DEVELOPMENT OF GLASS AND CRYSTALLINE CERAMIC FORMS FOR DISPOSITION OF EXCESS PLUTONIUM

James Marra [*], Alex Cozzi, Charles Crawford,
Connie Herman, John Marra and David Peeler

Savannah River National Laboratory
Aiken, SC, USA
[*] Corresponding author: james.marra@srnl.doe.gov

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ABSTRACT

In the aftermath of the Cold War, the United States Department of Energy (DOE) has identified up to 50 metric tons of excess plutonium that needs to be dispositioned. The bulk of the material is slated to be blended with uranium and fabricated into a Mixed Oxide (MOX) fuel for subsequent burning in commercial nuclear reactors. Excess plutonium-containing impurity materials making it unsuitable for fabrication into MOX fuel will need to be dispositioned via other means. Glass and crystalline ceramics have been developed and studied as candidate forms to immobilize these impure plutonium feeds. A titanate-based ceramic was identified as an excellent actinide material host. This composition was based on Synroc compositions previously developed for nuclear waste immobilization. These titanate ceramics were found to be able to accommodate extremely high quantities of fissile material and exhibit excellent aqueous durability. A lanthanide borosilicate (LaBS) glass was developed to accommodate high concentrations of plutonium and to be very tolerant of impurities yet still maintain good aqueous durability. Recent testing of alkali borosilicate compositions showed promise of using these compositions to disposition lower concentrations of plutonium using existing high level waste vitrification processes. The developed waste forms all appear to be suitable for Pu disposition. Depending on the actual types and concentrations of the Pu residue streams slated for disposition, each waste form offers unique advantages.

INTRODUCTION

The end of the cold war and subsequent downsizing of nuclear arsenals in the U.S. and Russia has resulted in excess weapons-useable plutonium. In 1994, the U.S. National Academy of Sciences declared that this excess plutonium represented a "clear and present danger" [1]. The National Academy of Sciences also stressed that the Pu must be safeguarded from theft and diversion and reintroduction into weapons. In the U.S. approximately 50 metric tons of plutonium has been declared excess. The majority of this plutonium is relatively pure and is suitable or can be made suitable for use in MOX fuel for burning in a nuclear reactor. The remaining Pu-containing materials have impurities or isotopic distributions that make use as a nuclear fuel difficult. In 1997, it was declared that about 17-18 metric tons of the excess plutonium should be immobilized and the immobilization form should be a titanate-based ceramic [2]. Furthermore, the preferred means to safeguard the immobilized plutonium was using an external radiation barrier method known as the can-in-canister approach [3]. In the can-in-canister approach, cans containing the immobilized plutonium waste form are placed inside of a high-level radioactive waste (HLW) canister and the canister is subsequently filled with HLW glass to provide a radiation barrier to the immobilized plutonium (FIGURE 1). There have been a number of programmatic changes in the U.S. plutonium disposition program since 1997 and the relative amounts and nature of the Pu materials requiring immobilization has changed significantly. Overall, the amount of material that is suitable for use in a MOX fuel has increased, resulting in a much smaller inventory requiring disposition via immobilization. However, the chemical nature of this smaller inventory is much less consistent and contains significantly higher levels of impurities. In the past few years, research efforts have concentrated on glass waste forms with proven tolerance to chemical impurities that can accommodate adequate quantities of plutonium in the glass structure.

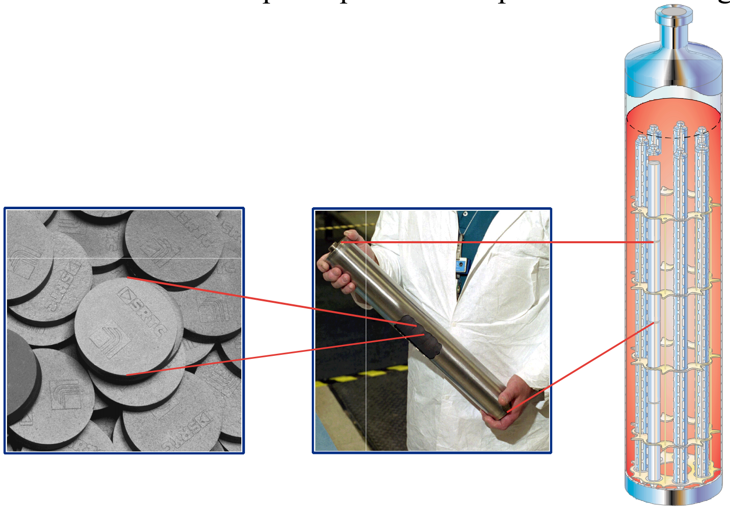

FIGURE 1. Schematic diagram showing the can-in-canister approach for a Pu ceramic.

Both ceramic and glass Pu immobilization options appear feasible. However, the attributes of the forms provide advantages and disadvantages relative to the quantity of Pu requiring disposition and the types and levels of impurities associated with the plutonium inventory. In this paper, ceramic and glass waste forms and fabrication processes will be discussed. The inherent advantages and disadvantages of the forms will also be identified.

TITANATE CERAMIC WASTE FORMS

A titanate ceramic was developed based on the previous Synroc compositions for stabilization of HLW and actinide-bearing wastes. The formulation selected for Pu immobilization was based on the Synroc-F and Synroc-FA compositions [4]. Researchers at Lawrence Livermore National Laboratory (LLNL) and Savannah River National Laboratory (SRNL) jointly developed the baseline composition for the Pu titanate ceramic [5]. The composition resulted in pyrochlore as the primary phase with smaller concentrations of brannerite, perovskite, rutile, zirconolite and glassy phase dependent on the impurities present (TABLE 1). The baseline composition contains approximately 12 wt % PuO_2 but it was demonstrated that up to nearly 30 wt % PuO_2 could be immobilized by removing the UO_2 from the composition resulting in a pyrochlore-rich ceramic with no undissolved PuO_2. The microstructure of the baseline composition is shown in FIGURE 2.

TABLE 1. Chemical Composition of Baseline Pu Ceramic Waste Form

Oxide	Wt.%	Purpose
PuO_2	11.9	To be immobilized
UO_2	23.7	Deplete U-235 decay product
HfO_2	10.6	Neutron poison
Gd_2O_3	7.9	Neutron poison
CaO	10.0	Form minerals
TiO_2	35.9	Form minerals

Phases formed (dependent on impurities)

Pyrochlore:	$(Ca,Gd)(Pu,U,Hf,Gd)Ti_2O_7$ (major phase)
Brannerite:	$(Pu,U,Hf,Gd)Ti_2O_6$ (minor phase)
Perovskite:	$CaTiO_3$ (minor phase)
Rutile:	$(Ti,Hf)O_2$ (minor phase)
Zirconolite:	$(Ca,Gd)(Hf,U,Pu,Gd)Ti_2O_7$ (minor phase)
Silicate phase:	Glass (minor phase)

The relative durability of the Pu ceramic was measured by a team of researchers using several different aqueous corrosion methods [6]. The relative release of Pu from the ceramic as measured by the Product Consistency - Method A (PCT-A) procedure was nominally 1×10^{-4} g/m^2 indicating the ceramic was very durable. The PCT-A is an aqueous test involving exposing crushed and sieved waste form to demineralized water at 90º C for 7 days [7]. The PCT-A is the reference method used to qualify a HLW glass for repository disposition in the U.S.

The process route developed to produce the Pu ceramic was a cold press and sinter route that resulted in ceramic “pucks” (nominally 7 cm diameter x 2.5 cm thick) as the final product. The process is shown schematically in FIGURE 3.

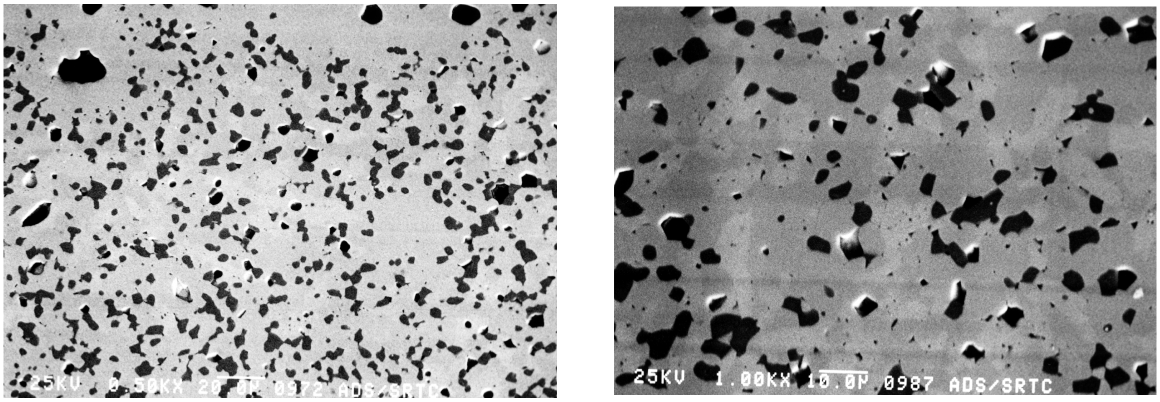

FIGURE 2. SEM micrographs of Pu ceramic (dark gray = pyrochlore, light gray = brannerite, small black = rutile, large black = porosity).

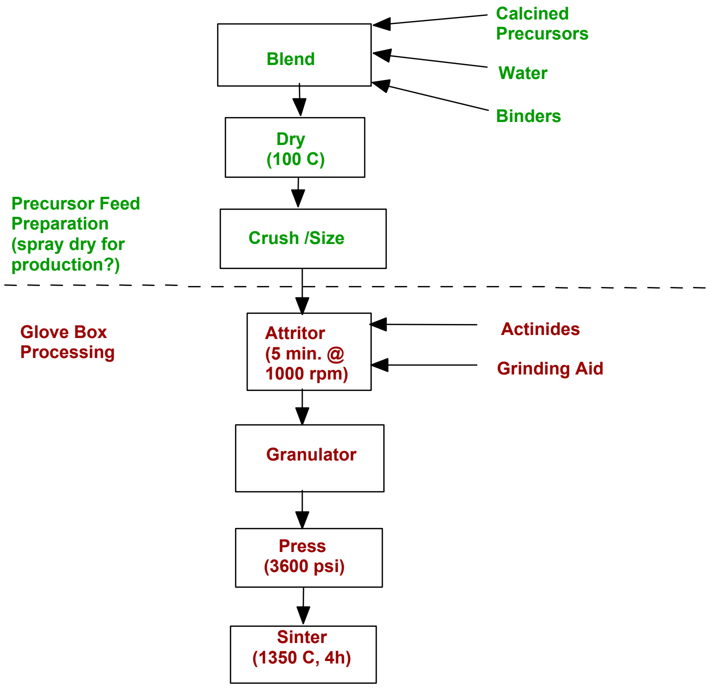

FIGURE 3. Schematic representation of the Pu ceramic process.

The Pu ceramic has distinct advantages regarding the ability to incorporate very high quantities of Pu within the primary pyrochlore phase. Therefore, if there is a large inventory of excess Pu requiring disposition, the ceramic waste form is attractive. The high relative durability of the ceramic also is an advantage for repository disposition. On the negative side, the tolerance of the ceramic form to impurities is limited with the potential to form phases that can influence the integrity and the performance of the ceramic [8]. Ceramic waste forms are also susceptible to alpha-radiation damage that can also influence product integrity and performance [9].

LANTHANIDE BOROSILICATE GLASS

High lanthanide glass compositions were developed commercially in the 1930s for use in optical applications [10]. This family of high lanthanide glasses has been used extensively in nuclear applications for protective purposes since many of the lanthanide elements have large thermal neutron cross-sections [11]. A series of glass compositions was developed based on the high lanthanide formulations to demonstrate that this family of glasses could accommodate high levels of plutonium within the glass structure. A lanthanide borosilicate (LaBS) glass showed that PuO_2 solubility could be as high as 13.4 wt % in the glass [12]. This glass composition was later denoted as LaBS Frit A. Additional LaBS glass compositions were developed to improve the Frit A composition. The LaBS Frit B composition added HfO_2 to the glass formulation to increase the amount of neutron absorbers in the glass [13]. The LaBS Frit X composition was developed recently to improve the processability of the glass. A significant increase in the amount of lanthanides in Frit X resulted in lower melting and glass liquidus temperatures [14]. The LaBS glass compositions have proven to be very tolerant to the impurities anticipated to be associated with the Pu feeds [15]. The LaBS glass compositions are given in TABLE 2.

TABLE 2. Lanthanide Borosilicate (LaBS) Glass Compositions

Oxide	FRIT A	FRIT B	FRIT X
Al_2O_3	21.5	21.3	10.00
B_2O_3	11.7	11.6	13.00
Gd_2O_3	8.6	12.8	13.50
HfO_2	--	6.6	7.0
La_2O_3	12.4	8.1	19.00
Nd_2O_3	12.8	8.2	15.00
SiO_2	29.2	28.9	20.00
SrO	2.5	2.5	2.50
ZrO_2	1.3	--	--

The LaBS glasses have been found to exhibit excellent aqueous durability [16]. Testing using the PCT-A method showed normalized elemental releases for Pu to be approximately 2×10^{-3} g/m^2. Additionally, looking at the PCT-A response for boron which is used as a measure of dissolution of the matrix glass indicated that the LaBS glass compositions were more than 2 orders of magnitude more durable than the HLW Environmental Assessment (EA) glass. The EA glass is the benchmark glass used to qualify HLW glasses in the U.S.

A vitrification process was developed for immobilizing Pu in a LaBS glass [17]. The dry process involved mixing and milling the Pu feed with the LaBS frit and melting in a Pt/Rh hot wall cylindrical induction melter (CIM) (FIGURE 4). The CIM can be operated at temperatures up to 1600º C. The design and size of the CIM provides for inherent criticality control during the melting process and straightforward fissile material accountability. The CIM is shown in FIGURE 5.

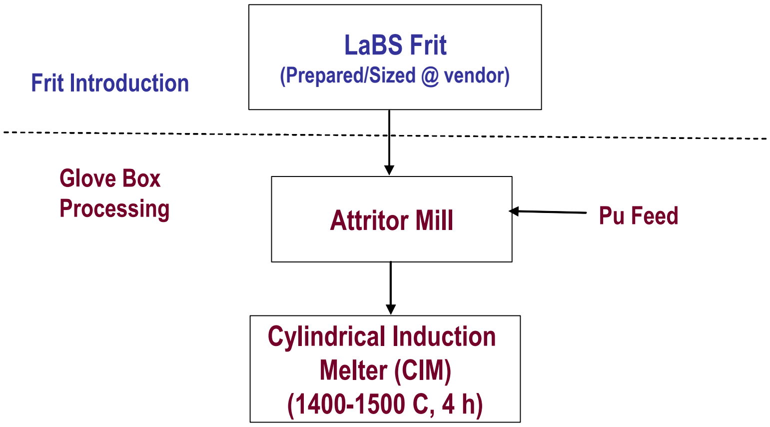

FIGURE 4. Schematic representation of the Pu LaBS glass vitrification process.

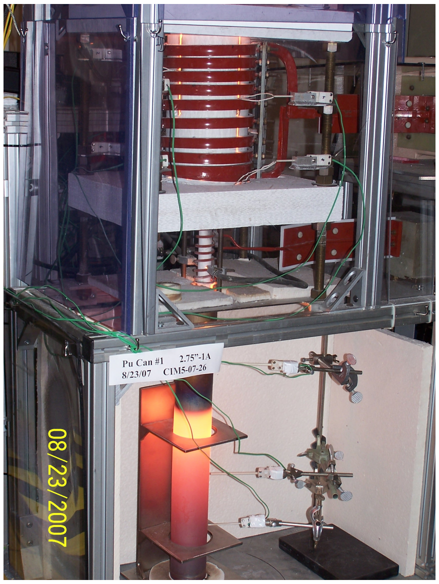

FIGURE 5. Cylindrical Induction Melter (CIM) during LaBS glass pour.

The advantages of the LaBS glass option for disposition of excess plutonium are the relatively high solubility for Pu, the tolerance to impurities, established vitrification and waste form qualification processes for radioactive waste glasses and radiation damage resistance. On the down side, the durability of the LaBS glass is not as high as the ceramic form and the radioactive dose of the glass is expected to be high due to (alpha, neutron) reactions occurring between the alpha-emitting Pu and the light elements in the glass [2].

ALKALI BOROSILICATE GLASSES

Alkali borosilicate glasses have been developed world-wide for vitrification of HLW, intermediate level waste (ILW) and low activity waste (LAW). Theses wastes have relatively low Pu content and, thus, the relatively low solubility of Pu in these glasses is not an issue. Recently, testing has been conducted at SRNL to investigate the solubility of Pu in a prototypical U.S. defense HLW glass. Testing was conducted at 0.5 wt % and 2 wt

% PuO_2 in the glass. The composition of the simplified waste glass evaluated was: Al_2O_3 = 9 wt %, B_2O_3 = 6 wt %, CaO = 2 wt %, Fe_2O_3 = 12 wt %, Na_2O = 14 wt %, Li_2O = 5 wt %, MnO = 2 wt %, and SiO_2 = 50 wt %. The glass was melted at the nominal HLW glass processing temperature of 1150º C. Both x-ray diffraction and scanning electron microscopy analysis of the glasses indicated that PuO_2 was fully dissolved up to 2 wt % (FIGURE 6).

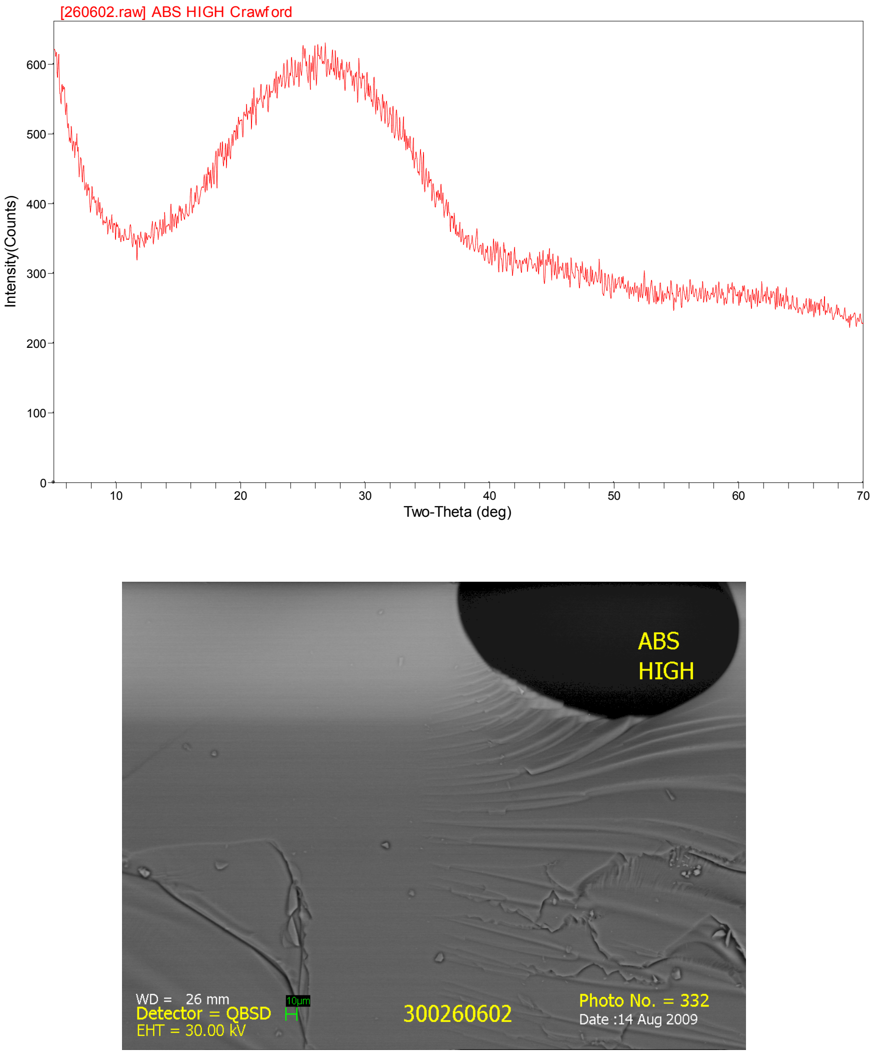

FIGURE 6. X-ray diffraction scan (top) and SEM micrograph of alkali borosilicate glass containing 2 wt % PuO_2 showing amorphous nature of glass. (green micron bar = 10 µm)

The alkali borosilicate glass option for Pu disposition allows for processing using existing HLW vitrification facilities. For example, the Defense Waste Processing Facility (DWPF) at the Savannah River Site, which has been in radioactive operation since 1996, could be directly used for the disposition of Pu. In this option, the Pu feed would be combined with the liquid HLW and transferred to the DWPF. In the DWPF, glass frit would be added to the waste and the glass would be melted using a Joule heated melter technology (FIGURE 7). This could result in significant cost savings if new facilities would need to be constructed for the other disposition options. The negatives with this option are that relatively low Pu concentrations can be incorporated into the glass matrix.

Additionally, material accountability and criticality controls involving a liquid feed containing Pu would need to carefully planned and executed. It should also be noted that the relative durability of alkali borosilicate glasses are lower than both the ceramic and LaBS glass options.

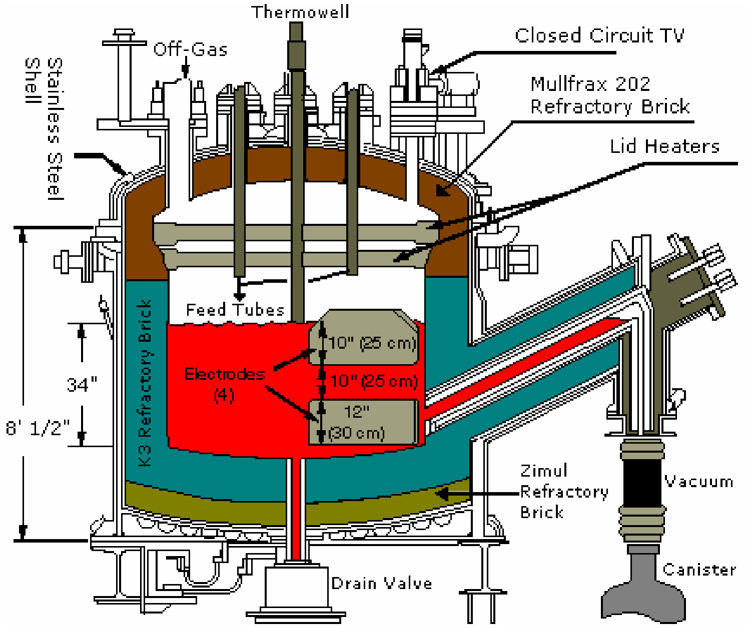

FIGURE 7. Schematic drawing of the Joule heated melter in DWPF.

CONCLUSIONS

Three waste form options have been identified and tested for the disposition of excess weapons-useable plutonium. All the options appear to be viable yet all three have inherent advantages and disadvantages. The titanate ceramic option can accommodate very high levels of plutonium into the primary pyrochlore phase. The crystalline ceramic also has very high aqueous durability. However, the ceramic has relatively low tolerance to impurities and can be susceptible to radiation damage. The LaBS glass can incorporate moderately high concentrations of PuO_2 into the glass structure and is highly tolerant of impurities. However, the glass has lower durability than the ceramic and generates a high neutron dose that could complicate glove box processing. The alkali borosilicate option could take advantage of existing glass processing facilities to significantly reduce disposition costs. However, the solubility of PuO_2 in alkali borosilicate glasses is relatively low. Additionally, specific attention would need to be given to criticality control and fissile material accountability in the aqueous feed process used in the HLW vitrification process.

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