Dealing with a Dangerous Surplus from the Cold War

The proliferation of nuclear materials is a threat to national security and world peace. This threat complicates the safeguarding and management of fissile materials that have become surplus since the end of the Cold War.

TEARING down the Berlin Wall in 1989 symbolized the end of the Cold War. However, the real work of ending the Cold War—sharply reducing the number of nuclear weapons—remains to be done.

The governments of the United States and Russia have taken the first steps toward nuclear arms reduction by negotiating the Strategic Arms Reduction Treaties. Under START I, which was ratified in 1991, both countries agreed to reduce their large nuclear weapons arsenals to approximately 6,000 warheads and have already begun to do so by dismantling between 1,300 to 2,000 weapons each year. START II, when it is ratified, will reduce the numbers further to between 3,000 and 3,500.

The dismantling of weapons and the cessation of new nuclear weapons manufacturing, while positive for world peace, have raised a problem: what to do about the fissile materials recovered from the weapons or in inventories that will remain unused. These materials—primarily plutonium and highly enriched uranium—are environmental, safety, and health concerns. But of more urgency is the threat they pose to national and international security if they fall into the hands of terrorists or rogue nations. As arms reduction continues and amounts of surplus fissile materials increase, the potential for such security breaches will increase.

As part of bilateral nuclear nonproliferation work, both the U.S. and Russia have initiated scientific studies to find a way to dispose of surplus fissile materials. In the U.S., the Department of Energy is the technical lead for the disposition studies, acting as a member of the Interagency Working Group of the White House Office of Science and Technology. In this capacity, DOE has mandated separate studies for disposing of plutonium and highly enriched uranium, because of their different chemical characteristics. Lawrence Livermore is focusing primarily on the study of plutonium disposition.

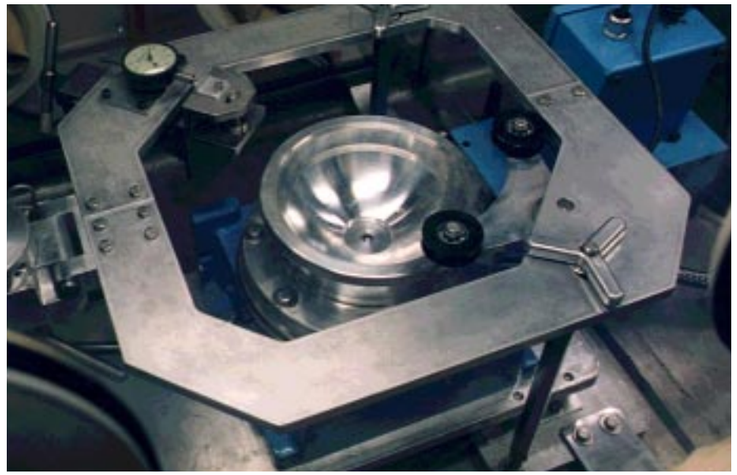

Figure 1. The prototype bisector was designed and tested at Livermore. Using a chipless cutting wheel, it can separate weapon pits into two half-shells in less than 30 minutes so that the plutonium in them can be recovered for disposition.

Plutonium Disposition

After a series of studies, including technical work for a preliminary environmental impact study, DOE selected three reasonable plutonium disposition alternatives for further study: using plutonium as reactor fuel; encasing it in other material, thereby immobilizing it and making it inaccessible; and burying it in a deep borehole.

Lawrence Livermore is involved in studying the front-end processes required to prepare plutonium for disposition and is performing research and development on two of the three specific disposition methods to determine their viability. Specifically, Lawrence Livermore is working with Los Alamos National Laboratory on a system for disassembling weapon pits (or cores, where detonation takes place), recovering the plutonium in them, and converting it into a disposable form. Livermore has also led the two teams studying the immobilization alternative and the deep burial alternative. Oak Ridge National Laboratory is studying the reactor-fuel alternative.

The *Programmatic Environmental Impact Statement* for plutonium disposition was published in December 1996. In January 1997, DOE announced its Record of Decision on plutonium disposition, recommending a dual disposition path: immobilize low-grade plutonium materials and use high-grade plutonium materials to fuel reactors. The alternative of burying surplus plutonium in a deep borehole ran into siting and licensing difficulties and was eliminated from consideration, despite the fact that Livermore studies proved it to be as technically feasible as the other two alternatives.

Recovery and Conversion

Lawrence Livermore and Los Alamos are designing a plutonium recovery and conversion system, the Advanced Recovery and Integrated Extraction System (ARIES). ARIES has five modules, which are used for: pit disassembly, converting plutonium into an oxide (for disposition), converting plutonium into a metal (for long-term storage), packaging plutonium for storage, and performing nondestructive assay to account for plutonium quantities. Lawrence Livermore is focusing on the first two modules.

Pit Disassembly

The pit disassembly, ARIES' first module, consists of a glovebox in which the weapon pit is received; remote handling devices that transfer pits onto a scale for weighing and then move them on to be inspected and have any appurtenant devices removed; and a bisector (Figure 1) that separates the pit into two half-shells by using a chipless cutting wheel. The bisector framework remains stationary while the pit is rotated.

The bisector design takes into account the dimensions, encapsulation methods, construction materials, and manufacturing techniques of these pits in order to incorporate the representative configurations that will be processed through ARIES. It also calls for a "no-hands-on" process to keep radiation exposures to the operator within acceptable limits.

Bisector improvements are being made and will be tested during 1997.

Producing Plutonium Oxide

To be suitable for most of the disposition methods, plutonium must first be converted into plutonium oxide, the job of ARIES's second module. Lawrence Livermore has been developing pyrochemical techniques to accomplish this conversion using various hydride/oxidation (HYDOX) reactions. Three such processes are being researched, all based on reactions in which pure hydrogen gas is used to remove plutonium from a pit by forming a plutonium hydride. The formation of the hydride causes the plutonium to break up into small particles and separate from the other pit materials. The plutonium hydride is collected and then converted to plutonium oxide either directly or after conversion to plutonium nitride.

The experiments on the HYDOX processes seek to minimize production cycle times and maintain safety while producing oxide particles to the required disposition specifications, particularly the more stringent specifications for oxide fuels used in reactors.

A prototype HYDOX furnace has been designed, assembled, and installed and is being used to test the various process options. An additional unit (Figure 2) is being assembled in a glovebox and will be installed and operated at Los Alamos as part of the ARIES demonstration.

The Spent Fuel Standard

Because most nations and even some terrorist groups are technically capable of converting surplus plutonium into nuclear weapons, the ideal disposition method eliminates the possibility of surplus plutonium being used for weapons. If a disposition method is not available within a reasonable time frame, the growing volume of plutonium surplus will make proliferation easier and render arms-reduction agreements meaningless.

Because total elimination is not a practical objective, a National Academy of Sciences study, commissioned by DOE's Office of Nuclear Energy, proposed the next best thing: minimized accessibility. Dubbed the "spent fuel standard" and accepted as the goal of plutonium disposition efforts by the U.S., Russia, and the seven other stakeholder nations, it defines "minimized accessibility" as equivalent to the accessibility of the plutonium found in spent reactor fuel. The spent fuel standard is a reasonable goal because the technology to accomplish it appears achievable within 10 years and implementation can be completed within 25 years. It is also a practical goal because, by definition, it excludes spent fuel plutonium—which comprises the larger part of the surpluses—from disposition and concentrates on weapons-grade plutonium.

Figure 2. To be suitable for most disposition methods, the excess weapons plutonium must first be converted into plutonium oxide by various hydride/oxidation (HYDOX) methods. The prototype HYDOX furnace design originated at Livermore and has been used to test various HYDOX process options. Livermore technicians William Kuhl (left) and Terry Ludlow assemble a HYDOX furnace in a glovebox. The unit will be used for further testing at Los Alamos National Laboratory.

The Immobilization Task

Lawrence Livermore is researching plutonium immobilization with the Savannah River Technology Center, Argonne National Laboratory, and Pacific Northwest National Laboratory. Several U.S. universities and private industries are also partners, as are several other nations (including Australia, the United Kingdom, France, and Russia) with interest and experience in immobilization.

Immobilization technology achieves the spent fuel standard by encapsulating plutonium inside a waste form specifically tailored for this function, adding a radiological barrier to increase inaccessibility to the plutonium, and sealing the resulting material inside a stainless-steel canister. Like spent reactor fuel, these canisters would be stored for an interim period before being placed inside a geologic repository. The size, weight, composition, and radiation barrier of the filled canister are intended to make the plutonium in it roughly as difficult to steal and recover as the plutonium in spent fuel.

Before the immobilization alternative can be fully developed and implemented, three decisions need to be made:

- What waste form is to be used for encapsulating the plutonium and what technology is to be used for encapsulation?
- Is the radiological barrier to be internal, that is, mixed with the plutonium, or external, in a separate container that surrounds the plutonium container?
- Where will the plutonium immobilization take place?

Immobilization Options

A great deal of information about stabilizing radioactive material by embedding it in another material has been published. An extensive literature search identified 45 forms considered previously for immobilizing radioactive waste.

These 45 forms were subjected to a formal, two-step screening process to derive top candidates for comprehensive technical evaluation. The two top-ranking forms were borosilicate glass and Synroc (synthetic rock), a ceramic material developed by scientists at the Australian National University, Lawrence Livermore, and Savannah River.

The glass and ceramic forms were evaluated in five variations of the immobilization process to look at various permutations of forms, radiological barrier concepts, and facilities in which the work could be done. As in all other disposition methods, the plutonium must first be converted into an oxide, and then a neutron absorber mixed with it for criticality control.

Three Glass Variations

Variation 1: Internal Radiation Barrier. In this two-stage process, plutonium oxide reacts with glass frit containing a neutron absorber to prepare a plutonium–neutron-absorber–glass frit (Figure 3a). First, 4 kilograms or less of plutonium as plutonium oxide are combined with neutron absorber and glass frit to form plutonium–glass frit.

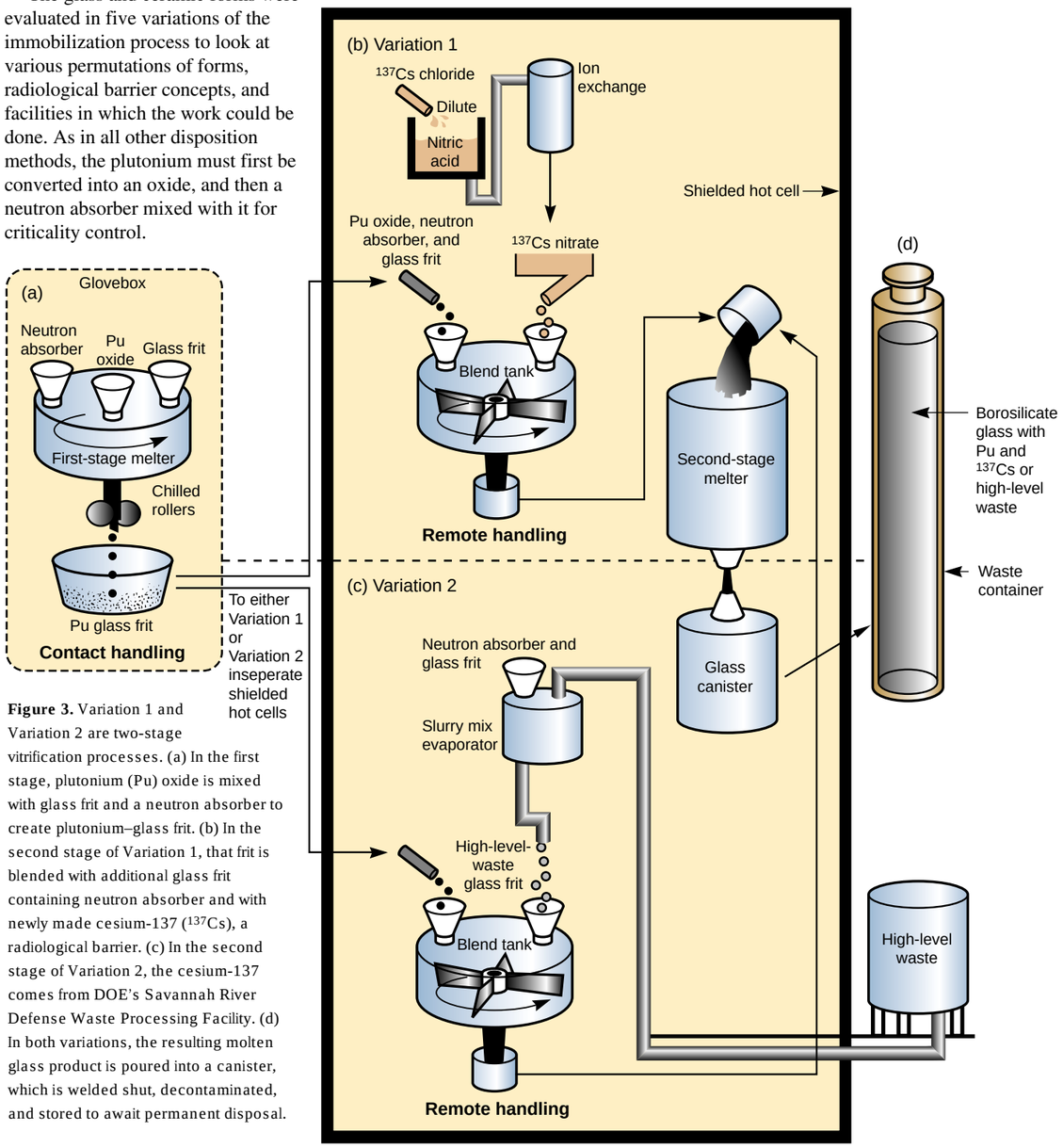

Figure 3. Variation 1 and Variation 2 are two-stage vitrification processes. (a) In the first stage, plutonium (Pu) oxide is mixed with glass frit and a neutron absorber to create plutonium–glass frit. (b) In the second stage of Variation 1, that frit is blended with additional glass frit containing neutron absorber and with newly made cesium-137 (^{137}Cs), a radiological barrier. (c) In the second stage of Variation 2, the cesium-137 comes from DOE's Savannah River Defense Waste Processing Facility. (d) In both variations, the resulting molten glass product is poured into a canister, which is welded shut, decontaminated, and stored to await permanent disposal.

The second step (Figure 3b) blends batches of 50 kilograms or less of plutonium as plutonium–glass frit with additional neutron-absorber-containing glass frit and cesium-137, where the cesium is used as a radiological barrier. The resulting molten glass product is poured into a canister, which is welded shut, decontaminated, and stored until permanent disposal in a high-level waste repository (Figure 3d).

Variation 2: Internal Radiation Barrier. This two-stage process is similar to Variation 1 but would use existing, modified facilities. The first-stage melt of plutonium oxide and borosilicate frit (containing a neutron absorber) is made in an existing facility at Savannah River, and the second-stage melt (Figure 3c), which incorporates the cesium radiological barrier, will be done at a new melter to be built next to Savannah River's Defense Waste Processing Facility. The high-level-waste fission product cesium-137 will come from the Savannah River tank farms.

Variation 3: External Radiation Barrier. This is a "can-in-canister" concept in which plutonium is immobilized in borosilicate glass that contains a neutron absorber. Then the mixture is poured into cans, which are in turn placed in canisters into which molten high-level-waste glass is poured (Figure 4). The high-level-waste glass comes from the Defense Waste Processing Facility at Savannah River.

Two Ceramic Variations

Variation 4: Internal Radiation Barrier. Plutonium oxide is first converted to plutonium nitrate and then blended with mineral-forming oxides (ceramic precursors), a neutron absorber, and a titanate that contains cesium. The mixture is calcined (heated but not fused), loaded into bellows, and hot pressed into a dense form (Figure 5). Twenty of these forms are loaded into a canister and packed with titanium oxide granules. The canisters are stored until they can be sent to a high-level-waste repository.

Variation 5: External Radiation Barrier. This is a can-in-canister approach similar to Variation 3. The ceramic form is made by blending plutonium oxide with ceramic precursor materials and a neutron absorber. The mixture is calcined, cold pressed, and sintered (heated but not melted) into a dense form that is loaded into small cans. The small cans are put inside a storage canister, where they are surrounded by glass made with high-level waste (Figure 6).

Progress Report

For the five process variations, the task team developed process flowsheets and preconceptual plant designs; gathered the required environmental data; and determined the workforce, cost, and schedule requirements for implementing them.

At the end of these tasks, the team recommended the can-in-canister concept to DOE and has proceeded to the research and development stage to determine whether glass or ceramic should be the immobilization form. Research on vitrification forms is being done with Savannah River, Pacific Northwest, and Argonne laboratories,

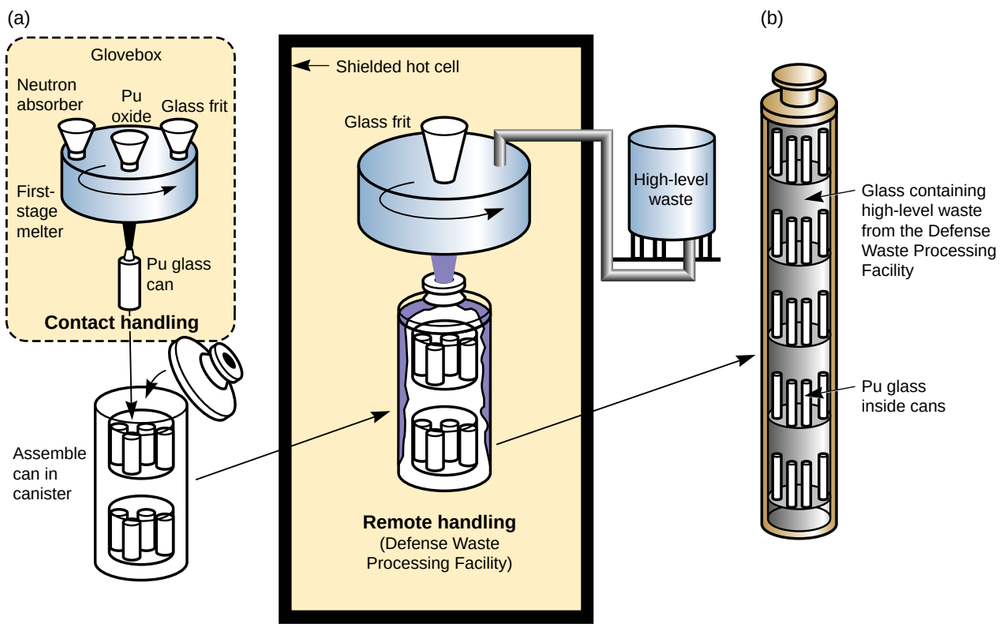

Figure 4. (a) Vitrification Variation 3 is a "can-in-canister" concept in which plutonium (Pu) immobilized in borosilicate glass is poured into a can, which is then placed in (b) canisters into which molten high-level-waste glass from the Defense Waste Processing Facility at Savannah River is poured. The outer canister provides an external radiation barrier.

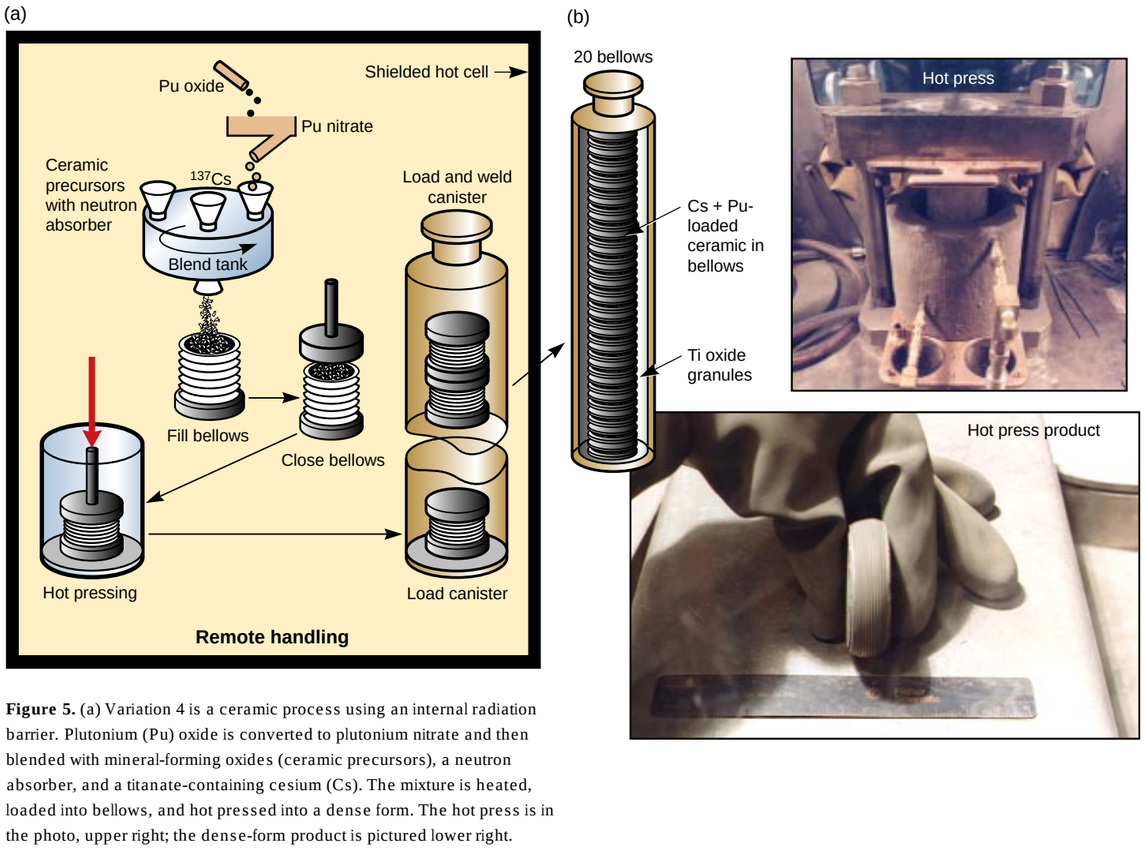

Figure 5. (a) Variation 4 is a ceramic process using an internal radiation barrier. Plutonium (Pu) oxide is converted to plutonium nitrate and then blended with mineral-forming oxides (ceramic precursors), a neutron absorber, and a titanate-containing cesium (Cs). The mixture is heated, loaded into bellows, and hot pressed into a dense form. The hot press is in the photo, upper right; the dense-form product is pictured lower right. Twenty of these products will be loaded into (b) a canister, packed with titanium (Ti) oxide granules, and sent, ultimately, to a permanent high-level-waste repository.

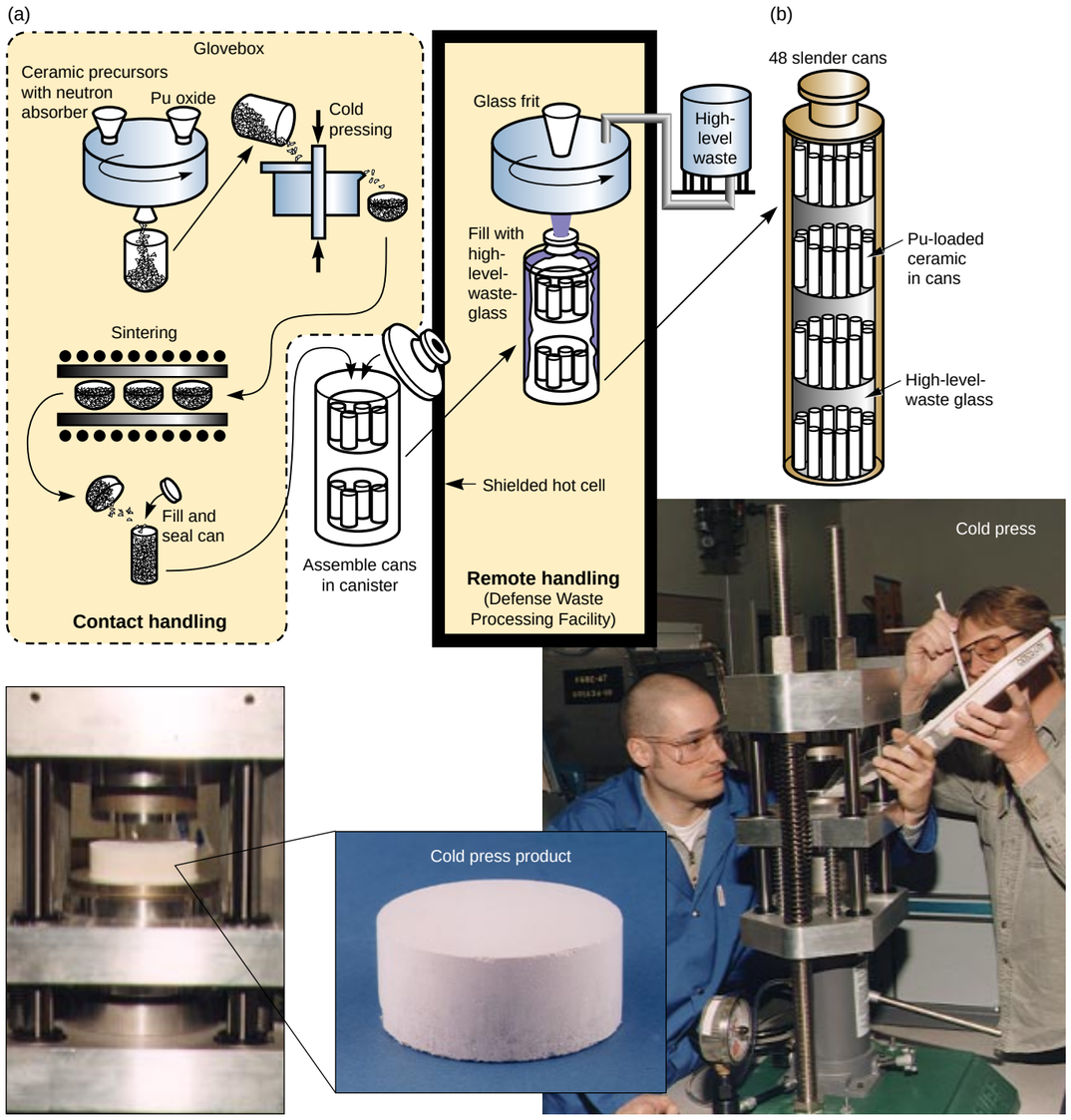

Figure 6. (a) Variation 5 is also a ceramic process, but it involves a "can-in-canister" (or external-radiation-barrier) approach like Variation 3. The ceramic form is made by blending plutonium (Pu) oxide with ceramic precursors and a neutron absorber. The mixture is heated, cold pressed, and sintered (heated but not melted) into a dense form. The cold press is in the photo, lower right; the dense-form product is pictured lower left. The ceramic product is loaded into small cans, which are put inside (b) a storage canister and surrounded by glass made with high-level waste.

while the Australian Nuclear Science and Technology Organisation (ANSTO) and Savannah River are Lawrence Livermore's partners in ceramic form research.

Desirable Glasses

All the ways to use glass to immobilize plutonium require further research into improving the solubility of plutonium in the glass melts, determining the most effective neutron absorber, understanding solubility interactions between the neutron absorber and plutonium, and analyzing how impurities affect the quality of the waste form. Glass-forming chemicals must be formulated to dissolve the greatest amounts of plutonium oxide, neutron absorber, and any uranium and other impurities present. Moreover, these chemicals should have the best processability and chemical durability characteristics. Finally, to prevent leaching, the glass product they form should ideally be homogeneous, with no separated crystalline or amorphous phases.

Two new candidate glasses have been formulated. The first, an alkali-tin-silicate (ATS) glass formulated at Argonne National Laboratory, was to be used in the process in which cesium would be an internal radiation barrier. However, because the preferred immobilization process appears to be the can-in-canister concept, work on this glass stopped.

A second glass formula, proposed for use in the can-in-canister process variation and now the preferred formulation for vitrification, produces glass similar to commercial Löffler optical glasses that contain 55% by weight or less of rare-earth oxides. (Because this glass requires a very high operating temperature, highly volatile cesium cannot be used as an internal radiation barrier.) The chemistries of actinides (the chemical family of plutonium) and rare-earth elements are similar, so the solubility of plutonium is expected to be comparably high in this formulation. In the latest experiments, this glass has dissolved greater than 10% by weight of plutonium. Now it is being optimized and further characterized for plutonium solubility, the influence of required additives such as the neutron absorber, tolerance to process variations, processability, resistance to radiation damage, and long-term chemical durability.

Ceramic Forms and Processes

Since the late 1970s, ceramic waste forms have been considered for use in immobilizing high-level waste. But no industrial experience base exists for this technology, so it is not as mature a technology as the borosilicate glass forms.

Like glass, ceramic forms must be characterized for plutonium solubility, the influence of required additives such as a neutron absorber, tolerance to process variations, processability, resistance to radiation damage, and long-term chemical durability.

The most advanced ceramic formulation to date is Synroc. ANSTO initiated development of Synroc in 1978 and completed a demonstration plant in 1987 that operated at a commercial scale of approximately 10 kilograms per hour and produced more than 6,000 kilograms of Synroc.

Fabrication processes for ceramic forms also determine how much plutonium may be incorporated into the forms. The best demonstrated process for ceramic fabrication, especially ceramic with an internal radiation barrier, is hot pressing. The process has been demonstrated full-scale with high-level-waste surrogates, but only on a laboratory scale with plutonium. At Livermore, a hot press capable of producing about 0.5-kilogram ceramic in a 7.5-centimeter-diameter bellows has been built and installed and has produced ceramic product containing about 60 grams of plutonium.

Repository Performance

An immobilization form is judged acceptable for disposal in a federal geologic repository according to a fitness-for-purpose criterion that includes regulatory, licensing, and long-term performance factors. The main long-term, post-emplacement performance considerations are criticality safety and the potential of the form to contaminate the biosphere. In the U.S., the regulatory performance period for high-level waste and spent fuel in a geologic repository has been specified as 10,000 years. (The pertinent regulations are currently under review and may change.) However, the emplaced plutonium and its uranium-235 decay product remain fissile over much longer periods (hundreds of thousands of years for plutonium and billions of years for uranium-235), over which criticality safety may need to be assured.

Scenarios for criticality events can be divided into three categories of criticality safety: safety of the essentially undisturbed emplacement waste package, safety of disrupted waste packages, and safety of disposed fissile materials released from the disposal form followed by possible transport within the repository or in the geosphere. In general, the criticality safety of the first category of scenarios can be assured with very high confidence, but assuring the safety of the latter two categories is more difficult and will depend on such factors as the fissile material content of the disposal form, canisters, and waste package; the geometry of the disrupted configuration; and the degree of degradation of the disposal form and its interactions with surrounding rock and water.

Notwithstanding the complexity of the problem, key properties of disposal forms that affect criticality safety have been identified. They are fissile loading of disposal forms, concentration of the neutron absorber, and neutron absorption properties of the immobilization matrix. Other factors are resistance of disposal form constituents to release and transport by groundwater and the rates and relative timing of releases of different components. Characteristics of elemental release from disposal forms may be very different for different disposal forms (especially glass and ceramic) and are affected by compositions of water and disposal form, solubility of the constituents, active surface areas available for reaction with water, compositional and thermal stability of disposal forms, physical and chemical homogeneity of disposal forms, and radiation effects (damage in disposal form and radiolysis in water). Researchers are particularly concerned about the susceptibility of the disposal form to cracking during fabrication and after emplacement and to the development of permeable channels within the disposal form caused by preferential dissolution of certain phases or along grain boundaries.

Lawrence Livermore and its partners are providing needed information for DOE's final immobilization technology decision, expected by September 1997. By then, they will have defined formulations for the glass and ceramic immobilization forms, characterized them for proliferation resistance and performance in the geologic repository, and developed the information needed to evaluate concepts for production processes.

Leonard Gray, the chief scientist for Lawrence Livermore's Excess Fissile Materials Disposition Program, with a prototype stainless-steel canister, which is 3 meters (10 feet) tall and 60 centimeters (24 inches) in diameter and weighs 1,680 kilograms (about 2 tons).

Science to End Cold War

The surplus weapons plutonium disposition program is but one of several programs to help implement political agreements and maintain safeguards and security for the nation. In light of the complexity of the disposition program, both in terms of scope and required scientific expertise, declaring the Cold War over was simpler than implementing its end. At Lawrence Livermore, scientific progress is being made to contribute to that end.

—Gloria Wilt

Key Words: ceramics, deep boreholes, fissile materials, immobilization, nuclear waste repository, plutonium disposition, plutonium oxide processes, spent fuel standard, Synroc, vitrification, waste forms, weapon pits.

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About the Livermore Team

Members of Livermore's Fissile Materials Disposition Program team (clockwise from lower left): MARK BRONSON holds a B.S. in metallurgical engineering and an M.S. in metallurgy from the University of Utah. In addition to being leader of the defense-related projects in the Isotope Separation and Advanced Manufacturing Program at Livermore, he leads the plutonium pyrochemistry work of the Fissile Materials Disposition Program. Particular accomplishments are development of the pit splitter for recovering excess plutonium from the cores of nuclear weapons and the hydride/oxidation process that converts plutonium to plutonium oxide prior to immobilization. He came to the Laboratory in 1988 by way of DOE's Rocky Flats facility in Colorado, where he concentrated on research and development in the field of plutonium pyrochemical technology.

BARTLEY EBBINGHAUS joined the Laboratory in 1991 after earning his doctorate in chemistry at the University of California, Berkeley. He is currently task leader for Livermore's ceramic immobilization work on DOE's Fissile Materials Disposition Program. He co-designed the formula and fabrication process for the proposed ceramic form (a variation of a material called Synroc) that is able to incorporate and immobilize excess plutonium. He has also demonstrated the successful preparation of a large plutonium-bearing ceramic pellet that meets preliminary design expectations.

GUY ARMANTROUT joined the Laboratory in 1965. He holds a doctorate in electrical engineering and physics from Purdue University. He is a project leader in the Fissile Materials Disposition Program responsible for the development and demonstration of production-scale processing systems for the immobilization of plutonium in glass and ceramic in preparation for disposal in a geologic repository.

LEONARD GRAY (Ph.D., University of South Carolina) has been a part of DOE's Fissile Materials Disposition Program since its inception in 1990, when he was asked to organize and lead an international team responsible for developing the immobilization portion of the program. After a 20-year career as a staff chemist at DOE's Savannah River Site, he joined the Laboratory in 1988 as a section leader for plutonium process development in the Special Isotope Separation Program. He is currently chief scientist for Livermore's contributions to the Fissile Materials Disposition Program.

Abstract

Dealing with a Dangerous Surplus from the Cold War

In the aftermath of the Cold War, the management of surplus fissile materials has become an urgent task with profound environmental, national, and international security implications. Lawrence Livermore is a key player in a study launched by the Department of Energy to find a way to dispose of surplus weapons plutonium. The Laboratory's work consists of engineering to retrieve plutonium from nuclear weapon pits and to process it into a form usable for disposition as well as research and development for two disposition methods—immobilization by a ceramic or glass waste form and burial in deep geologic boreholes. DOE recently selected immobilization as one method of the dual disposition path it will implement for plutonium. Lawrence Livermore's work continues with research in ceramic and glass formulations to provide a scientific basis for DOE's decision on the method for immobilizing plutonium.

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