CONF-950401--31

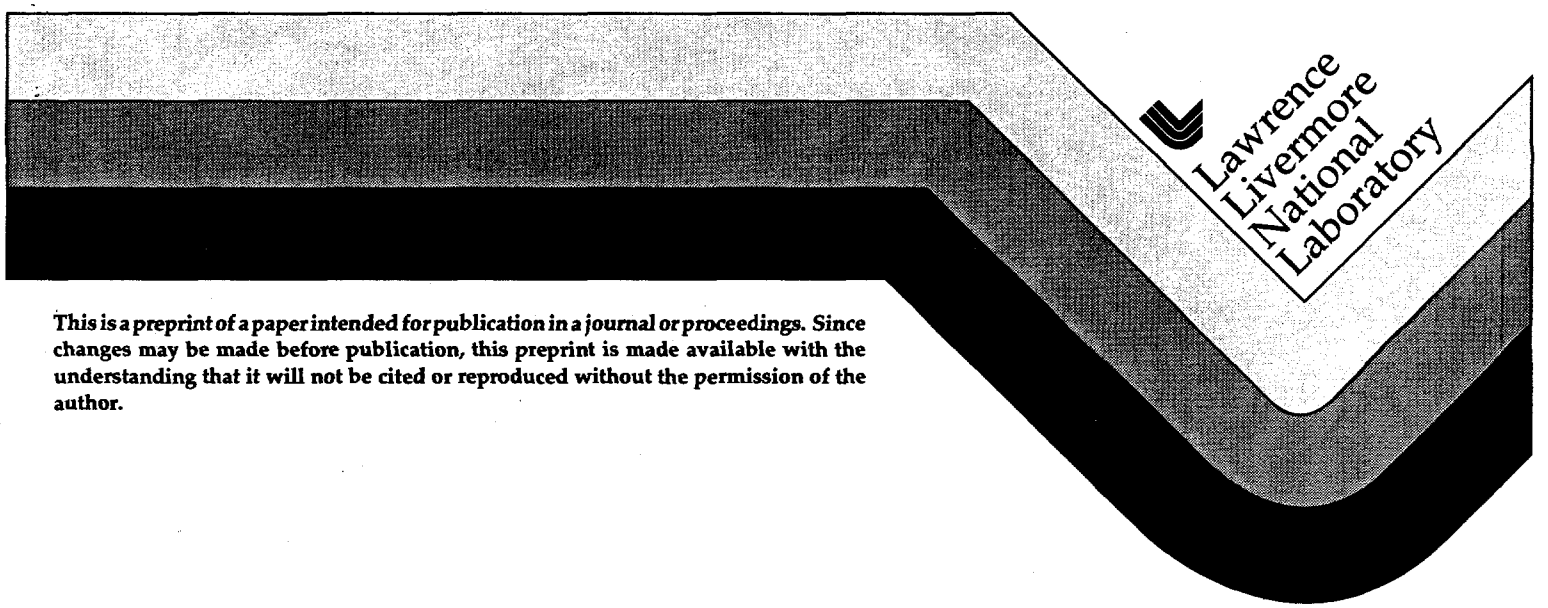
UCRL-JC-118846
PREPRINT

Immobilization as a Route to Surplus Fissile Materials Disposition

L. W. Gray
T. Kan

This paper was prepared for submittal to the
International Symposium on the Environmental Issues & Waste Management Technologies in Ceramic and Nuclear Industry
Cincinnati, Ohio
April 30-May 5, 1995

April 27, 1995



DISCLAIMER

IMMOBILIZATION AS A ROUTE TO SURPLUS FISSILE MATERIALS DISPOSITION

Leonard W. Gray and Tehmau Kan, Lawrence Livermore National Laboratory, Livermore, CA

In the aftermath of the Cold War, the U. S. and Russia have agreed to large reductions in nuclear weapons. To aid in the selection of long-term management options, DOE has undertaken a multifaceted study to select options for storage and disposition of plutonium (Pu) in keeping with the national policy that Pu must be subjected to the highest standards of safety, security, and accountability. One alternative being considered is immobilization. To arrive at a suitable immobilization form, we first reviewed published information on high-level waste (HLW) immobilization technologies in order to identify 72 possible Pu immobilization forms to be prescreened. Surviving forms were screened using multiattribute analysis to determine the most promising technologies. Promising immobilization families were further evaluated to identify chemical, engineering, environmental, safety, and health problems that remain to be solved prior to making technical decisions as to the viability of using the form for long-term disposition of plutonium. All data, analyses, and reports are being provided to the DOE Fissile Materials Disposition Project Office to support the Record of Decision that is anticipated in the fourth quarter of FY96.

INTRODUCTION

With the Cold War over, we have an opportunity to dismantle thousands of nuclear weapons. Nuclear powers are now faced with management of tonnes of Pu outside of national security needs. If agreed reductions are implemented, perhaps 100 metric tonnes (MT) of Pu will no longer be needed for military purposes. Although disarmament offers hope for improving world security, disposition of surplus fissile materials (FM), especially plutonium (Pu) used in nuclear weapons, may also have significant international security implications. The U.S. Department of Energy (DOE) has undertaken a multifaceted study to select options for storage and disposition in keeping with the national policy that excess Pu must be subjected to the highest standards of safety, security, and international accountability. Disposition is defined as a process of use or disposal of materials that results in the remaining material being converted to a form substantially and inherently more proliferation-resistant than the original form. Disposition options must take into account technical, nonproliferation, environmental, and economic considerations. As a part of the overall disposition program, Russia and other nations with relevant interests and experience will be invited to participate in the overall disposition study.

The disposition process (Fig. 1) can be divided into three distinct but overlapping phases—dismantling, intermediate storage, and long-term disposition. Dismantling of U.S. and Former Soviet Union (FSU) weapons and storing FM are already under way. Conversion of residue materials and long-term disposition of all the FM will take far longer to accomplish.

One disposition alternative considered for Pu is immobilization. In support of the DOE Materials Disposition (MD) Project Office's Programmatic Environmental Impact Statement (PEIS) for Disposition of Pu, Lawrence Livermore National Laboratory was selected as Lead Laboratory to study and recommend methods for transforming Pu into long-term immobilized forms meeting environmental, safety, and security objectives; to provide appropriate input to

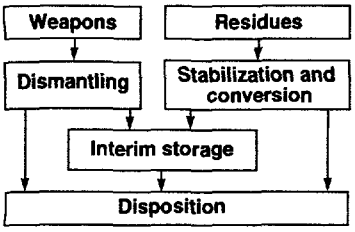


Figure 1. Steps in control and disposition of surplus FM.

other Disposition Tasks Teams so as to assess technical feasibility of immobilization as a long-term disposition option; and describe infrastructures required to dispose of Pu.

Support laboratories include Westinghouse Savannah River Technology Center, Argonne National Laboratory, Oak Ridge National Laboratory, Pacific Northwest Laboratory, Rocky Flats Environmental Technology Site, and Westinghouse Hanford Company.

Immobilization would embed Pu in a tailored ceramic, borosilicate glass, or other suitable material, alone or mixed with radioactive fission products to produce a suitable disposal form. To be viable, the Pu concentration of the form must be in the 0.4 to 10 wt% range. To arrive at suitable forms, published information on HLW immobilization technologies was reviewed; 72 uniquely named forms were identified. After prescreening, surviving forms were screened using multiattribute utility analysis to determine the more promising technologies. Promising immobilization families (glass, ceramics and metals) were further evaluated to identify and seek solutions for chemical, engineering, environmental, safety, and health (ES&H) problems remaining to be solved prior to making technical decisions as to their viability for long-term disposition of Pu. We are also assessing modifications required to existing U.S. high-level waste immobilization approaches, ES&H implications, costs, and schedule. All data, analyses, and reports are being provided to the DOE/MD to support the Record of Decision that is anticipated in the fourth quarter of FY96.

SPENT FUEL STANDARD

An important consideration in evaluating disposition options for surplus Pu is the "spent fuel standard." This term, which was coined by the U.S. National Academy of Sciences (NAS), is described as follows: ". . . disposition of weapons Pu should seek to meet a 'spent fuel standard'—that is, to make this Pu roughly as inaccessible for weapons use as the much larger and growing quantity of Pu that exists in spent fuel from commercial reactors."

The standard consists of four parts: radiological, physical, chemical, and nuclear properties. Three characteristics directly influence requirements, regulations, and practices for applications of domestic and international safeguards and security; therefore, these characteristic must be met to satisfy the standard. Pu isotopic composition has only secondary effects. This topic is discussed in more detail elsewhere.[1]

SELECTION OF WASTE FORMS FOR IMMOBILIZING PU

A literature search identified 72 waste forms[2] by unique names (but only 45 unique forms) that have been considered for immobilizing radioactive wastes. Individual forms can be grouped into families that share common chemical and physical characteristics: (1) calcine, (2) cementitious, (3) ceramic, (4) glasses, (5) glass-ceramic, (6) metallic, (7) multibarrier, and (8) polymeric. Distinct waste forms are distinguished by unique physical and chemical properties. A screening process was implemented to select the best waste forms for the plutonium disposition application. A more detailed discussion of the screening process is given elsewhere,[3] but the following sections summarizes the process.

A two-stage approach (Fig. 2), based on decision analysis techniques, was adopted for screening. This allowed the use of more rigorous selection techniques as options became more closely matched. Stage 1 applied limited criteria to a large number of forms; this

quickly removed forms that were clearly inappropriate for Pu immobilization. Stage 2 more closely evaluated remaining forms with the goal of selecting a small set (<3) of the best forms. This involved a more formal comparison of waste form characteristics using multiattribute utility analysis techniques from decision analysis principles.

The results for individual and combined technical assessments, and value and tradeoff assessments, are shown in Table I. "Utility" is the overall figure of merit for a form.

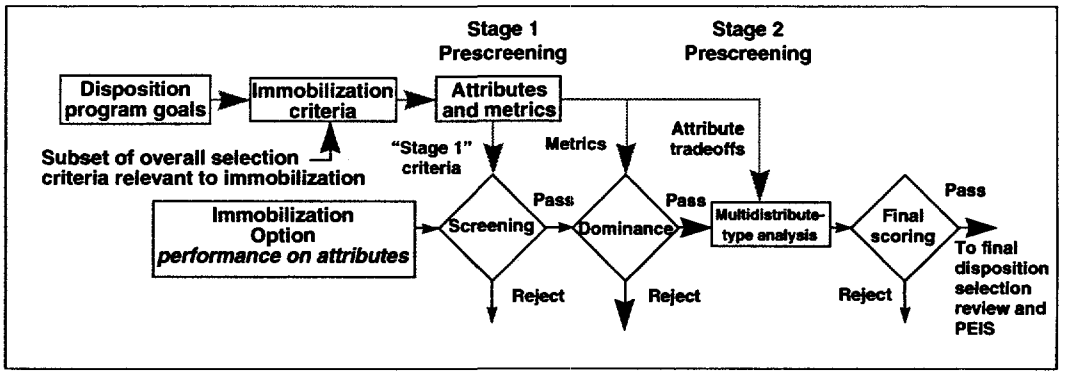


Figure 2. Pu immobilization prescreening process.

Table I. Ranking of forms according to weightings and utility curves.

Form	Utility
Borosilicate glass	0.89
Synroc	0.66
Phosphate glass	0.55
Monazite	0.49
Metallic alloy	0.47
High-silica glass	0.44
FUETAP concrete	0.40
Hot-pressed concrete	0.25
Phosphate-bonded ceramic	0.17
Silicon-zirconium phosph.	0.17
Ceramics in concrete	0.13
Iron-enriched basal	0.13
Ceramic pellets in metal	0.13
Supercalcine	0.08
Glass-ceramic monoliths	0.03
Cermet	0

IMMOBILIZATION OPTIONS

Seven immobilization options comprising three technologies are being evaluated in the PEIS process:

- Vitrification
  - Internal radiation barrier
  - External radiation barrier
  - Glass Materiel Oxidation and Dissolution System (GMODS)
- Ceramics
  - Internal radiation Barrier
  - External radiation Barrier
- Electrometallurgical Treatment.

Vitrification

Vitrification of Pu as borosilicate glass is a technically viable immobilization option. Its technical basis derives from nearly 40 years of international development and decades of commercial production of this type of glass for the stabilization of HLW. Borosilicate glass is internationally accepted as the waste form for HLW.[3] Vitrification of HLW and low-level radioactive wastes (LLW) is becoming commonplace worldwide. Preliminary work has shown that Pu can be immobilized in this fashion and that Pu glass can be developed into a relatively safe, durable, accountable, and monitorable form.[4–7]

Internal Radiation Barrier: This vitrification option immobilizes Pu in a borosilicate glass. The product of the vitrification facility is a homogeneous glass monolith (Fig. 3a) within a DWPF type canister. The glass contains both the Pu and the ^{137}Cs or other radiation source uniformly distributed in the glass matrix.

External Radiation Barrier: This immobilization alternative vitrifies Pu in glass. The plutonium-glass is poured into small stainless-steel cans, seal-welded, and placed into interim storage. The small Pu-glass cans are then inserted into standard Defense Waste Processing Facility (DWPF)-type waste canisters, and borosilicate glass containing HLW is poured around the cans to form a radiation barrier (Fig. 3b) Since the plutonium-bearing glass does not have to incorporate the volatile cesium, higher-temperature (more-durable) glass compositions can be used to immobilize the plutonium.

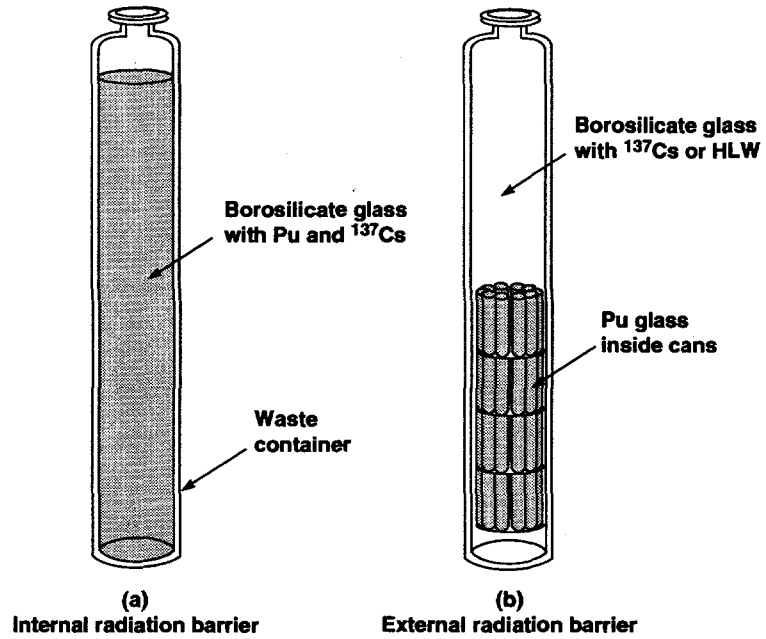


Figure 3. Two options for vitrification of Pu.

GMODS: The GMODS process[8] immobilizes FM into a Pu, low-enriched uranium (LEU), HLW, borosilicate glass. The process involves two steps: (1) Convert FM to an intermediate glass containing the FM without addition of other radioactive materials; (2) Convert the intermediate glass and miscellaneous spent nuclear fuel (SNF) and other highly radioactive

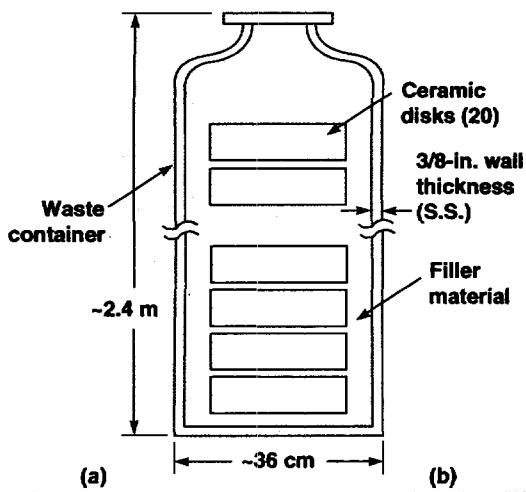
materials into a Pu, LEU, HLW, borosilicate glass. The final HLW glass will meet both the requirements for surplus fissile materials disposition and repository waste acceptance.

Ceramics

Small-scale demonstrations have shown that a high concentration of actinides can be incorporated into an extraordinarily stable and leach-resistant ceramic commonly referred to as Synthetic Rock (Synroc).[9,10] These ceramics were developed specifically for immobilizing HLW created from processing SNF. Various different formulations have been tested, depending upon the maturity of the technology and the composition of the waste to be immobilized. Although variations exist, a primary component is always TiO_2, which is a refractory oxide and is extremely resistant to dissolution, thus providing the basis for a good waste form. The specific formulation that is most likely to be suitable for disposition of surplus FM is Synroc-C, a mixture of zirconolite ($CaZrTi_2O_7$), perovskite ($CaTiO_3$), hollandite ($BaAl_2Ti_6O_{16}$), and rutile (TiO_2). Zirconolite and perovskite will immobilize actinides, and hollandite will immobilize radioactive cesium, which is added as a radiation barrier to proliferation.

Internal Radiation Barrier: This immobilization option incorporates Pu in a titanate ceramic. The product is an assembly of homogeneous ceramic disks within a metal canister (Fig. 4a). The ceramic contains both the Pu and ^{137}Cs or other radiation source distributed in the ceramic matrix.

External Radiation Barrier: This immobilization option incorporates Pu in a titanate ceramic. The product is an assembly of homogeneous ceramic disks within a metal canister Fig. 4b). The ceramic disks contains Pu only. The ^{137}Cs or other radiation source is incorporated into a separate ceramic medium that fills the void between the ceramic disks and the product canister (Fig. 4b)



	Internal radiation barrier	External radiation barrier
Ceramic	Ceramic with Pu and ^{137}Cs	Ceramic with Pu
Filler	Inert material (TiO_2 powder)	Solidified $Na_2Ti_3O_7$ with ^{137}Cs

Figure 4. Two options for immobilizing Pu in a ceramic.

Electrometallurgical Treatment

The electrometallurgical treatment process immobilizes Pu in a metal or a mineral waste form that is denatured with fission products, primarily ^{137}Cs. The mineral form is derived by converting a zeolite containing fission products and TRU elements to a leach-resistant monolith in which the fission products and actinides are contained in stable, naturally occurring minerals. This mineral form is similar to the foregoing ceramic form and is referred to here as the "mineral waste form" to distinguish it from the ceramic form. The metal form is a Zr-Fe alloy containing up to 10 wt% actinides; alloys with either high zirconium or high iron content are being considered. Pellets of the mineral waste form containing cesium and other fission products are placed in cavities cast in the metal waste form ingot.

The processes involved in two immobilization technologies; vitrification and ceramics are reviewed in more detail below.

GLASS AND CERAMIC IMMOBILIZATION TECHNOLOGIES

Vitrification of Plutonium in Borosilicate Glass

Various processes and equipment are in worldwide commercial use, producing borosilicate glass for a variety of large- and small-scale commercial applications, both with and without radioactive elements. These technologies could be adapted to produce Pu borosilicate glass. Although there are many differences among these applications and the associated equipment (including feed compositions, melter designs, scale of equipment, and heating methods), the basic compositions and properties of the final glass products are similar. Heating methods in common use include joule, radiant energy, induction, microwave, and plasma heating. The choice of heating method depends on the particular application, the scale of the equipment, feed composition, final form requirements, and other considerations.

The most thoroughly demonstrated process for HLW vitrification is the one developed in France at Marcoule,[11] which is being used, with minor alterations, in the United Kingdom, France (LaHauge), and Japan. This two-step process first calcines a liquid acidic waste. The resulting dry calcine material is then fed to an induction glass melter. In the United States, most HLW is alkaline and contains significant quantities of sodium and aluminum. It is more appropriate to use a single-step vitrification process in which the waste in the form of a liquid slurry is fed directly to the melter. The DWPF at the Savannah River site (SRS) is scheduled to be ready for hot (i.e., radioactive) operation late this year. The DWPF melter incorporates both joule and radiant heating. It also has a water cooling jacket that freezes the glass in contact with the metal shell and maintains the exterior of the melter at a low temperature to prevent updrafts of contaminated air in the processing cell. Other vitrification plants for HLW will soon be operating in Germany, the United States, and Japan. Vitrification plants for LLW are even more commonplace.

Figure 5 is a block flow diagram for a generic process to vitrify Pu in borosilicate glass. In this process, the gamma radiation field is assumed to be provided by ^{137}Cs in the form of CsCl from the inventory presently stored at the Hanford Site.[12]

Although HLW vitrification is relatively well developed, Pu vitrification requires that we investigate several issues before a production plant can be built. First, we must determine the optimum glass composition to achieve a durable product with an acceptably low Pu leach rate. In addition, processes and equipment must be developed for the various plant unit operations to reduce the risks in deploying the production plant. And third but not least, the issues associated with criticality must be addressed for each step of the immobilization

process from preparation of the input feed material to production of the final waste form.

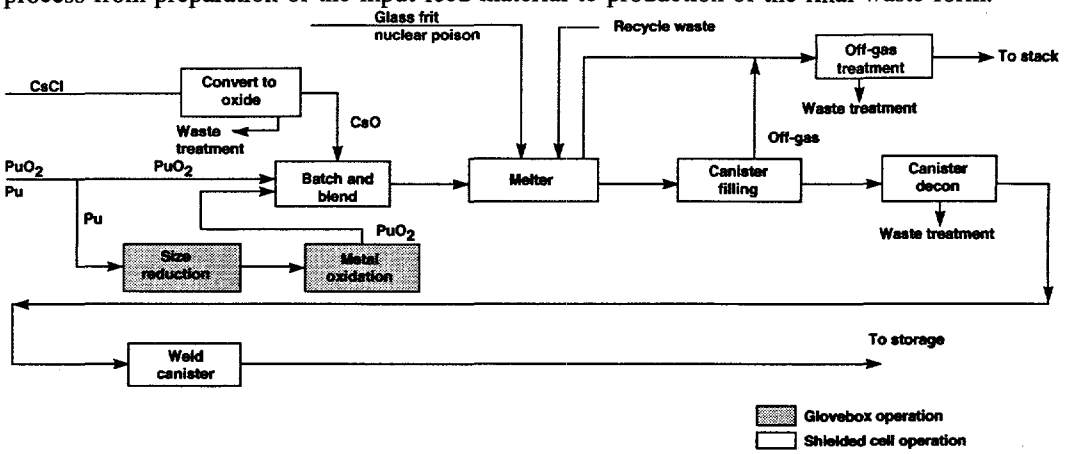


Figure 5. Vitrification block flow diagram.

Processing is performed in glove boxes or shielded concrete cells. Pu processing prior to addition of ^{137}Cs is conducted in shielded glove boxes. Processing of Cs and Pu after ^{137}Cs has been added is conducted in remotely operated shielded cells.

Ceramic Base Case Process Description

The ceramic is assumed to be similar to Synroc-C, containing the mineral phases zirconolite, hollandite, perovskite, and rutile. This material was developed at theAustralian Nuclear Science and Technology Organisation and the Australian National University. Hollandite is the host for Cs; and zirconolite and perovskite are hosts for rare earths and actinides. Actual phases selected will be the result of a research program. It is assumed that the composition of ceramic-forming chemicals (precursors) will not affect the processing equipment or sequence.

The feed materials are Pu oxide and metal, cesium chloride, and nonradioactive ceramic precursor materials. Gadolinium is added as a nuclear poison for criticality control during ceramic processing and final storage. The Pu and Gd are mixed as soluble compounds to ensure intimate mixing and to prevent settling should agitation be lost.

The final ceramic product is contained in canisters and stored on-site until it is transported to its final disposition. Each product canister contains about 660 kg of ceramic, which includes 80 kg of Pu, 52 kg Gd, and 1 kg (87,000 Ci) of cesium. Figure 6 is a simplified block flow diagram for ceramic immobilization.

SUMMARY

The literature was surveyed for waste forms suitable for immobilizing Pu. The waste forms found were then screened by a two-stage process to narrow the field to three primary forms—borosilicate glass, titanate-based ceramics, and metals—for further evaluation. Preliminary flowsheets have been developed for the immobilization of plutonium using these three forms that meet the "spent fuel standard" proposed by the U.S. NAS. Cost estimates are being developed for deployment of these options, assuming that the required time to immobilize approximately 50 MT of surplus plutonium is about 10 years.

ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

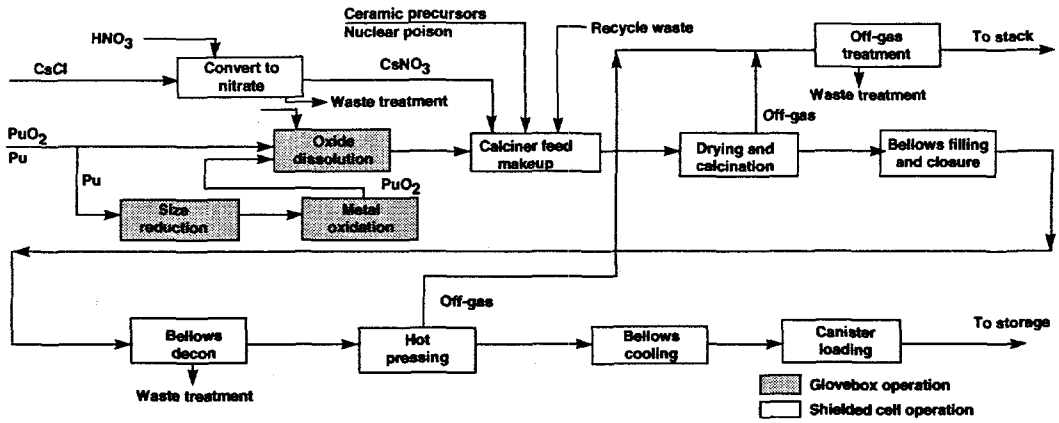


Figure 6. Ceramic immobilization block flow diagram

REFERENCES

1. National Academy of Sciences, *Management and Disposition of Excess Weapons Plutonium* (National Academy Press, Washington, DC, 1994).
2. *Screening of Alternate Immobilization Candidates for SFM Disposition*, Predecisional Draft, Lawrence Livermore National Laboratory, Livermore, CA (1995).
3. W. Lutze and R. C. Ewing, Eds., *Radioactive Waste Forms for the Future* (North-Holland, Amsterdam, 1988).
4. G. G. Wicks, J. M. McKibben, and M. J. Plodinec, "Vitrification of Excess Plutonium," accepted for presentation at Waste Management '95, Tucson, AZ, and to be published in the proceedings (1995).
5. J. M. McKibben and G. G. Wicks, "Vitrification of Excess Plutonium," presented at the International Policy Forum: Management and Disposition of Nuclear Weapons Materials, Leesburg, VA (1994).
6. J. M. McKibben, R. W. Benjamin, D. F. Bickfor, L. P. Fernandez, W. N. Jackson, W. R. McDonnell, E. N. Moore, P. B. Parks, M. J. Plodinec, W. M. Rajczak, S. K. Skiles, and G. G. Wicks, *Vitrification of Excess Plutonium* (U), WSRC-RP-93-755, Predecisional Draft, Westinghouse Savannah River Company, Aiken, SC (1993).
7. G. G. Wicks, "Nuclear Waste Glasses," *Treatise on Materials Science and Technology, Glass IV*, M. Tomozawa and R.H. Doremus, Eds. (Academic Press, Inc., New York, 1985), Vol. 26, pp. 57–188.
8. C. W. Forsberg, E. C. Beahm, and G. W. Parker, "Direct Conversion of Radioactive and Chemical Waste Containing Metals, Ceramics, Amorphous Solids, and Organics to Glass." *Proc. Spectrum '94: Nuclear and Hazardous Waste Management International Topical Meeting*, Atlanta, GA (American Nuclear Society, La Grange Park, IL, 1994).
9. G. R. Lumpkin, K. L. Smith, M. G. Blackford, K. P. Hart, P. McGlinn, R. Geire, and C. T. Williams, "Prediction of the Long-Term Performance of Crystalline Nuclear Waste Form Phases from Studies of Mineral Analogues," *Proc. 9th Pacific Basin Conf.*, Sydney, Australia, 1994 (National Conference Publication No. 94/6, 1994), p. 10.
10. A. Jotsons, "Status of Synroc Development," *Proc. 9th Pacific Basin Conf.*, Sydney, Australia, 1994 (National Conference Publication No. 94/6, 1994).
11. C. G. Sombret, "The Vitrification of High-Level Radioactive Wastes in France," *Nucl Energy* **24**(2), 85 (1985).
12. R. R. Jackson, "Hanford Waste Encapsulation: Strontium and Cesium," *Nucl. Technol.*