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Evaluation of Candidate Glass and Ceramic Forms for Immobilization of Surplus Plutonium

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EVALUATION OF CANDIDATE GLASS AND CERAMIC FORMS FOR IMMOBILIZATION OF SURPLUS PLUTONIUM

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ABSTRACT

The U. S. Department of Energy (DOE) is pursuing the development of an immobilization technology for the disposition of excess plutonium. This paper summarizes an evaluation of the can-in-canister (CIC) and homogeneous concepts for packaging surplus plutonium with high level waste, and an evaluation of the leading glass and ceramic forms for immobilizing the plutonium. Based on technical considerations, the lead laboratory (Lawrence Livermore National Laboratory) for the Plutonium Immobilization Project recommended to the DOE office of Fissile Materials Disposition that the surplus plutonium to be immobilized should be incorporated in a ceramic form using the can-in-canister packaging concept.

I. INTRODUCTION

The U. S. Department of Energy (DOE) has elected to pursue a duel path strategy for disposition of excess weapons-usable plutonium. One component of this strategy is irradiation of mixed oxide fuel in commercial reactors. The second component of this strategy is immobilization of plutonium in a suitable glass or ceramic material.

Lawrence Livermore National Laboratory (LLNL), in its role as the lead laboratory for the development of plutonium immobilization technologies for DOE's Office of Fissile Materials Disposition (MD), was requested by MD to recommend an immobilization package design, immobilization form, and material processing technology.

Alternative immobilization technologies involving different packaging designs, immobilization forms, and processing methods were evaluated with respect to criteria that reflect programmatic and technical objectives.

Two basic types of immobilization package concepts were considered: homogeneous and can-in-canister[1] (CIC). Two basic material types, glass and ceramic, were considered as matrices for immobilizing the plutonium. The combination of packaging concepts with glass and ceramic forms resulted in six immobilization technologies being evaluated and screened for future development. These concepts are described in the next section.

The criteria used in the evaluation were a subset of criteria previously used by MD to choose from among a broader range of disposition options, and are documented in DOE's ROD[2]. The evaluation of the alternative immobilization technologies was performed in two phases. First, the homogeneous and can-in-canister package concepts were evaluated, and a preferred concept (can-in-canister) was chosen for further study.

In the second phase, the glass and ceramic technologies for the chosen CIC concept were evaluated in a three step process. First, experts from within the Plutonium Immobilization Project (PIP) compiled and evaluated materials research and engineering data for the two leading forms with respect to the decision criteria[3]. Second, LLNL experts conducted an integrated assessment of the candidate technologies with respect to weighted criteria and other programmatic objectives,

Table 1. Immobilization Technology Alternatives

Packaging (Radiation Barrier) Approach	Immobilization Technology and Alternatives
External barrier (can-in-canister)	1. Glass (existing facilities) 2. Ceramic (existing facilities)
Homogeneous or internal barrier	3. Glass–new facilities (Greenfield) 4. Glass–adjunct melter (existing/new facilities) 5. Ceramic–new facilities (Greenfield) 6. Electrometallurgical treatment (existing/new facilities)

leading to a recommendation to DOE/MD on the preferred material form and processing technology based on technical factors[4]. Finally, a peer review panel of independent experts assessed the decision process, evaluations, and recommendation [5].

II. IMMOBILIZATION PACKAGE CONCEPTS

Two types of "waste" packaging concepts were evaluated for immobilizing the surplus plutonium. The first concept involves a fission product radiation barrier that is external to the plutonium-bearing form (can-in-canister concept). As indicated in Figure 1, small cans of plutonium-bearing material (glass or ceramic) would be placed in a rack that is inside a large stainless steel canister. This large canister is then filled with high level waste (HLW) glass. The prototype is the canister used for high level waste glass in the Defense Waste Processing Facility (DWPF) at the Savannah River Site. This canister is 3 m in height, 0.6 m in diameter, and contains approximately 1700 kg of HLW glass.

The second waste package concept would incorporate a homogeneous mixture of HLW or Cs-137 and plutonium within a large solid form of glass or ceramic. This homogeneous form would be encapsulated within a large stainless steel canister.

In both concepts, the fission products in the canister would generate a radiation barrier of at least 100 R/hr at 1 m from the package surface 30 years after initial fabrication. Both approaches are intended to mimic the physical and radiological

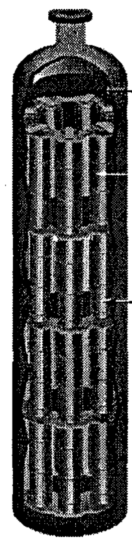

Figure 1. Can-in-Canister Design

characteristics of spent nuclear fuel, and to meet the spent fuel standard as articulated by the National Academy of Sciences[6] and implemented by DOE.

The can-in-canister (CIC) and homogeneous concepts were evaluated for both ceramic and glass plutonium-bearing forms. In addition, new and existing facility concepts for each of the immobilization technologies were defined in order to evaluate the overall merit of the alternatives. The combination of packaging concepts, glass and ceramic plutonium forms, and facility concepts resulted in six alternative immobilization technologies considered in this evaluation (Table 1). Facility concepts included block flow diagrams, mass balances and rate data for unit operations, equipment lists and layouts, reviews of regulatory and operational considerations, and facility sizing for 25 kg of plutonium per day for 200 operating days per year.

Initially the homogeneous and can-in-canisters concepts were compared, based on DOE's decision criteria referenced previously. Metrics for these criteria were developed in order to facilitate the comparison. The criteria used were:

1) Theft and diversion
2) Host nation extraction
3) Technical viability
4) Environment, safety, and health
5) Cost effectiveness
6) Timeliness

The homogeneous concept scored slightly higher with regard to the first two (non proliferation) criteria because the plutonium is intimately mixed with the fission products. However, both concepts appear to meet the "spent fuel" standard for proliferation resistance[6]. If needed, there are several relatively simple methods for enhancing the proliferation resistance of the can-in-canister package. These include: welding the plutonium-containing cans to each other and to the supporting frame, and reinforcing the cans with either steel rebar or armor.

The CIC concepts scored significantly higher than the homogeneous designs with regard to technical viability. The homogeneous forms and processes were much less developed than those of the can-in-canister concepts. Thus, the CIC technologies pose a significantly lower development risk than the homogeneous forms and could be deployed much earlier (timeliness). Furthermore, the homogenous forms involve processes that are generally more complex, and that require coprocessing of ^{137}Cs (which has a relatively high vapor pressure) with plutonium in a high-temperature formation process.

With regard to the ES&H criterion, the differences between the two concepts are minor, with a small advantage for the can-in-canister approach. The only noteworthy difference is the more extensive shielding of the plutonium operations required by the homogenous forms.

The CIC concept was conceived for the purpose of making extensive use of existing facilities and infrastructure at DOE sites, particularly the HLW vitrification facilities at SRS or those planned for Hanford. The use of existing facilities combined with the lower processing complexity results in the CIC glass and ceramic concepts being much less expensive (factor of about 1/2) than the homogeneous forms.

Based on the assessment summarized above, the glass and ceramic CIC technologies were chosen for more detailed evaluations to determine the preferred immobilization technology.

III. CIC GLASS FORM

The proposed glass form for the plutonium immobilization mission is a single-phase lanthanide borosilicate (LaBS) glass specially formulated to accommodate high concentrations of actinide elements (~16 wt%). Leaching tests indicate that the baseline LaBS glass has higher durability than both the EA Standard Glass and the Defense Waste Processing Facility (DWPF) HLW glass. Because of the high lanthanide and actinide content in the LaBS glass, the melting temperature is much higher than that for the traditional borosilicate waste glasses (1500° - 1550° C).

The production process for immobilization of plutonium in LaBS glass includes the following steps:

a) Attritor mill to co-grind PuO_2/UO_2 and glass making frit
b) Screw feeder to seven melters
c) Melter feed hopper
d) Melters for vitrification including off-gas system
e) Glass pour into cans
f) Can cool down
g) Trim can
h) Inspection
i) Load glass can in outer can
j) Bagless loadout

The incoming baseline feed consists of the PuO_2 powder admixed with incoming oxidized uranium feeds. In step a), these oxide materials are co-milled with the prefabricated, prefused LaBS frit in an attritor mill. The PuO_2/UO_x/frit mixture is then milled to the baseline ~20 microns to enhance solubility in the melt. Next the material is then fed directly to seven melters via a screw conveyer within a hard-piped closed system to eliminate dusting of silica and plutonium/uranium oxides. The melter, illustrated in Figure 2, is an induction-heated cylindrical ZGS (zirconia grain stabilized) platinum-rhodium alloy vessel containing a platinum-rhodium agitator rod to enhance mixing and ensure homogeneity.

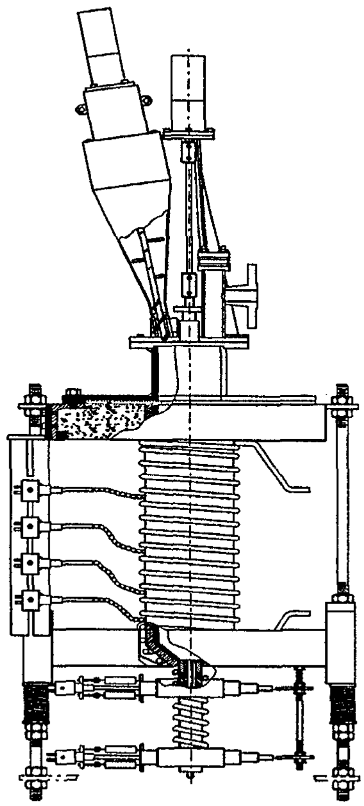

Figure 2. Glass melter

Melt temperature is 1500 °C. The melter and associated equipment comprise a complex system made up of the following major components: the melter and drain tube, melter and drain tube induction heating systems, feed system, off-gas system, and control system.

After pouring and cooling, the cans are trimmed with a commercially available pipe cutter above the meniscus. Each can containing plutonium-glass is then placed within an outer can (which protrudes outside the glove box). The outer can is sealed and detached from the glove box via a bagless transfer system. After the double plutonium-glass cans have been removed from the glove box, they are temporarily stored until ready for the canister loading step. Plutonium-glass cans are subsequently loaded into frames for insertion into empty DWPF canisters.

Essentially all material handling must be performed with automated, hands-off, equipment in heavily shielded glove boxes. The (α,n) reaction in boron, a major constituent in the LaBS glass, produces a high neutron radiation field which requires special design considerations for the layout of equipment.

IV. CIC CERAMIC FORM

The proposed ceramic form is a pyrochlore-rich ceramic that also contains zirconolite, brannerite, and rutile as secondary and tertiary phases. The pyrochlore-rich titanate ceramic was chosen for plutonium immobilization to ensure high loadings of plutonium, uranium, and the neutron absorbers gadolinium and hafnium. The neutron absorbers are present to ensure criticality control in the repository. High loadings of ^{238}U (natural or depleted uranium is added as part of the precursor oxides) are intended to provide additional criticality control in the repository over the long term through the limitation of the $^{235}U/^{238}U$ ratio as ^{239}Pu decays to ^{235}U. Plutonium and uranium are interchangeable in pyrochlore. The precursor composition consists of 55.7 wt% TiO_2, 16.5 wt% HfO_2, 15.4 wt% CaO and 12.4 wt% Gd_2O_3. Actinide loadings of 11.9 wt% PuO_2 (10.5 wt% plutonium) and 23.7 wt% UO_2 (20.9 wt% uranium) complete the mix.

A cold press and sintering process, which is similar to the MOX fuel processes in use in Europe, was developed and demonstrated for both the zirconolite- and pyrochlore-based forms. The production process for immobilization of plutonium in ceramic, illustrated in Figure 3, includes the following steps:

a) Conditioning mill to size reduce UO_2 and PuO_2
b) Attritor mill to blend PuO_2/UO_2 and oxide precursor
c) Granulator
d) Feed hopper to single press
e) Cold press
f) Conveyer to six furnaces
g) Sintering furnaces including off-gas system and Ar purge
h) Disc cool down
i) Inspection
j) Load discs into can
k) Bagless loadout

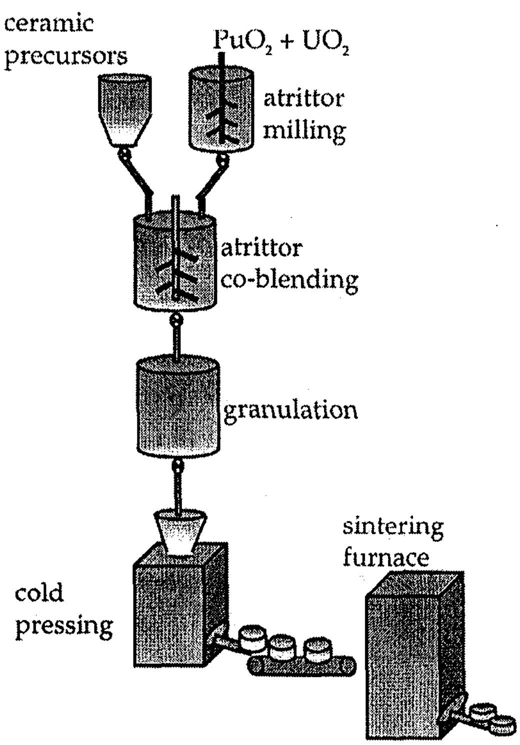

Figure 3. Ceramic process

In the ceramic immobilization process, PuO_2 and UO_2 are size-reduced and blended with ceramic precursors, titanium, hafnium, calcium and gadolinium oxides (TiO_2, HfO_2, CaO, Gd_2O_3), to make an overall mixture. The mixture is then pressed into disks at approximately 14 MPa (2,000 psi). The green disks are then reactively sintered at 1350 °C in argon for 4 hours. After sintering, the plutonium-bearing ceramic product achieves an after-fired density of 5.5 gm/cm^3 with phases of pyrochlore (90 wt%), brannerite (5 wt%), rutile (5 wt%), and less than 1 wt% plutonium-uranium-rich oxide. When impurities are added to the feed streams, the zirconolite phase (polyform of pyrochlore) is formed in significant amounts (up to 30 wt%).

After sintering, the ceramic disks are removed from the oven, inspected, and loaded into a "bagless transfer" can. The can is sealed and removed from the glove box via a bagless transfer system - basically the same system and operations described for glass. After removal from the glove box line, the ceramic-containing cans are stored until they are ready for canister loading. These cans are loaded into frames, which are then inserted into an empty DWPF canister.

V. GLASS-CERAMIC COMPARISON

The glass and ceramic forms were compared with regard to each of the six technical criteria established by DOE. To facilitate the comparison, metrics were assigned to each of the criteria. The criteria and metrics are listed in Table 2.

Table 2. Decision criteria, and metrics and weighting factors

Criterion 1. Resistance to theft or diversion by unauthorized parties
a. Low inherent attractiveness
b. Minimization of transportation, facilities, and sites
c. Minimization of processing
d. Safeguards and security assurance
e. Difficulty of retrieval, extraction, and use by a clandestine group or rogue nation
Criterion 2. Resistance to retrieval, extraction, and reuse by the host nation
a. Difficulty of retrieval, extraction, and reuse
b. Assurance of detection of diversion and extraction
Criterion 3. Technical viability
a. Technical maturity (considered as impacts on cost and timeliness)
b. Viability risks (considered as impacts on cost and timeliness)
c. Repository acceptability of disposal form
Criterion 4. Environmental, safety, and health compliance
a. Public and worker health and safety
b. Waste minimization
c. Known and manageable waste forms
Criterion 5. Cost effectiveness
a. Life cycle cost:
b. Investment and start-up cost
c. Establish product acceptability requirements
d. Potential for cost sharing, dollars
e. Utilization of existing Infrastructure
f. Cost estimate certainty
Criterion 6. Timeliness
a. Time to start disposition/time to open facility
b. Time to complete
c. Impacts on existing or future missions

Theft and Diversion

Because of its lower plutonium loading and higher neutron field, the glass form is considered slightly less attractive as a theft or diversion target prior to its incorporation in the HLW glass canister. However, this higher neutron field would make material accountability measurements more difficult for glass. More importantly, recovery of plutonium from glass would be simpler than recovery from the ceramic form. Recovery from glass can be achieved with a modification to an existing (published) plutonium recovery process while recovery from the ceramic form would require a more chemically complex process that has not been developed for plutonium-bearing titanate minerals. Overall, the ceramic form was judged to have a small to moderate advantage over glass for this criterion.

Host nation reuse

The ceramic form offers a slight advantage with respect to recovery and extraction by the host nation. It is likely that the extensive resources of the host nation would be sufficient to develop the processes for recovery of plutonium from the ceramic form. For the host nation, recovery of plutonium from either of the can-in-canister forms would be comparably as difficult as recovery from spent nuclear fuel. Detection of actions to recover plutonium on a large scale from either form would be relatively easy.

Technical Viability - Repository Acceptability

The ceramic form offers a small to moderate advantage due to its expected higher durability under repository conditions and its lower potential for long term criticality. This factor is composed of several metrics, principally: dissolution or corrosion rate, expected surface area, and effects of radiation damage (from α decay). The major performance issue is the ability of the candidate forms to provide assurance against a long term criticality event in the repository. With regard to technical maturity and risk, both forms were judged to be essentially equivalent. However, both forms have offsetting advantages that could impact cost and schedules (see below).

Environmental, Safety, and Health

Immobilization operations are expected to produce little radiation exposure to the public, and both forms were judged equal in this area However, there is a difference between the two forms with regard to potential worker dose. The ceramic process has an advantage over the glass process due to the much higher neutron radiation source strength associated with the glass form. This stems from the (α, n) reaction that occurs in boron, a key constituent in the LaBS glass. The high neutron rate occurs beginning with the glass frit-plutonium feed milling/blending step through canister operations prior to entry into the DWPF canyon. The glass and ceramic forms are likely to be similar in terms of contamination potential and waste generation.

Cost Effectiveness

The ceramic form offers a small to moderate cost advantage relative to glass. Because the plutonium loading of glass is lower than the ceramic, the glass form displaces more high level waste glass and requires manufacture of additional high level waste canisters. In addition, design and operational impacts associated with the higher radiation source term for glass might result in higher costs for automation, shielding, or use of enriched boron to reduce the dose rate.

With regard to cost uncertainty, no significant difference between the two forms were identified. Glass has a small advantage over ceramic in the area of product knowledge and control. The ceramic form needs additional testing to verify its ability to produce acceptable products across the expected range of feed materials. This glass advantage is offset by the lower maturity of the high-temperature induction-heated melter system for glass, compared to the more mature MOX fabrication technology being adapted for the ceramic form. Neither of these issues is believed to be a potential "show stopper" or to represent a significant risk to the immobilization project.

Timeliness

There is no discernible difference between the two forms with regard to timeliness in the baseline schedule. However, two areas of risk were identified: waste form qualification for the ceramic and melter development for the glass. Difficulty in addressing these issues could lead to schedule slippage.

Overall Assessment

Assessment of the information currently available indicated that both the ceramic and glass technologies provide acceptable forms for the immobilization of plutonium. However, the ceramic technology is superior to the glass technology because of the accumulation of small to moderate advantages for a number of important decision factors. These include proliferation resistance, repository performance and acceptability of the waste form, potential worker dose, and cost effectiveness. Glass, on the other hand, has only a slight advantage for one nonproliferation factor (attractiveness level) as well as some small advantages in specific areas that are offset by ceramic advantages in related areas.

IV. SUMMARY AND CONCLUSIONS

Based on the previously described evaluation of alternative immobilization technologies, the can-in-canister concepts were judged to be clearly superior to the homogeneous form technologies[1]. Both glass and ceramic forms were found to be acceptable for plutonium immobilization using the CIC packaging approach[3,4]. However, the ceramic technology offers a number of advantages over glass, notably:

- The ceramic form is more proliferation resistant.
- The ceramic form is expected to be more durable in a repository environment.
- The ceramic form has a significantly lower radiation source term that reduces the potential for worker exposure during fabrication.
- The ceramic form and process offer potential cost savings relative to the glass technology.
- The ceramic technology is more flexible, and can better accommodate modifications to programmatic and technical requirements.

Therefore, the lead laboratory for Immobilization, LLNL, recommended that the ceramic form and process technology be developed for eventual deployment in a plutonium immobilization plant using the can-in-canister approach[4]. This recommendation was concurred with by the independent peer review panel[5], and by the DOE Office of Fissile Materials Disposition[7].

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