPP. Characterization requires knowing the physical, chemical, and radiological properties of the waste to make sure it contains only materials allowed to be shipped to and accepted by WIPP. Once received at WIPP, and before they are buried, the wastes must be confirmed to contain only those materials allowed to be disposed at the site.

Safely disposing and storing the accumulated waste from almost 60 years of nuclear research is a daunting task. WIPP is a critical part of the DOE’s effort to clean up this legacy waste and protect the public and the environment. In the articles that follow, we take a look at several issues of nuclear waste, including technologies Los Alamos is using to safely store and track waste, how Los Alamos researchers are assisting the cleanup effort at Rocky Flats, and a guest editorial on WIPP’s first three years of operation.
In May 1999, I was appointed manager of the Department of Energy (DOE) Carlsbad Field Office, which is responsible for the DOE’s Waste Isolation Pilot Plant (WIPP) and the National Transuranic Waste Management Program. WIPP is a deep geologic repository located near Carlsbad, N.M., for the disposal of defense-generated transuranic (TRU) waste. The National Transuranic Waste Management Program coordinates the characterization of this waste at DOE sites across the country and the transportation of the waste to WIPP for disposal.

Upon arriving in Carlsbad, I immediately realized the need to accelerate TRU waste shipments to WIPP. At the time, WIPP was receiving one to two shipments of TRU waste per week. At that rate, it would take the facility 255 years to complete its mission! Clearly, something had to be done, so I challenged WIPP employees and organizations to “fill the pipeline” to achieve and sustain 17 shipments per week.

I am proud to say that three years later, WIPP is receiving 17 shipments per week and is now ramping up to receive 25 per week. Let me tell you how our team achieved this goal.

Filling the pipeline required a culture change as much as anything else. For years, WIPP focused on preparing the facility for opening. This meant passing literally hundreds of audits by regulators, oversight groups, and internal review teams. After the facility finally opened for TRU waste disposal operations on March 26, 1999, most WIPP employees and organizations continued to focus their attention “inside the fence”—to improving the WIPP waste handling process and facility operations.

Our challenge was to get these employees and organizations to shift some of their focus to “outside the fence”—improving TRU waste characterization and transportation. Changing a culture can take years, but we did not have that kind of time. So, we launched a full-scale communication blitz to effect a change in their focus.

But, communication is not enough to effect a culture change—you must hold organizations and employees accountable. WIPP became one of the first DOE facilities to use a new method of contractor accountability: the performance-based incentive. Through a number of performance-based incentives, we made sure that the contractor had incentives to accelerate waste shipments to WIPP. Not only was the contractor held accountable, my own DOE employees were as well.

A truck carries three Transuranic Package Transporter Model II—or TRUPACT-II—containers to the WIPP site. The stainless steel containers are approximately eight feet in diameter, ten feet high, and can hold up to fourteen fifty-five-gallon waste drums.
In addition to changing the culture at WIPP, many technical initiatives were also necessary to aid in filling the pipeline. Researchers at Los Alamos National Laboratory had previously designed and produced a TRU waste mobile loading unit, and we accelerated its deployment and use at the Savannah River Site in South Carolina. The mobile loading unit contains a suite of equipment capable of loading 55-gallon TRU waste containers into TRUPACT-IIIs (the shipping casks we use for transport to WIPP).

The Central Characterization Project is another accomplishment of the past year. This project is a mobile waste characterization system consisting of four parts. Nondestructive assay instrumentation is used to characterize the radiological content of each drum, while nondestructive evaluation equipment (real-time radiography) is used to examine the physical contents of each drum.

The characterization system also includes a visual examination capability (in a glove box) for confirming a statistical subset of the real-time radiography examinations, and headspace gas sampling and analysis equipment to draw and composite air in the headspace of each container for analysis for a broad spectrum of volatile organic compounds. The mobile/modular units currently do not have the capability to core and analyze homogeneous solids, such as cemented drums.

The mobile waste characterization system is accompanied by a mobile loading unit. These units give sites the ability to characterize and stage transuranic waste destined for shipment to WIPP in accordance with all necessary requirements and to meet WIPP’s disposal requirements. Currently, the Environmental Protection Agency and the New Mexico Environment Department have approved the project for use on a specific waste stream located at the Savannah River Site.
To date, these efforts have resulted in several critical accomplishments during the past three years. WIPP has ramped up from receiving one to two waste shipments per week to 17 shipments per week, for a total of just over 700 shipments received. The site also has surpassed one million employee-hours without a lost-time accident and has achieved more than one and a half million safe transportation shipment-miles.

To put this in perspective, in our first three years of operation we have safely emplaced almost ten percent (1,250 kilograms) of the weapons-grade plutonium in the baseline inventory projected for disposal. Interestingly, we have received almost the same number of curies of americium-241, since we accepted shipments early on of some of the reprocessing sludge from the Idaho National Engineering and Environmental Laboratory. The more than 67 kilocuries of americium-241 in WIPP today are roughly equivalent to that in a common smoke detector for each person on the planet.

Another surprising fact deals with the amount of hazardous volatile organic compounds that has been shipped to WIPP in the first three years of operation. With all the emphasis on organic hazardous materials in TRU waste destined for WIPP, the total amount of volatile organic compounds that WIPP is required to track as stipulated in our Resource Conservation and Recovery Act permit with the State of New Mexico is less than 28 liters of gas. No, that’s not a typo.

There are nine specific “contaminants of concern” in the volatile organic compound monitoring requirements of the WIPP permit. If all of the approximately 18,000 drums of TRU waste in WIPP today had been treated to extract these volatile organic compounds from the headspace gas, they would result in a total of 28 liters at standard temperature and pressure.
Recently, a new proposal has been made to construct an Actinide Chemistry and Repository Science Laboratory (ACRSL) adjacent to the Carlsbad Environmental Monitoring and Research Center (CEMRC), which is a part of New Mexico State University. In conjunction with DOE’s Office of Science and Technology (EM-50) and Los Alamos, we transferred the Contaminant Analysis Automation trailer from Los Alamos to CEMRC last year. The Contaminant Analysis Automation technology will become a significant part of the ACRSL, which will be operated by CEMRC.

The Los Alamos Carlsbad Office will perform radiochemistry experiments needed to address issues related to nuclear waste characterization and repository performance in these new facilities. Sandia National Laboratories will also conduct actinide chemistry experiments here. These studies will help address specific scientific and technical issues related to waste characterization, repository performance, and enhanced operations of the repository.

Several experiments are planned. Researchers will study the effects of WIPP-relevant materials—such as reductants—and potential radiolysis by-products—for example, hypochlorite and peroxide—on the oxidation states and speciation of plutonium, americium, uranium, thorium, and neptunium. They also hope to study the effects of organic ligands on the mobility of plutonium and other actinide elements in WIPP-relevant brines, the demobilization of actinides by borehole fill materials, and the efficacy of oxidation state analogs for predicting the behavior of the actinides.

Space is too limited here to describe all the other initiatives the WIPP project is pursuing to fill the disposal pipeline with waste actinides. We are exploring many streamlined ways of characterization, and there are numerous transportation enhancement opportunities, including a rail option. We plan a subsequent contribution to “Actinide Research Quarterly” next year with an update on how the WIPP project is solving the nation’s TRU waste disposal problem.

It has been a challenging three years. By accelerating waste shipments to WIPP, we are making a positive contribution to our national safety and security, as well as paving the path forward for the nuclear industry.
New Initiatives in the Laboratory’s Handling of Legacy Transuranic Waste

Anyone in the Laboratory who works with actinides potentially generates transuranic (TRU) waste destined for the Waste Isolation Pilot Plant (WIPP) in Carlsbad, N.M. Because a high volume of legacy TRU waste also exists in storage here, reducing waste volume and efficiently managing legacy waste are topics that should be of concern to us all.

The Lab’s new programs for handling legacy waste date back to 1994–95 when the State of New Mexico intervened to request that nearly 17,000 drums of solid mixed and TRU waste be placed in an inspectable and retrievable configuration. So began the transuranic waste inspectable storage project (TWISP).

The drums had been stored for nearly 20 years at TA-54 on above-grade asphalt pads in dense-pack arrays under plywood, plastic, and soil. Facility and Waste Operations (FWO) Division ultimately retrieved the drums from three such pads, and after washing and venting them, transferred them into six domes at TA-54. Here, they are inspected weekly, at minimum, and daily on any day when a Laboratory staff member enters a given dome.

And happily for both taxpayers and Lab administrators, TWISP was completed two years ahead of schedule and $18 million under budget.

Another concern in the arena of TRU waste management has been the profusion of what are known as “RFP crates”—Fiberglas™-reinforced boxes containing a diversity of equipment ranging from glove boxes to high-efficiency particulate air (HEPA) filtration systems contaminated with both TRU and other types of waste, such as beryllium and low-level waste (LLW).

Often these crates are very large, and almost always, the items inside were packaged without much attention to space efficiency. This waste issue has spawned the Decontamination Volume Reduction System (DVRS) Project, an initiative to process RFP crates by characterizing their waste, reducing its volume, and enclosing it in crates for shipment to WIPP if TRU, or storage at Los Alamos if LLW. A relative of a good old-fashioned “Escort-Eldorado equalizer” proved invaluable in this project.

The basic methodology involves unsheathing each crate, segregating its waste (if relevant) into TRU and LLW, and if feasible, decontaminating each component by such techniques as paint-stripping, surface abrasion, and the use of chemical cleaners and surfactants. Each component is then reduced in volume by “Big Blue,” a massive compactor, kin to those that compress both luxury and subcompact vehicles into the rectangular jumbles of metal that we often see being transported to recycling sites.

The resulting secondary waste must then be repackaged to meet WIPP-approved...
procedures if TRU, and Los Alamos waste acceptance criteria if LLW. And because safety is always first priority, the DVRS facility has a double firewall, each wall rated for a two-hour fire protection delay.

Along the way, other techniques have proved useful during this process of waste categorization and reduction. For example, gas sampling of the crate interiors allows the detection of explosive or acid gases, mercury vapor, and loose radiological contamination.

And during the FWO Division’s exploration of options for noninvasive crate-content identification, an ingenious gamma-radiography adaptation was proposed. Because many crates are larger than the size limits of most radiography machines, a solution was discovered in the form of the machines used by Border Patrol agents to scan tractor-trailer rigs for drugs and/or illegal immigrants—machines large enough to handle most or all RFP crates.

Unfortunately, the events of Sept. 11 necessitated a temporary withdrawal of the offer of radiography personnel participation in the screening project, but it is hoped that this aspect of the operation will soon become reality.

There are also technological improvements in the offering in the waste-reduction arena. For example, a carbon dioxide decontamination blaster has shown promise in removing surface layers of actinide-contaminated items. The blaster produces a residue from which carbon dioxide evaporates, leaving a greatly reduced volume of TRU and an actinide-decontaminated remainder that can be disposed of as LLW. Other chemical-decontamination methods are also being researched.

“If we can get the money to do this stuff, we will,” said Ray Hahn of Solid Waste Operations (FWO-SWO). One possible source of income may be the FRPs from other laboratories in the DOE complex. If an acceptable means of transport to Los Alamos can be found for their FRPs, Lawrence Livermore and other laboratories may ship them here for decontamination and reduction on a fee basis.

—Vin LoPresti
WITS is Central to a Cradle-To-Grave Waste Management System

Innovative Tracking System Improves Accountability, Eliminates Paper Trail, Reduces Inventory Time

Researchers in the Waste Management and Environmental Compliance Group (NMT-7) have developed an innovative system for tracking the Nuclear Materials and Technology (NMT) Division’s radioactive and contaminated waste. It will store this retrievable information in a central database accessible to other Laboratory organizations.

The Waste Inventory Tracking System (WITS) is central to NMT’s “cradle-to-grave” approach to waste management because it provides one source for information gathering and archiving.

WITS also minimizes the possibility of human error by automating the characterization process through the use of bar codes and a hand-held personal digital assistant (PDA) to track waste shipments. This information is also vital to staff at the TA-54 Waste Disposal Site, where the waste is received and staged or disposed, depending upon its classification.

WITS was designed in collaboration with Beta Corporation International and Intelligent Programming, LLC, over a two-and-a-half-year period beginning in 1998. The PDA is used to read the bar code on each container of waste. This bar code, which is created at the waste source, identifies the contents of each container; exactly what’s in it and how much of it there is by weight. This information goes directly into a database that prints out a complete inventory of each container and maintains a searchable archive that is available to all authorized employees.

The system eliminates the paper trail and all the shortcomings associated with cumbersome files and human error.

Besides streamlining the information-building process, WITS also drastically reduces the time it takes to create the inventory.

Bernadette Martinez, the technical lead for information management in NMT-7, says that it used to take about three hours to characterize one dumpster shipment of 90 low-level radioactive waste boxes and fill out the per-dumpster waste acceptance forms.

This process now takes about 20 minutes and includes an electronic-signature feature. The waste acceptance form is still used, but a printout of the waste contents as well as photographs to document the shipment now accompanies it. The increased accuracy and overall cost-saving benefits are substantial.

WITS also reduces the time and effort to process the waste data at TA-54. Before WITS, NMT-7 personnel completed a Chemical Waste Disposal Request (CWDR) for each waste package. The information on the CWDR was entered by hand into the computerized Chemical/Low-Level System at TA-54. To ensure accuracy, the data was entered a second time and compared. The paper copy of the CWDR was filed and maintained as a waste management record.
WITS eliminated the need for double data entry and the management of the paper CWDR. Martinez says, however, that the “key thing about WITS is its ability to integrate information among divisions.” This across-the-Laboratory integration is important for several reasons: It creates a database that is accessible to anyone who needs it; it increases the Laboratory’s accountability; and it decreases the time and effort involved in delivering, maintaining, and retrieving paper-only records.

Currently, WITS is used for compactable waste such as low-level radioactive room trash and noncompactable waste containing metal and wood. However, the incorporation of chemical and hazardous waste into WITS requires additional refinements in the system.

WITS may have many applications outside of waste management. Martinez has been contacted by other national laboratories, several British companies, and Toyota Motor Manufacturing North America, Incorporated, for information about WITS and its possible applications to general inventory management.

One notable, nonwaste use of WITS was made last year when a contamination incident at TA-55 resulted in workers having to check every compression fitting in the production building. WITS’ functionality was used to document the checking of approximately 25,000 fittings with a “fitting tracker” software module. After the fittings were documented as tight, check/leak verifications were performed. The estimated 50,000 total checks performed over a three-month period resulted in a quick resumption of operations. Members of NMT Division won a Los Alamos Achievement Award for their effort.

This innovative system may have other uses at the Lab, says Martinez. Because WITS requires only a two-hour operator training to use the system, it could be used as a cost-effective tracking system in any number of work situations, including a basic inventory of everything from computers to lock-out/tag-out accounting.

—Ed Lorusso

Egan McCormick of the Waste Management and Environmental Compliance Group (NMT-7) performs a field inventory of low-level waste boxes using a hand-held personal digital assistant—or PDA. The PDA has a built-in bar code reader that scans a bar code on the container and uploads the information to a database. This bar code, which is created at the waste source, identifies the contents of each container; exactly what’s in it and how much of it there is by weight. The technology is part of the Waste Inventory Tracking System (WITS) developed by NMT-7 to track radioactive and contaminated waste.
The Rocky Flats Environmental Technology Site (RFETS) is an environmental cleanup site located about 15 miles northwest of downtown Denver. Formerly known as the Rocky Flats Plant, this site made components for nuclear weapons using various radioactive and hazardous materials until December 1989, when plant operations were shut down.

Nearly 40 years of nuclear weapons production left behind a legacy of contaminated facilities, soils, and surface water. Two decades of routine monitoring have shown that the environment around RFETS is contaminated with actinide elements (uranium, plutonium, and americium) from site operations.

More than 2.5 million people live within a 50-mile radius of the site; 300,000 of those live in the Rocky Flats watershed. The Environmental Protection Agency designated the site a Superfund cleanup site and a massive accelerated cleanup effort began in 1995.

The key priority of site management and surrounding community leaders is the safe, accelerated closure of Rocky Flats. Kaiser-Hill, the company in charge of the cleanup, and the Department of Energy (DOE), in close coordination with Rocky Flats stakeholders, are working aggressively to substantially complete the cleanup and closure of Rocky Flats by 2006. The price tag for the closure is estimated to be between $6 billion and $8 billion.
**Chemical speciation studies**

Researchers at Los Alamos are assisting the cleanup effort by studying contaminated soils from the site using x-ray absorption spectroscopy at Stanford Synchrotron Radiation Laboratory. Earlier studies of the site have shown that plutonium is present in surface soils and that there is a clear west-east trend in contamination away from an old drum storage site known as the 903 Pad. More than 90 percent of the plutonium is contained within the upper 10 to 12 centimeters of soils downwind of the 903 Pad.

The Los Alamos team has been studying the application of synchrotron radiation techniques to plutonium environmental behavior, and their most recent study has resulted in the first spectroscopic confirmation of the chemical speciation of plutonium in soils at RFETS. The speciation of contaminants (i.e., the elemental identities of the contaminants, their physical states, oxidation states, host-phase identities, molecular structures, and compositions) controls their toxicity, bioavailability, transport, and fate in the environment.

The data acquired from the Los Alamos study (combined with other site-specific studies) are key to choosing proper remediation strategies, the correct model for assessing public health risks, and aiding decisions for future land configuration and management.

The probability of the release of plutonium from RFETS soils to the surrounding environment depends on the solubility of its compounds in groundwater and surface waters, the tendency of plutonium compounds to be adsorbed onto mineral phases in soil particles, and by the probability that the colloidal forms of plutonium will be filtered out by the soil or rock matrices, or adsorb or settle out during transport.

The 903 Pad was used in the 1950s and 1960s for storage, on bare ground, of approximately 4,000 drums of plutonium-contaminated solvents and oils. A major release of plutonium to the environment occurred when plutonium-contaminated waste oil leaked from these drums. The drums were removed in 1967 and 1968 after radioactive contamination was detected.

Plutonium-contaminated soil was dispersed by the wind during remediation activities, and an asphalt pad was installed in 1969 to control the spread of plutonium contamination. The area around the 903 Pad continues to be one of the major sources of plutonium contamination at the Site.

Los Alamos researchers used synchrotron x-ray absorption spectroscopy on plutonium-contaminated soils from the 903 Pad to identify the chemical form (or speciation) of plutonium in these soils to assess its environmental behavior and to assist the site in assessing cleanup strategies.
Using XANES Spectroscopy to Determine Oxidation States

When a beam of x-rays passes through matter, it loses intensity via interaction with the matter. A plot of the x-ray absorption as a function of energy (the graph on the top) shows a decrease in absorption with increasing energy, the presence of a sharp rise at certain energies called edges, and a series of oscillatory wiggles (or fine structure) at energies above these edges. It is these characteristic energy regions where x-rays are strongly absorbed (referred to as absorption edges) that are used in x-ray absorption spectroscopy.

The x-ray absorption near edge structure (XANES) can be used to determine the oxidation state of the target (x-ray absorbing) element in solution or in the solid state. The energy at which an absorption edge appears depends on the ionization potential of the ion. This ionization potential increases with the ion’s valence, so in general, the absorption shifts to higher energy with increasing oxidation state.

Los Alamos researchers used this effect to determine the oxidation state of plutonium in contaminated soils and concrete samples from the Rocky Flats Environmental Technology Site. In XANES spectra of plutonium (the graph on the bottom), there are distinct differences in the energy of the rising absorption edge, the intensity of the peak (sometimes referred to as the “white line”), and the structure in the absorption features at the higher energies beyond the absorption peak.

All of these features change with the changing oxidation state of plutonium. These differences in the XANES spectra are used to identify the oxidation state of plutonium in RFETS samples.

These factors are largely governed by the chemical oxidation state and its associated chemistry. Plutonium in lower oxidation states tends to form complexes with extremely low solubilities and stronger sorption to mineral surfaces under most environmental conditions. Plutonium in the higher oxidation states tends to form complexes with relatively higher solubilities and weak sorption to mineral surfaces.

Scientific techniques that provide information on the nature of plutonium oxidation states in the environment are therefore of great interest.

Synchrotron-based methods are extremely powerful for the study of speciation in the environment because they can be used under environmentally relevant conditions, namely, in the presence of water at ambient pressures and temperatures, and at dilute metal ion concentrations.

The chemical oxidation state and electronic properties can be determined from the X-ray Absorption Near Edge Structure (XANES). X-ray Absorption Fine Structure (XAFS) spectroscopy probes the local chemical environment of a material, providing information on the identity of atoms in the first coordination sphere of the central metal ion, the number of neighboring atoms, and their interatomic distances.

Because the samples do not need to be crystalline, XAFS is ideally suited to the study of highly disordered solids and amorphous materials that are likely to be found as a result of accidental environmental contamination.
The Los Alamos team examined x-ray absorption spectroscopy of a series of well-characterized standard compounds followed by samples of contaminated RFETS soils and concrete collected from the site. These studies used Stanford Synchrotron Radiation Laboratory’s new Molecular Environmental Science Beam Line.

The XANES measurements on RFETS soil from the 903 Pad and concrete from a contaminated building clearly show that the oxidation state of plutonium is Pu(IV), and the XANES spectral signatures are very similar to that of solid plutonium dioxide (PuO$_2$) in both soil and concrete samples. One of the soil samples was concentrated enough that XAFS data could be studied. XAFS data analysis revealed local structure features nearly identical to that of the solid PuO$_2$ standard.

Los Alamos x-ray absorption studies therefore show unambiguously that plutonium in RFETS soils taken from the 903 Pad is in oxidation state (IV) and in the chemical form of insoluble PuO$_2$. For decades it had been presumed that plutonium in RFETS soils existed as PuO$_2$, but this hypothesis had never been proven.

Using XAFS Spectroscopy to Determine Local Atomic Structure

X-ray Absorption Fine Structure (XAFS) spectroscopy reveals information on the solid-state structure of a sample, even if the sample is amorphous, noncrystalline, or dissolved in solution. XAFS provides information about the number of atoms and their interatomic distance from a central target atom.

In the case of plutonium dioxide (PuO$_2$), the crystalline structure has cubic symmetry and is shown here from the perspective of a central plutonium atom (dark green). If we probe the x-ray absorption of plutonium in this sample, we will extract the local structural environment around a plutonium atom in the sample. For PuO$_2$, there are eight near-neighbor oxygen atoms (shown in red) that all sit at a 2.33 angstrom distance from the central plutonium atom in the structure. In the cubic PuO$_2$ structure, there are also 12 neighboring plutonium atoms (light green) at an interatomic distance of 3.81 angstroms from the central plutonium atom. Finally, in this example, there is another “shell” containing 24 distant oxygen atoms (shown in pink) at an interatomic distance of 4.66 angstroms.

It is this combination of the number of near-neighbor atoms, their elemental identities, and their interatomic distances that uniquely define the chemical structure using XAFS spectroscopy.
Synchrotron Studies

The Los Alamos study is the first spectroscopic confirmation of the speciation of plutonium in soils at RFETS. This finding is consistent with the observed insolubility of plutonium in site-specific waters and supports a growing body of evidence that physical (particulate) transport is the dominant mechanism for plutonium migration at RFETS.

This recognition not only identified the need for the site to develop a soil-erosion model, but also significantly helped in gaining public trust that an erosion model was the correct model for the site and that soluble transport models are inappropriate for plutonium in RFETS soils.

Plutonium XAS measurements have developed into a decision-making tool for Kaiser-Hill LLC, saved the company millions of dollars by focusing site-directed efforts in the correct areas, and will aid the DOE in its effort to clean up and close the RFETS by 2006.
Third Plutonium Futures Conference
Set for July 2003 in Albuquerque

The next Plutonium Futures Conference is scheduled for the summer of 2003 in Albuquerque at the Marriott Hotel. The conference, the third in a series, is sponsored by Los Alamos National Laboratory, in cooperation with the American Nuclear Society.

In 2000, the Plutonium Futures Conference hosted more than 400 visitors from 15 countries. The conferences, held every three years, provide an international forum for presentation and discussion of current research on physical and chemical properties and environmental interactions of plutonium and other actinide elements.

A number of issues surrounding plutonium and other actinides deserve and receive significant national and international attention, including the safe storage and long-term management of surplus weapons materials and the management of large inventories of actinides from civilian nuclear-power generation. The technical basis for addressing these issues requires intensive and increasing understanding of the underlying plutonium and actinide science and technology.

Scientists, engineers, and university students throughout the world, as well as the national laboratories and the Department of Energy’s nuclear complex, are expected and encouraged to participate and make technical contributions.

A second announcement and call for papers will be issued this summer. To sign up to receive more information, visit the website at www.lanl.gov/Pu2003, or contact Kathy DeLucas at duke@lanl.gov, (505) 665-3618.


ARQ wins publication award

Three issues of the “Actinide Research Quarterly” have won an Award of Merit from the Kachina Chapter of the Society for Technical Communication’s 2001 Technical Publications Competition. The issues submitted were 4th Quarter 2000, 1st Quarter 2001, and 2nd Quarter 2001. The award was presented to K.C. Kim, chief scientist of Nuclear Materials Technology (NMT) Division, former editor Ann Mauzy, editor Meredith Coonley, and designer Susan Carlson. Mauzy, Coonley, and Carlson are with Communication Arts and Services (IM-1).