

Immobilization of Excess Weapon Plutonium: A Better Alternative to Glass

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The United States plans to immobilize several metric tons of excess weapons plutonium in a solid matrix. The selected material must achieve the short-term goal of deterring proliferation through theft or host-nation reuse, and the long-term goal of preventing plutonium exposures over geologic time. The Department of Energy, after internal review, has recently decided on Synroc, a crystalline ceramic, to immobilize the plutonium. This paper presents an independent technical comparison of glass versus ceramic immobilization options, and reaches similar conclusions to those of the Department of Energy. On a technical basis, Synroc performs better than glass in a number of areas. It is more proliferation resistant than glass due to the more complicated and less well-known extraction process that would be required to separate the plutonium. Synroc is more chemically durable than borosilicate glass and can dissolve more depleted uranium than glasses to address future criticality problems. Now that the Department of Energy has selected Synroc as the waste form of choice for plutonium disposition, it should also be reconsidered for immobilization of high-level nuclear waste.

INTRODUCTION

Both Russia and the United States are faced with decisions on how to dispose of plutonium and highly enriched uranium recovered from dismantled warheads, and from various nuclear weapons facilities. In the U.S., the Department of Energy (DOE) estimates that 50 or more metric tonnes (MT) of weapons plutonium and hundreds of metric tonnes of highly-enriched uranium (HEU) will be considered "excess." Disposition of these materials is essential for national and international security reasons. The disposition of excess HEU is a relatively straightforward process in which it is mixed with natural uranium to dilute it to the low-enriched composition used in commercial nuclear reactor fuel. In contrast, the disposition of plutonium is not so simple; dilution with other plutonium isotopes will not render it "safe" because

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all isotopes of plutonium can be used to make nuclear weapons. However, the National Academy of Sciences' Committee on International Security and Arms Control¹ advanced the "Spent Fuel Standard" criterion to provide a guidepost for plutonium disposition. The Spent Fuel Standard requires that the weapons plutonium be converted to a form as inaccessible as plutonium in spent fuel from commercial nuclear reactors.²

In addressing excess weapons plutonium disposition in the United States, the Department of Energy (DOE) and the Clinton Administration have adopted a dual-track approach that will give the DOE the option both (1) to mix plutonium oxide with uranium oxide to form MOX fuel, which will be burned in selected light-water reactors, and (2) to immobilize plutonium in solid form such as glass or ceramic.³ It is the latter option that forms the focus of this paper. Despite the dual-track approach, it is certain that at least 17 MT of the excess plutonium will be immobilized rather than converted to MOX. This is a substantial part of the plutonium metals, scraps, and residues located at 8 major sites in the United States including Pantex in Texas, Rocky Flats in Colorado, and Hanford in Washington (Figure 1)⁴ which are in forms that would be prohibitively expensive to purify sufficiently for use as MOX fuel.⁵

Immobilization of excess weapons plutonium will almost certainly use a can-in-canister method, where 20 small stainless steel cans containing plutonium incorporated in ceramic or glass will be loaded onto a frame inside a large (3 m long by 0.6 m diameter) stainless steel canister (Figure 2).⁶ Each can will contain about 2.56 kg of plutonium immobilized in the waste form, for a total of 51.2 kg Pu per canister.⁷ After the small cans are loaded onto the frame, borosilicate glass containing defense high-level nuclear waste will be poured into the large (1,800 kg) canister, and a lid will be welded onto the canister. The high-level waste glass contained in the outer canister will provide a gamma radiation barrier to deter theft of the plutonium.

The canister design, employing borosilicate glass, will be common to whichever waste form—glass or ceramic—is used for the can; and it is the choice of this waste form that the remainder of the paper will examine.

Because plutonium is extremely toxic, a grave proliferation risk, and has a half-life of 24,100 years, it is essential that the waste form into which it will be incorporated be able to both (1) prevent reuse in nuclear weapons by both host nations and terrorists and (2) safely contain it for a very long time to prevent exposures to humans and the environment. Although the United States along with many other major nuclear countries has favored the use of glass for high-level nuclear waste immobilization, plutonium, a fissile material, requires additional considerations, and there now appear to be a number of waste form

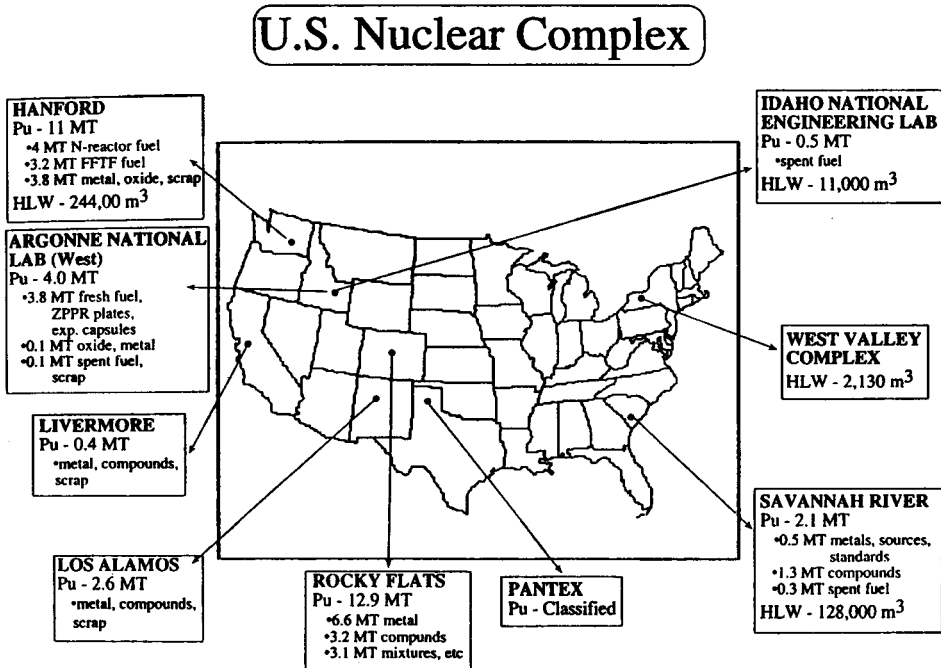


Figure 1: Map of locations of excess weapons Pu in the United States.²⁴

options that have significant advantages over glass. This paper will focus on two types of waste form, crystalline ceramics and glass, and compare their properties and production technologies.

It is widely assumed that the immobilized waste is eventually destined for a geologic repository. For this reason, it is important to try to understand the repository environment over time-scales greater than a few thousand years. However, it is actually easier to model the behavior of some waste forms over a geologic time-scale than it is to model the hydrology or seismicity associated with the repository environment. Past repository performance assessments

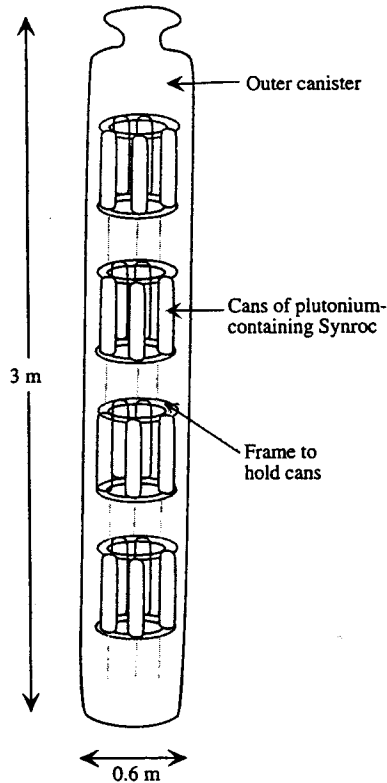


Figure 2: Schematic of the can-in-canister design. Twenty cans of plutonium-containing waste form are attached to a frame and inserted into a larger canister. The canister is filled with high-level radioactive waste glass to provide a radiation barrier for nonproliferation purposes.⁷

have concluded that plutonium would not be a major contributor to environmental radiation doses on the basis of the low solubility of plutonium put in groundwater (on the order of 10^{-8} gm/cm³).⁸ Recent findings on plutonium mobility at the Nevada Test Site, however, suggest just the opposite, that relatively rapid transport of plutonium in the repository environment may occur from colloidal transport of species.⁹ In light of the uncertainty associated with plutonium transport in geologic media coupled with large uncertainties in performance assessments of repositories (due to uncertainties in future volcanic activity, seismicity, flow in the unsaturated zone, climate change, etc.) it would be prudent to choose a waste form that ensures containment of radionuclides,

regardless of repository performance. This conclusion was reached by the National Research Council's Committee on Vitrification of Radioactive Wastes, which stated that "sensitivity analyses used to evaluate waste form performance should emphasize the material properties of the waste form, not the total system performance."¹⁰ This is the approach taken in this paper.

Nevertheless, the waste form should to some degree be appropriate for the particular type of geologic repository. Yucca Mountain, Nevada, the location of the planned high-level waste geologic repository, is composed of tuff, a fine-grained silicic rock solidified from volcanic ash flows. It is dominated by SiO_2 , Al_2O_3 , K_2O , Na_2O , and CaO , as is crystalline rock, such as granite or gneiss, under consideration in Europe as repository media. This contrasts with bedded salt, the repository lithology at the Waste Isolation Pilot Plant in Carlsbad, New Mexico. Because of the different lithologies, the groundwater compositions, pH, and redox conditions will vary in these different geologic environments. The selected waste form must be able to perform well under the conditions that will exist.

AN INTRODUCTION TO THE WASTE FORMS

Over the years, researchers have considered a number of materials to encapsulate high-level nuclear waste. These materials include, but are not limited to, glasses of various compositions, including silicate glasses¹¹ and phosphate glasses;¹² ceramics of a wide variety of formulations;¹³ glass-ceramic compounds;¹⁴ cements;¹⁵ coated particles or particles in metal matrices;¹⁶ and pyroprocessed metals.¹⁷ Based on present familiarity with production technology, the two best candidate materials for high-level nuclear waste and plutonium disposition are glasses and crystalline ceramics.¹⁸

Glass

Glass is a noncrystalline solid in which a wide range of waste impurities or material can be dissolved.^{19, 20} Glass may be relatively susceptible to damage from radioactive decay, although this has yet to be proven experimentally.²¹ As discussed in the Appendix, a number of countries have developed successful industrial-scale vitrification technologies to solidify their HLW.²² For these reasons, glass has received the most attention as a potential waste form for the immobilization of plutonium. On the other hand, glass is thermodynamically unstable and over geologic time may devitrify (crystallize), especially at the elevated temperatures (100°–300°C) expected to be encountered in a geologic repository.²³

Table 1: Compositions of glasses for plutonium immobilization in weight percent.

Oxides	Borosilicate glass ^a	LaBS1 glass ^b	LaBS2 glass ^c
Al ₂ O ₃	3.84	20.77	21.5
B ₂ O ₃	7.97	11.35	11.7
BaO	0.22	-	-
BaSO ₄	0.22	-	-
CaO	1.16	-	-
CaSO ₄	0.12	-	-
Cr ₂ O ₃	0.10	-	-
Cs ₂ O	0.08	-	-
CuO	0.40	-	-
Fe ₂ O ₃	12.47	-	-
Gd ₂ O ₃	-	7.45	8.6
K ₂ O	3.47	-	-
La ₂ O ₃	-	8.6	12.4
Li ₂ O	4.4	-	-
MgO	1.36	-	-
MnO	2.05	-	-
Na ₂ O	8.58	-	-
Na ₂ SO ₄	0.10	-	-
NaCl	0.31	-	-
Nd ₂ O ₃	-	8.6	12.8
NiO	0.74	-	-
PbO	-	-	-
PuO ₂	-	11.36	-
SiO ₂	49.61	28.16	29.1
Sm ₂ O ₃	-	-	-
SrO	-	2.43	2.5
ThO ₂	0.36	-	-
TiO ₂	0.65	-	-
U ₃ O ₈	0.53	-	-
ZrO ₂	-	1.27	1.3
Total	98.74	99.99	99.90

a. Standard Defense Waste Processing Facility borosilicate glass composition.²⁴

b. Lanthanum borosilicate glass based on Löffler glass composition, developed at Lawrence Livermore National Lab.²⁵ Plutonium has already been added to this composition, unlike the other LaBS glass.

c. Lanthanum borosilicate glass based on Löffler glass composition, developed at the Savannah River Site.²⁶

Borosilicate glass, as opposed to other compositions such as phosphate glass, is preferred for high-level nuclear waste. It has the advantage of being more durable than many other glass compositions and can be produced at lower temperatures than other glasses.²⁷ Table 1 shows three glass compositions that may be suitable for excess weapons plutonium material. In the standard glass composition being used at the Savannah River Defense Waste Processing Facility (DWPF), B and Li are present to improve the properties of the glass, such as lowering the viscosity of the melt. The glass composition for plutonium disposition is a lanthanide borosilicate (LaBS) glass because of the higher solubility of plutonium and greater chemical durability. Overall, glass can accept a wider range of impurities than ceramic, but with limits. For example, LaBS glass can accept only a limited amount of uranium, as will be discussed in a later section of this paper. Borosilicate glasses are commonly processed between 1,100°–1,200°C whereas LaBS will be processed at 1,475°C.²⁸ For the DWPF borosilicate glass composition of Table 1, waste loadings for plutonium are on the order of 2–4 wt percent.²⁹ One study suggests that higher waste loadings in borosilicate glass, on the order of 7 wt percent, would be possible.³⁰

Two formulations of lanthanide borosilicate (LaBS) glasses are shown in Table 1. Gadolinium and Hafnium in the LaBS glass are added as neutron absorbers. Lawrence Livermore National Laboratory developed the LaBS 1 composition, in which plutonium is already part of the composition. The LaBS2 glass, developed by the Savannah River Site, will be used as a base composition from which the final composition will be developed. The measured solubility of plutonium in the LaBS glass at 1475°C was observed to be greater than 10 wt percent in stirred crucible experiments, although a maximum of 8.5 wt percent Pu was observed in an unstirred crucible melt of a 1 kilogram monolith of LaBS glass.³¹

Natural analogs of waste form material provide the only data available data on long-term performance of these materials under geological conditions. Many geologic examples of glass exist in the natural world. These glasses fall into two compositional categories: those highly enriched in silica, such as rhyolitic glasses and tektites (70–75 wt percent SiO₂) and those less enriched in silica, such as basalt glasses (45–50 wt percent SiO₂).³² Tektites are impact glasses that form under extreme conditions of temperature and pressure, whereas rhyolite and basalt glasses form during extrusive volcanic events (low pressure, high temperature). Natural volcanic glasses are generally much younger than 40 million years of age.³³ A few rare glasses, lunar glasses, are much older, on the order of 10⁸ years, but have probably survived for so long because of their lack of contact with water in the lunar environment.³⁴ Comparison of the silica content of these glasses with the LaBS glasses (29–35 wt percent SiO₂) in Table 1 indicates that neither the rhyolites or the basalts

Table 2: Compositions of ceramic waste forms for plutonium immobilization.

Phase assemblage	Phase	Composition	Crystal system	Synroc-C modal % ^a	LLNL Synroc modal % ^b
Single phase	Zircon	ZrSiO ₄	Tetragonal		
Single phase	Monazite	CePO ₄	Monoclinic		
Single phase	Apatite	Ca ₅ (PO ₄) ₃ F	Hexagonal		
Single phase	Baddelyite	ZrO ₂	Tetragonal (high T)		
			Isometric (T < 1,200°C)		
Single phase	Cubic zirconia		Isometric		
Synroc	Zirconolite	CaZrTi ₂ O ₇	Monoclinic	30	
	Pyrochlore ^c	CaUTi ₂ O ₇	Isometric		80
	Hollandite	Ba _{1,2} (Al,Ti) ₈ O ₁₆	Tetragonal or monoclinic	30	
	Brannerite	(U,Pu)Ti ₂ O ₆	N/A		12
	Perovskite	CaTiO ₃	Orthorhombic	20	
	Rutile	TiO ₂	Tetragonal		8
	Other ^d			20	0.5

a. Classic synroc-C composition.³⁵

b. Most recent formulation of synroc composition for plutonium disposition at Lawrence Livermore National Laboratory.³⁶

c. May or may not be present with zirconolite.

d. For synroc-C, these are Ti oxides (rutile) and Ca-Al titanates and alloys;³⁷ for LLNL synroc, this is HfO₂ or (U,Pu)O₂.³⁸

would be reasonable natural analogs for the LaBS glass composition. For HLW on the other hand, basalt glasses would be justifiable analogs to the DWPF borosilicate glass in Table 1. Few natural glasses contain alpha-emitters in large enough quantities to provide a reasonable estimate of the effect of radioactivity on glass over geological time.

Ceramics

Ceramics, in contrast to glass, are crystalline materials in which radionuclides from nuclear waste are accepted into the crystal structure by substituting for the components that constitute the phase. Consequently, it is usually possible to predict where an element will go in the crystal structure, based on its ionic radius and charge. A number of different compositions of ceramics may be appropriate for the immobilization of nuclear waste, such as zircon, monazite, apatite, baddelyite, cubic zirconia, or Synroc (Table 2).³⁹ To geologists, crystalline ceramic materials are simply minerals or mineral assemblages, the building blocks of rocks. Many natural analogs exist for the ceramics suggested above.

For plutonium immobilization, Synroc, zircon, monazite, baddelyite, or cubic zirconia may be appropriate waste forms. For simplicity of discussion in this paper, I will focus on three of the most promising possibilities, Synroc, zircon, and monazite. Zircon and monazite are single-phase species that in nature contain significant amounts of actinides (zircon contains U and monazite, U and Th). In fact, both minerals are common in crystalline rocks and are used by geochronologists for the determination of age of crystallization or metamorphism with the U-Pb method of dating. Zircon from the Canadian shield was used to determine the age of one of the oldest known rocks on earth, a 4.02 billion-year-old gneiss.⁴⁰ The oldest known monazite is over 2 billion years of age.⁴¹ These phases are extremely durable, resistant to corrosion and radiation damage, and consequently have survived for extremely long periods of time.

The best known multi-phase ceramic waste form, Synroc, is composed of some combination of the following minerals: zirconolite, pyrochlore, hollandite, perovskite, rutile, and minor oxides and alloys.⁴² Synroc-C included hollandite, zirconolite, perovskite and alloys, and was designed to accommodate high-level waste from the reprocessing of spent nuclear fuel from commercial power reactors (Table 2).⁴³ Hollandite hosts fission products such as Cs, Ba, Rb, K, and Cr.⁴⁴ The tetravalent actinides, Th, U, Pu, and Zr are immobilized in zirconolite or pyrochlore, whereas perovskite accommodates Sr, Na, trivalent actinides and rare earth elements. The alloy accepts Tc, Mo, Ru, Pd, S, and Te.⁴⁵

Although Synroc itself does not exist in nature, all of the major phases in it do. Zirconolite is found in igneous rocks such as carbonatites and ultramafic assemblages. The oldest known zirconolite, over 2.5 billion years old, is from a layered mafic complex in Australia.⁴⁶ Pyrochlore, known as a source of rare elements such as Nb, Ta, and W, is found in carbonatites and both nepheline syenites and granite pegmatites.⁴⁷ Pyrochlore is known to range in age from 16 million years to at least 1.4 billion years old.⁴⁸ Perovskite is usually found in rocks with low SiO₂ content and thus is a common mineral in the upper mantle of the earth. Hollandite is found in rare volcanic rocks with compositions high in K₂O, BaO, and TiO₂ and low in SiO₂.⁴⁹ Rutile is a very common accessory mineral found in a wide variety of rock types.

Table 2 gives the compositions of these waste forms. It includes two formulations for Synroc—the standard Synroc-C formulation, developed by Ringwood⁵⁰ and the most recent compositions used in trials at Lawrence Livermore National Laboratory (LLNL).⁵¹ One of the LLNL formulations is predominantly pyrochlore, of which zirconolite is a derivative structure, and could accommodate a high percentage of plutonium. Lawrence Livermore National Laboratory has recently done experiments on the incorporation of impurities into Synroc. For the expected range of impurities and impurity loading based on the waste stream, Synroc accommodates them by forming the phases pyrochlore, zirconolite, brannerite ((U, Pu) Ti₂O₆), rutile/silicate, and an actinide oxide in varying amounts.⁵² Pyrochlore has the additional benefit of accepting large quantities of U into its structure (U is one of the major elements in pyrochlore), which will offset two problems: that of high quantities of U in the waste stream and the possible need to purposefully include depleted U to decrease the likelihood of a criticality event from U-235 after Pu-239 decays (further detail on this topic is covered later in this paper).

The selection criteria for a waste form to immobilize excess weapons plutonium must address both short-term and long-term goals: to secure plutonium from reuse by both terrorists and host nations and to prevent doses of plutonium to humans and the environment, respectively. In the short term, the waste form should (1) be resistant to recovery of plutonium and (2) have a mature production technology and low production costs and timing. In the long-term the waste form must have (1) good chemical durability over geologic time, (2) an ability to accommodate radiation damage from radioactive waste, and (3) an ability to avoid criticality.

The Appendix presents a systematic comparison of glass and ceramics in terms of these criteria.

CERAMIC AND GLASS: A COMPARISON OF UNCERTAINTIES AND ADVANTAGES

Some of the questions associated with Synroc and LaBS glass issues may be resolved in the short term, whereas other issues require intensive, long-term work. Table 3 displays a comparison of uncertainties concerning LaBS glass and Synroc. Uncertainties associated with glass fall into the categories of glass production, chemical durability, and radiation damage. In glass production the largest uncertainties are related to the reliability and safety of the high-temperature melting process behavior of the glass during the first and second glass pours, such as the effects of glass fracturing on chemical durability, and the significance of PuO_2 crystallization. Experiments on the effects of water on microfractures in glass and others on the behavior of crystalline PuO_2 with respect to chemical durability, radiation damage, and proliferation resistance will most likely require more than a few months to complete, if any have been planned by the DOE.

In terms of chemical durability, the effect of colloid behavior on the transport of actinides, and in particular, plutonium, is another uncertainty associated with LaBS glass, which will not soon be resolved. LaBS glass is a new composition about which there is scant available data. As a result, we know little about the type and conditions of formation of colloids and less about their ability to bind up plutonium and transport it. Many leaching experiments require long reaction times (years). Another long-standing and unresolved issue is that of radiation damage to glass, specifically to the LaBS glass composition. I would argue that our understanding of radiation-damaged glass is in the early stages. We are still learning which questions are appropriate to ask, and we will learn more only after considerable research on the topic. Furthermore, no natural analogs exist to provide an understanding of radiation damage in glass over geologic time.

In ceramics a number of uncertainties also await clarification. As with glass, the effect of radiation damage on the chemical durability of ceramics remains an unresolved question. With ceramics we have the advantage of using natural analogs as an indication of the effects of radiation damage. Although most radiation-damaged minerals remain chemically durable with regard to actinide retention, the underlying question of radiation effects from plutonium over geologic time may not be resolvable. Like glass, the role of colloids in leaching of ceramics requires more research. Another uncertainty associated with ceramic production involves the effects of density on chemical durability for current Synroc formulations. If lower density Synroc is found to be deficient, then variations in production methodology should be investigated

Table 3: Uncertainties associated with glass and Synroc.

Uncertainty	Glass Experiment needed for resolution	Timing	Uncertainty	Synroc Experiment needed for resolution	Timing
<i>Glass production Safety & reliability</i>	Melter development	Long-term	<i>Chemical durability</i> % Theoretical maximum density effects on durability	(1) adjust production methods, temperature of sintering, pressure of pressing, size of powders (2) Leach tests on current lo-density synroc products	Short-term Long-term
Fracture effects on chemical durability	Leaching tests on fractured and microfractured samples	Long-term	Colloid formation	Leach tests in flowing and static water	Long-term
Significance of PuO ₂ crystals	Leach tests, radiation effects tests, dissolution in acid tests on PuO ₂	Short-term	<i>Radiation damage</i>	Leach tests on actinide-doped samples and further comparison with natural samples	Long-term
<i>Chemical durability</i>	Leach tests in flowing and static water	Long-term			
<i>Radiation damage</i>	Radiation damage tests and leach tests on actinide-doped samples	Long-term			

Table 4: Advantages of glass and synroc.

Glass	Synroc
<ul style="list-style-type: none"> • Ability to accept impurities. • Potential ability to withstand radiation damage. 	<ul style="list-style-type: none"> • Better proliferation resistance. • Ability to accommodate at least twice as much U-238 and Pu-239. • No effects from 2nd HLW glass pouring. • Chemical durability over time. • Production safety.

to address the density problem. It will take considerable time to perform adequate leach tests to assess the affects of low density. The ability of Synroc to produce plutonium-binding colloids during alteration also requires attention over the long-term.

Ceramics and glass appear to be basically equivalent in terms of maturity of production technology, timing of waste form production, and in cost of production. However, with respect to other criteria, each waste form appears to have certain advantages. These are summarized in Table 4.

Glass has advantages over ceramic in its theoretical ability to accept a wide range of impurities into its structure and its potential ability to withstand radiation damage. Ceramics and Synroc in particular, on the other hand, are proven to have corrosion rates at least one or more orders of magnitude lower than glass, and thus should better contain the waste over the geological time frames necessary for plutonium disposition. In addition, Synroc is more stable thermally than glass, and, unlike glass, its chemical durability will not be affected by high temperatures that may be encountered in the geologic repository. Furthermore, Synroc is able to withstand the temperatures of reheating that the waste form will experience during the second pour of HLW glass with only minor effects. Synroc can easily accommodate more depleted U than glass to address the problem of decay of Pu-239 into mobile U-235. The dilution of the enriched U by depleted U will help prevent future criticality events that might be caused by U-235 in a geologic repository. Ceramics in general are not soluble in nitric acid, unlike glass, and accordingly the PUREX process cannot be easily adapted for plutonium extraction. The failure modes of Synroc production are more benign than those of glass production.⁵³ Worker safety should be an important consideration for a large-scale effort for excess weapon plutonium disposition.

THE POLICY CHOICE

The criteria that form the basis for the waste form decision should be proliferation resistance, production technology, chemical durability, and criticality safety. In the short term, proliferation resistance is the most important selection criterion. Ceramics (in particular, Synroc) are more resistant to extraction of plutonium than glass. This basic difference sets ceramics apart from glass. Because extraction of plutonium from ceramics would require major modifications to presently-existing separation facilities and construction of new ones, such activity would be easier to detect through safeguards than extraction from glass.

Among the selection criteria that apply to the long-term, chemical durability and criticality safety are the most significant. Considering the large uncertainties in predicting future geologic events and the state of a repository environment, we should rely on the material most likely to resist alteration and corrosion and impede the release of actinides into the environment, which is ceramic.

Whereas criticality safety was not a criterion in the selection of a waste form for HLW immobilization, it should be for plutonium disposition. To prevent criticality events due to Pu-239's mobile daughter-product, U-235, depleted U should be added to the waste form to dilute U-235. Only ceramic can adequately support the addition of large amounts of actinides to its composition.

In September 1997, the Materials Disposition office at the DOE announced its decision to use Synroc to immobilize excess weapons plutonium.⁵⁴ The decision was based on five criteria, and in four of these areas the DOE judged that ceramic held advantages over glass.⁵⁵ The criteria and findings were similar to those of this paper. In evaluating waste form performance, criterion (1) focuses on the repository environment. DOE found that ceramics would be more durable than glass, and a DOE panel found that ceramic would provide better criticality assurance because it can incorporate more U-238 than can glass.⁵⁶ Criterion (2) was environment, health, and safety. DOE disclosed that workers handling the glass product would be exposed to eight times the neutron dose rate of the ceramic product due to alpha-n reactions from boron in the glass.⁵⁷ Criterion (3) was costs, and it was noted that increased worker protection against radiation from handling the LaBS glass would result in increased costs. Also, costs for LaBS glass would be higher than for ceramic as a result of the higher loading of plutonium in ceramic. Overall, this would result in fewer cans of immobilized plutonium requiring fewer canisters of high-level waste glass. For the final criterion (4), nonproliferation, DOE found that ceramic provides an advantage over glass due to its greater resistance to plutonium extraction. DOE noted that the plutonium extraction process from ceramic is more complicated and less well

developed than that from glass. In terms of detection of theft or diversion of plutonium during waste form processing, ceramic provides the additional advantage of easier non-destructive assay. Alpha-n reactions from B in glass interfere with the verification of plutonium concentration.

Although DOE is currently advancing ceramic as the waste form of choice for plutonium immobilization, it does so by issuing tepid statements on the advantages of ceramic over glass. Overall, the DOE emphasized that the advantages of ceramic over glass were small. Even though there was a shortage of data on the two waste forms to make an adequate comparison, DOE moved the waste form decision up a year, and clearly not all necessary experiments could be completed in such a shortened time frame.

CONCLUSION

Recently, both LaBS glass and Synroc ceramic were competing waste forms for the can-in-canister option to immobilize excess weapons plutonium. On the basis of the technical information presented in this paper, ceramics are the preferable waste form for plutonium immobilization. Ceramics perform better than glass in terms of their chemical durability, their thermal stability, their proliferation resistance, their ability to withstand heating that they will encounter during the pouring of the canister HLW glass, and their ability to dilute U-235 formed from the transmutation of Pu-239. Synroc ceramic is equivalent to LaBS glass in terms of maturity of production technology and timing of production according to DOE estimates.

This comparison can be extended to the immobilization of HLW. Although this material has different properties than plutonium (for example, higher beta and gamma emission and volatilization problems), it is time to reconsider ceramics as a waste form for HLW. For long-term disposition, the main concern for HLW, ceramics are superior to glass due to their greater chemical durability. We should begin to explore in earnest other promising phases such as zircon, monazite, and baddelyite and develop new Synroc assemblages. Nuclear waste and fissile materials are presently abundant and it is our responsibility to deal with them in the best manner available.

APPENDIX: SELECTION CRITERIA FOR THE WASTE FORM

RECOVERABILITY

Unfortunately, no completely irreversible disposition methods exist for plutonium. Nonetheless, the form and design used should be the most irreversible possible. If it is more difficult for the host nation to extract plutonium from the immobilized form than spent fuel, both in terms of cost and institutional capability, then the waste form is successful. In comparison to host nations, it is assumed that terrorists would want a much smaller quantity of plutonium. However, even one canister of immobilized plutonium would contain enough material for 12 weapons (at 4 kg Pu per bomb).

In the case of both glass and ceramic, the can-in-canister design will discourage terrorist attack by the sheer mass of the canisters (each will weigh over a ton) and the radiation barrier of 200–500 R/hr at 1 m from the surface of the canister 30 years after fabrication of radioactive HLW glass.⁵⁸ If terrorists were able to steal these canisters, they may somehow be able to break the cans containing plutonium out of the radioactive canisters, but this is much more likely accomplished by a host nation, which would have the facilities, institutional networks, and funding to organize such a process. If the design is successful and the cans are an integral part of the canisters, then both host nations and terrorists would have to handle the material remotely, and would have to dissolve the entire canister to extract plutonium. This process would be easier for host nations, who have the institutional support, but it would prove expensive for both parties.

Two recent DOE reports have criticized the can-in-canister design as not adequately meeting the spent fuel standard.⁵⁹ The Red Team Report⁶⁰ claims that the cans are mechanically separable from the HLW glass relatively rapidly and with simple equipment. Once the radiation barrier is gone, the plutonium-containing cans could easily be removed and handled because shielding would no longer be required. The DOE is now beginning tests to ascertain how separable the cans are from the glass matrix.⁶¹ If the cans are determined to be easily separable, a new design would be required in which the cans are made an intrinsic part of the HLW glass. This could be accomplished by making the cans fracture with the HLW glass if the canister is breached or by using small pellets of plutonium-containing ceramic or glass.⁶²

A recent study of the proliferation resistance of borosilicate glass suggested that a critical mass of Pu (4.7 kg) could be recovered from only 613 kg of borosilicate glass with a waste loading of 2 wt percent Pu using simple bench-

top methods (a recovery rate of 27 percent).⁶³ For comparison, one canister of glass is expected to weigh approximately 1,800 kg,⁶⁴ suggesting that for homogeneously mixed plutonium at 10 wt percent, it could produce over 70 kg plutonium. To extract plutonium, the glass would first have to be crushed, ground, and dissolved in nitric acid, and then the PUREX process could be applied to separate plutonium.⁶⁵ To this end, the United States could augment already-existing PUREX facilities at Hanford, the Savannah River Site, and the Idaho National Engineering Laboratory with new large-scale crushing, grinding, and dissolving facilities. Consequently, it would be about as easy to extract plutonium from a glass waste form as from spent fuel.

More importantly, LaBS glasses were developed to serve as a temporary storage form for the actinides americium and curium, which have commercial value. Recent research on the dissolution of LaBS and Sr-Al-borosilicate glasses to recover americium and curium was conducted by Savannah River Site scientists. Erbium was used as an analog for Am and Cm in the experiments in which the glasses dissolved completely after 2 hours in nitric acid at 110°C.⁶⁶ Workers were able to recover 100 percent of the lathanides from this process. Thus, from the point of view of the host nation, LaBS glass offers little resistance to extraction of plutonium, certainly the same or less than that of spent fuel.

The proliferation resistance of ceramics is not as well documented as that of glass, although one DOE study suggests that ceramics would be more difficult to grind and dissolve.⁶⁷ Ebbinghaus and others⁶⁸ claim that titanate-based ceramics, like those used in Synroc, are not soluble in nitric and hydrofluoric acids, those used in the PUREX process. The acids in which Synroc is soluble actually interfere with the PUREX process, and consequently the process cannot be easily adapted for use to extract plutonium.⁶⁹ The difficulty in dissolving ceramic materials is illustrated by the techniques used to put these materials into solution for industrial and experimental purposes. Peterson and others⁷⁰ investigated the use of perovskite, a component of Synroc-C, as a source of titanium. They achieved over 90 percent recovery of titanium for dissolution in acid concentrations above 70 percent H₂SO₄ (with best results for solutions above 90 percent H₂SO₄), at temperatures above 200°C for 35-mesh size particles and above 150°C for <100-mesh-size particles.⁷¹ The time required for dissolution ranged from a few minutes to 6 hours, depending on the above parameters. Similarly, zircon and monazite require complete dissolution for the U-Pb method of geologic age-dating. The experimental procedure for dissolving these materials follows a well established procedure of combining the minerals with 6N HF and a small amount of HNO₃ in a teflon "bomb" at 240°C for 2 days.⁷² The teflon "bomb," a screw-top teflon bottle, creates a pressurized environment when heated.

Based on the above data, the only proliferation resistance offered by LaBS glass is that of the canister design, which will be common to both waste forms. Ceramics, on the other hand, offer the additional resistance of having no established industrial-scale processes or facilities to dissolve and extract plutonium. Acids such as HF and H₂SO₄ are necessary for plutonium extraction, but these acids are not used in the standard PUREX process. As a result, a host nation that was determined to extract plutonium from its ceramic waste form would need to build new facilities and develop new technologies to extract large quantities of plutonium. In comparison to extraction of plutonium from spent fuel, then, it is more difficult to extract plutonium from ceramic, but as easy or easier to extract plutonium from LaBS glass.

Production Technologies

There is already much experience in the production of glass to contain HLW (see Figure 3). Initially, two main vitrification processes were developed, one by France (AVM) and one by Germany.⁷³ Glass production in France began in 1969 with the PIVER (*Pilote Verre*) plant, which operated until 1972, producing a total of 12 MT of glass.⁷⁴ In 1978, the *Atelier de Vitrification de Marcoule* (AVM) facility began producing HLW glass using a continuous vitrification process and by 1995 had produced 857.5 MT of glass.⁷⁵ The feed solution is first dried and calcined and then mixed with glass frit in an induction-heated metal melter. The U.K. adopted the AVM process for its Waste Vitrification Plant at Sellafield.⁷⁶

The PAMELA facility in Belgium, begun in 1985, uses the German process. The material is vitrified in a single-step in a ceramic melter, where glass frit and HLW are loaded into the melter and drying, calcining, and melting occur in sequence.⁷⁷ China, still in the R & D stage, plans to adopt the German process.⁷⁸ Russia has vitrified HLW in phosphate glasses at their Mayak facility where operations began in 1987, operated for 1.5 years, and restarted in 1991, producing a total of 1,800 MT of glass by 1995.⁷⁹ Russia is now developing a borosilicate glass to handle an increased radionuclide content.⁸⁰ Japan is also in the process of developing a borosilicate glass composition for its newly-built vitrification facility at Tokai, although this facility may have been affected by recent shutdowns.⁸¹

The United States presently has two operating vitrification facilities, the Defense Waste Processing Facility (DWPF) at the Savannah River Site and the West Valley, New York, facility. The DWPF, which began processing radioactive waste from defense installations in April 1996, employs a complex procedure. The HLW must first be processed to remove mercury and organic materials prior to mixing with glass frit in a melter.⁸² The DWPF will produce 6,000 canisters of HLW glass, at 1,800 kg per canister, over the next 25

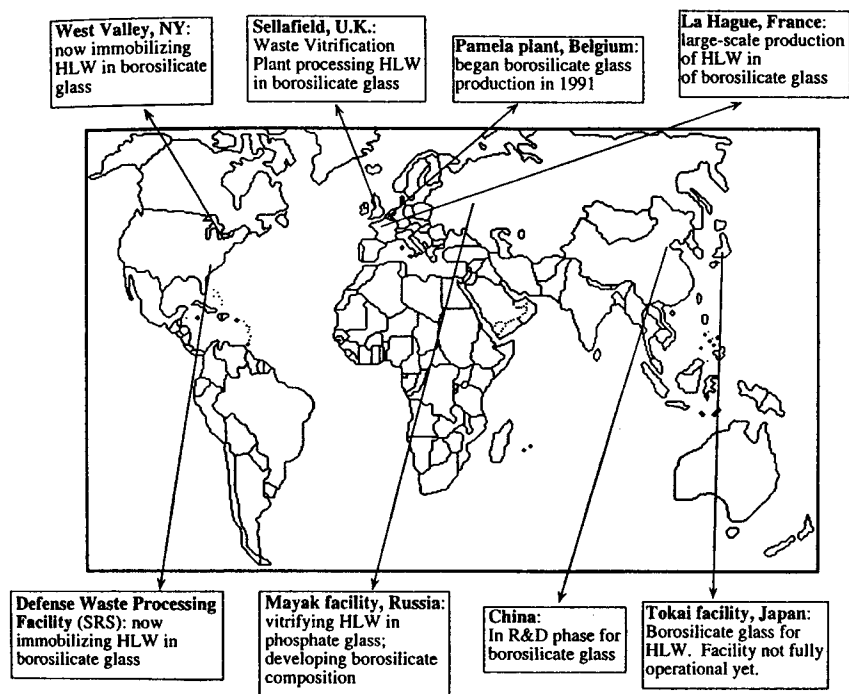


Figure 3: Map of vitrification technologies and accomplishments in various countries.

years.⁸³ In contrast, the lifetime of the West Valley facility will be only 2.5 years, and the metal melter will produce approximately 300 canisters.⁸⁴ Other vitrification facilities are in the R & D phase.

However, although HLW glass has been produced on an industrial scale for the past few decades, the technology to immobilize plutonium in glass requires special conditions, such as glove-box-size apparatus and significantly higher processing temperatures and is not as advanced as regular borosilicate glass technology.⁸⁵ Although ceramics have not been used to immobilize HLW at an industrial scale in any country, a group at ANSTO (the Australian

Nuclear Science and Technology Organization) have been producing Synroc using large-scale production technology at the Synroc Demonstration Plant (SDP) since 1987,⁸⁶ and since this technology may be used as a benchmark to compare with glass production technology, such a comparison of production technologies for ceramics and glass suggests that they are at similar levels for the immobilization of plutonium. In fact, DOE estimates of production time schedules for the can-in-canister option for both ceramic and glass cans are exactly the same.⁸⁷ Cost estimates for the ceramic and glass can-in-canister options are also identical.⁸⁸ On the basis of cost and scheduling estimates, it appears that the DOE sees little difference in the difficulty of production for either glass or ceramic.

LaBS glass will be produced using melter technology substantially modified to handle fissile materials. Workers at the Savannah River Site are planning to use bottom-pour, inductively heated melters, with platinum-rhodium crucibles and platinum stir rods.⁸⁹ To the LaBS glass base composition will be added 1.5 kg of 5-10 μm PuO_2 powder.⁹⁰ The residence time in the melters is approximately 4 hours at a temperature of 1,475°C.⁹¹ The melters will be scaled for glove-box work, and the geometry of the melters will provide some prevention against criticality events.

A number of pitfalls face the planned glass production technology. First is the safety issue of failure modes. In a melter system failure, workers are dealing with a plutonium-rich corrosive liquid at temperatures of 1,475°C, which has the potential to be extremely dangerous. Secondly, devitrification and crack formation result from quenching the glass melt. Further devitrification and crack formation occur during the pouring of the canister HLW glass. Cracking, as discussed earlier, can lead to accelerated rates of leaching. In a number of experiments, the second glass pour resulted in the formation of PuO_2 crystals in the LaBS glass.⁹² The presence of these crystals may not affect the long-term performance of the material, but we know little about the behavior of PuO_2 in a geologic environment. Not much information is available on the chemical durability of PuO_2 (will plutonium be leached out of the solid), radiation damage effects on PuO_2 , or the proliferation resistance of PuO_2 (how easy is it to dissolve and extract plutonium). In addition, formation of PuO_2 crystals raises questions about the homogeneity of PuO_2 in the glass. It is important for criticality and nonproliferation reasons to ensure that PuO_2 is distributed homogeneously in the glass. Areas of concentrated PuO_2 crystals may not receive adequate neutron absorption, leaving open the possibility of criticality. Glass may pose a problem in terms of materials counting and accountability in that the plutonium needs to be distributed homogeneously to detect it with low uncertainty. The Red Team Report suggests that this homogeneity in glass may be difficult to achieve.⁹³

Ceramics can be produced by a number of methods such as cold pressing followed by sintering, hot pressing, and hot isostatic pressing. At ANSTO, the Synroc Demonstration Plant has been on-line since 1987 and has fabricated more than 6000 kg of Synroc with simulated HLW.⁹⁴ The method they follow is to calcine the acid HLW and Synroc-C powders at 700°C for 1–2 hrs., add 2 wt percent Ti powder, load the mix into bellows, and hot press at 1,150°–1,200°C at 14–21 MPa for 2 hrs.⁹⁵ This method produces Synroc-C at 99 percent of its theoretical maximum density.⁹⁶ In contrast the Department of Energy intends to use a cold-press-and-sinter method to produce Synroc, similar to the production methodology for MOX pellets for nuclear fuel. Hot pressing usually produces a denser material, but it is more expensive than cold pressing. At the Lawrence Livermore National Laboratory, Synroc is processed by first mixing 5 μm -size component powders and calcining them at 600°C for 1 hour, then 1–5 μm -size PuO_2 powder is added and the mix is cold pressed at 15–20 MPa and then sintered at 1,350°C for 4 hours.⁹⁷ The final product has greater than 90 percent of its theoretical maximum density.

Synroc production is not without its own set of pitfalls. One disadvantage it shares with glass production is that of the fine particle size of the PuO_2 and other component powders. One to five microns is a respirable size and these powders have a tendency to disperse within the glove boxes used to handle them. Prior to the initiation of ceramic or glass production the DOE must deal satisfactorily with this issue. In addition, Synroc that is produced by cold pressing and sintering reaches only 90–95 percent of its theoretical maximum density. The most serious problem resulting from low density Synroc is its reduced chemical durability over the long term. Static leaching experiments on Synroc suggest that leach rates are lowest for densities of at least 98 percent; the leach rate for some species in Synroc increases by at least 2 orders of magnitude for a density decrease of 98 percent to 90 percent.⁹⁸ At present, there is no information on the leach rates of plutonium as a function of density for the proposed composition of Synroc. As a result, it is important for the Department of Energy program to try to increase the density of the plutonium-containing Synroc.

The Lawrence Livermore National Laboratory has also done a number of experiments trying to produce zircon and monazite by the cold-press-and-sinter method, with only partial success. Zircon component powders that were cold pressed and sintered at 1,650°C for 1 hour resulted in theoretical densities of 65–75 percent.⁹⁹ Monazite that was sintered at 1,350°C resulted in a theoretical density of 71 percent.¹⁰⁰ In neither the zircon or monazite experiments did all the material react to form the intended phases. Ultimately, zircon and monazite may be promising waste forms for HLW and plutonium in

terms of chemical durability and ability to withstand radiation damage, but their production technology is too immature to immobilize excess weapon plutonium in a timely manner.

Chemical Durability

The chemical durability of a material refers to its ability to resist corrosion and chemical alteration, which usually result from exposure to aqueous solutions. In the case of a waste form, corrosion can result in the release of radionuclides. In a geologic repository, radionuclides may be transported in the groundwater to the biosphere. Chemical durability is usually measured as a corrosion rate, dissolution rate, or leach rate. Leach rate is measured in $\text{gm/m}^2\text{day}$ and commonly varies between 10^{-4} – ~ 1 $\text{gm/m}^2\text{day}$ for borosilicate glasses and Synroc ceramics.¹⁰¹

A number of variables affect the corrosion rates of different waste forms. The composition and ionic strength of the leachate, the pH of the leachate, and the temperature are the three most important parameters that affect corrosion rate.¹⁰² The flow rate of the leachate, the redox potential, the waste package materials, the waste loading, and radiolysis of the leachate are also factors that affect corrosion rates.¹⁰³ For ceramics, the production methodology (hot pressing versus cold pressing, for example) can also affect chemical durability.¹⁰⁴ For a material such as Synroc, it is important to consider the corrosion behavior of each phase separately. In the case of plutonium immobilization, the leachability of pyrochlore or zirconolite are the most significant, because they are host phases for plutonium.

Workers have done numerous experiments on borosilicate glass corrosion under a wide range of conditions.¹⁰⁵ Under experimental conditions of constantly flowing deionized water at 90°C , the range of corrosion rate for borosilicate glass is from 0.5 – 5 $\text{g/m}^2\text{day}$.¹⁰⁶ Compare this range to long-term corrosion rates of 0.01 – 0.001 $\text{g/m}^2\text{day}$.¹⁰⁷ The difference in corrosion rate ranges may have to do with silica saturation of the leachate. Under static groundwater conditions, the leachate becomes saturated in SiO_2 relatively rapidly, and the corrosion mechanism slows. Werme and others¹⁰⁸ found a corrosion rate of 10^{-3} $\text{g/m}^2\text{day}$ in silica-saturated conditions (static conditions) and a rate of 1.5 $\text{g/m}^2\text{day}$, over 3 orders of magnitude higher, for silica undersaturated conditions (flowing conditions).

When glasses corrode, they form alteration layers on their surfaces. A typical cross-section of these surface layers shows that adjacent to the uncorroded glass is an amorphous layer, including colloidal species, followed by an outer layer of crystalline phases, such as analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$).¹⁰⁹ The phases

that form depend on the temperature and the compositions of the glass and the leachate. Colloids, fine particles 1 nm–1 μm in size that remain indefinitely suspended in aqueous solutions, are particularly problematic for nuclear waste immobilization.¹¹⁰ Originally, it was assumed that the waste form would break down and dissolve and that radionuclide release was controlled by the solubility of individual nuclides in ground water, the flow rate of the ground water, and the ability of other species to sorb them out of solution. Recent studies¹¹¹ have found that colloids form on the glass surfaces during alteration, and these colloids can bind Am, Cm, and Pu (but not Np). Under repository conditions, the formation of colloids is supplemented by colloidal material formed from the surrounding bedrock and backfill.¹¹² In some experiments, actinides like Pu, Am, and Cm continued to be released after the solubility limit had been reached due to the formation of colloids binding these actinides.¹¹³ Vernaz and Gordon¹¹⁴ report that for plutonium-containing borosilicate glass, after leaching for one year at 90°C, over 80 percent of the leached plutonium was in colloidal form. Consequently, transportation of Pu (and Am and Cm in the case of high-level waste) depends on the behavior of colloidal phases under repository conditions. A recent study compared models of transport of plutonium as a solute in groundwater with that of plutonium in colloids and found that plutonium transported as colloids traveled five times as far.¹¹⁵ It is not yet known how rapidly and to what extent ceramics will produce colloidal species during aqueous alteration.

In general, some ceramics appear to have chemical durability at least 2–3 orders of magnitude higher than that of glass.¹¹⁶ Species like zircon, zirconolite, and monazite can release radionuclides by two methods: grain boundary (or volume) diffusion, which is usually extremely slow at low temperatures, and dissolution of the phase in aqueous solution, the more probable route for radionuclide release under repository conditions.¹¹⁷

Monazite has a corrosion rate of $<0.002 \text{ g/m}^2\text{day}$ in 90°C water in static conditions.¹¹⁸ Similar low corrosion rates exist for Synroc-C. Calcium, one of the most mobile elements in Synroc,¹¹⁹ is leached at a rate of $0.02 \text{ g/m}^2\text{day}$ in 90°C water in static conditions; whereas Zr is released at a rate of $<8 \times 10^{-4} \text{ g/m}^2\text{day}$ and Ti is leached at a rate of $<2 \times 10^{-4} \text{ g/m}^2\text{day}$ in 90°C water in static conditions.¹²⁰ The actinides leach from Synroc at rates of $2 \times 10^{-5} - 5 \times 10^{-4} \text{ g/m}^2\text{day}$.¹²¹ Moreover, a recent study has shown that the long-term leach rate for plutonium (from zirconolite) is $1 \times 10^{-7} \text{ g/m}^2\text{day}$ at 70°C, with the water changed daily (this approaches flowing water conditions, i.e., undersaturation).¹²²

In terms of actinide-containing phases in Synroc, the chemical durability varies. Natural zirconolite rarely shows evidence of alteration (chemical attack followed by dissolution of the species).¹²³ Natural pyrochlore, on the other hand, is more commonly altered. At high temperatures (350°–550°C and

300–400 MPa) pyrochlore alters by ion exchange in the tunnels of the pyrochlore structure.¹²⁴ This type of ion exchange in pyrochlore is limited to ions with low valence, so that Th and U in natural samples are not released.¹²⁵ At low temperatures and pressures, pyrochlore alters only by leaching mechanisms, and again, the phase retains its actinides.¹²⁶

A comparison of corrosion rates between glass and ceramics indicates that ceramics perform better than glasses in terms of chemical durability. The glass data are predominantly for borosilicate glasses, not LaBS glass, and the Synroc data are for the Synroc-C composition, not the modified composition planned for plutonium disposition.¹²⁷ In general, it is presently very difficult to make an absolute comparison of leaching rates of plutonium from the waste forms, not simply because target waste form compositions are not used in experiments, but the experimental conditions and reporting vary. Grain size, measured as surface-to-volume (S/V) ratio, leach time, pH, temperature, plutonium concentration, and static/flowing/daily change water conditions need to be equivalent for an absolute comparison of glass and ceramic plutonium leach data, and they are not.

Enough data exists on leaching of plutonium from glass and ceramic to conclude that more systematic studies are required. Vernaz and Gordon¹²⁸ tested R7T7 borosilicate glass¹²⁹ containing 0.85 wt percent PuO₂. In static tests with a S/V ratio of 50 m⁻¹ at 90°C, the leach rate of Pu-238 after 182 days was 0.38 g/m²day at a pH of 8.6. Under the same conditions, after 182 days the leach rate of Pu-239 was 0.087 g/m²day at a pH of 9.5. The discrepancy in leach rate between the two isotopes of plutonium could be due to the difference in pH.¹³⁰ Bates and others¹³¹ recently reported results from plutonium leach tests on the Defense Waste Processing Facility borosilicate glass composition with 7 percent Pu (P7 glass) and 2 percent Pu, 2 percent Gd (G2 glass) added. Static tests using an S/V ratio of 20,000 m⁻¹ at 90°C over 182 days resulted in plutonium leach rates of 3.8×10^{-6} g/m²day for P7 at a pH of 11.3 and 1.6×10^{-5} g/m²day for G2 (pH unreported).¹³² These rates are much lower than those reported by the French scientists and may have to do with the differences in grain size (powder versus monolith), pH, concentration of plutonium, or initial glass composition.

Vance and others¹³³ describe plutonium leach tests on a Synroc composition that contains 70 wt percent zirconolite, 15 wt percent rutile, and 15 wt percent nepheline (NaAlSiO₄) with a PuO₂ concentration of 10.9 wt percent. Leach tests were done on Synroc with a S/V ratio of 10 m⁻¹. After 28–84 days, plutonium leach rates were between $1.9\text{--}3.7 \times 10^{-6}$ g/m²day at 90°C (pH not reported).¹³⁴ At 200°C under the same conditions, plutonium leach rates ranged between $2.1\text{--}3.8 \times 10^{-6}$ g/m²day. Increased temperature appears to have had little effect on plutonium release rate in Synroc. These leach rates

are 4–5 orders of magnitude less than the plutonium leach rates of Vernaz and Gordon,¹³⁵ but similar to those of Bates and others.¹³⁶ A number of procedural discrepancies exist between the results of Vance and others and those of Bates and others, including grain size, pH, time, and plutonium concentration. Consequently, it is difficult to draw definitive conclusions from this data.

The only data on plutonium leaching from LaBS glass originates from ongoing work at Lawrence Livermore National Laboratory. Initial comparisons of the durability of LaBS glass with that of synthetic zirconolite show that zirconolite is one to three orders of magnitude more durable than glass at both high and low pH. For example, for test conditions of 70°C and a flowing buffer solution at a pH of 4, zirconolite had a minimum dissolution rate of 0.001 g/m²day.¹³⁷ In comparison, at a pH of 2, LaBS glass (the LaBS 1 composition) had a dissolution rate of 3 g/m²day and at a pH of 5, LaBS glass had a dissolution rate of 0.08 g/m²day, suggesting that at a pH of 4, assuming linear behavior, LaBS glass has a dissolution rate of 0.3 g/m²day, more than an order of magnitude higher than that of zirconolite.¹³⁸

Aside from chemical durability is the related issue of thermal stability. Ceramics in general are stable at high temperatures (>200°C), whereas glasses often are not. Initial borosilicate glass compositions dissolved completely over a period of a few days at temperatures > 300°C.¹³⁹ Little recent data is available for leach tests on glasses performed at temperatures greater than 90°C. One study notes severe cracking in the French R7T7 borosilicate glass at temperatures above 250°C.¹⁴⁰ Synroc, in contrast, is quite stable at temperatures of 200°C, as is suggested by leach data on plutonium at 200°C discussed earlier. The issue of thermal stability is important in consideration of geologic repository environment. For the proposed Yucca Mountain repository, limited repository space and costs will require close-packing of thermally hot spent fuel, with which immobilized plutonium canisters will be interspersed. Local repository temperatures may reach 200°C, at least for the first 300 years of the repository's existence.¹⁴¹ Thus the waste form needs to remain stable at high temperatures.

Another issue that has received almost no attention but pertains to the chemical durability of glass and ceramic is that of the effect of fractures on the durability of these materials. Fractures will be present in the glass product immediately after production due to the effects of quenching. Additional fractures and devitrification may result from the second pouring of HLW glass for the can-in-canister concept. These fractures provide more surface area on which corrosive aqueous liquids can act. In addition, the presence of water on microfractures creates stresses, which will cause the fractures to propagate. Alternatively, cracks in glass may form in response to devitrification where

contrasts in the coefficient of thermal expansion will cause stresses to mount at these locations in the glass and will create microcracks.¹⁴² Fractures may also be present in Synroc but studies show that over time fractures and cracks in glass propagate faster than those in crystalline materials.¹⁴³ One estimate of time to complete dissolution for a glass log canister containing plutonium is 100,000 years,¹⁴⁴ based on modeling that assumes that fracturing would increase the surface area by 5 times. Fracturing is a dynamic process and fracture growth over time may increase the surface area by 50 times.¹⁴⁵ Such an increase in surface area would reduce the lifetime of the log to 10,000 years and would definitely affect the transport models on plutonium.

Radiation Damage

Because both glass and ceramic will contain significant amounts of plutonium, an alpha emitter, they both have the potential to sustain radiation damage. They will also receive a lesser dose of gamma radiation. Alpha decay releases an alpha particle (4–6 MeV) with a range of 20 μm , which releases energy by exciting electrons and creating about 100–200 atomic displacements in the crystal structure.¹⁴⁶ Alpha decay also emits the more damaging alpha-recoil nucleus (0.1 MeV) with a range of 0.02 μm . The recoil nucleus does its damage by elastic collisions with other atoms, creating 1,000–2,000 atomic displacements.¹⁴⁷ In contrast, beta particles create a maximum of only 1 atomic displacement per beta emission event.

Glass and crystalline material sustain radiation damage differently, because of the structural differences between the two. Relatively little is known about the effects of radiation on glass, especially from high concentrations of alpha decay events that will be encountered in plutonium waste glass.¹⁴⁸ What is suspected is that glasses sustain volume changes from phenomena such as bubble formation. Volume changes could lead to microcracking and as a result, increased surface area and accelerated radionuclide release. When helium from alpha decay accumulates in glass at high alpha doses (at 10^{18} α -decay events/g), it forms He bubbles.¹⁴⁹ Oxygen bubbles form in some glasses in response to radiolytic decomposition, which occurs as a result of the ionizing effects of gamma and beta radiation.¹⁵⁰ Maximum volume changes produced by radiation damage of 10^{18} α -decay events/g are on the order of 1.2 percent.¹⁵¹ Radiation may have an effect on devitrification in glass, but this is not yet known.¹⁵²

In the case of crystalline material, damage from alpha recoil breaks bonds and makes the materials amorphous. Amorphization results in volume increases that may lead to microcracking, and consequently, to increased corrosion rates. In natural samples, both increased temperatures and geologic time spans result in annealing or recrystallization that corrects radiation

damage. Zircon becomes fully metamict at 10^{19} α -decay events/g.¹⁵³ This amorphous form, named cyrtolite, shows a corrosion rate of 10^{-5} g/m²day, comparable with undamaged species.¹⁵⁴ Amorphous monazite exhibits a corrosion rate of $<2 \times 10^{-3}$ g/m²day in static water at 90°C.¹⁵⁵ Zirconolite becomes fully metamict at 5×10^{18} α -decay events/g and anneals at temperatures above 100°C.¹⁵⁶ At saturation, when zirconolite is fully amorphous, it swells 6 vol. percent at 25°C and 4.3 vol. percent at 200°C.¹⁵⁷ Although the volume increase is high relative to that of glass, plutonium leaching is increased by only one order of magnitude in fully amorphosed zirconolite.¹⁵⁸ Pyrochlore is fully metamict at 3.1×10^{18} α -decay events/g, although it is still crystalline at 0.6×10^{18} α -decay events/g.¹⁵⁹

To put these numbers in perspective, zirconolite that contains 10 wt percent plutonium will experience 2.5×10^{20} α -decay events/g by one million years, long beyond 20 half-lives of plutonium (approximately 500,000 years).¹⁶⁰ Many natural minerals have retained actinides for millions to billions of years after receiving comparable doses of radiation. For instance, 211 million-year-old pyrochlore from British Columbia and 1.3 billion-year-old pyrochlore from New Mexico sustained doses of $0.89\text{--}8.4 \times 10^{19}$ α -decay events/g and $0.2\text{--}36 \times 10^{19}$ α -decay events/g, respectively.¹⁶¹ Some of these pyrochlore samples are amorphous, but others have recrystallized by annealing, and they have not experienced U or Th loss. Natural zirconolite that was exposed to $1\text{--}3 \times 10^{20}$ α -decay events/g have retained their actinides for over 1.5 billion years.¹⁶² In pyrochlore's favor, over long time periods, natural samples anneal alpha-decay damage 2–5 times faster than zirconolite.¹⁶³ Although the ceramic materials clearly show increased swelling in response to amorphization relative to glass, the use of pyrochlore over zirconolite in Synroc may counteract a tendency to microcrack. Pyrochlore is an isometric mineral and will consequently swell isotropically, whereas zirconolite is monoclinic and will increase in volume anisotropically. Therefore, an increase in volume in pyrochlore may put less stress on the overall crystalline structure than a similar increase in zirconolite.¹⁶⁴ Some of these gains could be counteracted by a less dense Synroc, which is affected to a greater degree by radiation damage than denser material.¹⁶⁵ Lumpkin and others¹⁶⁶ suggest that microcracking from volume expansion can be avoided by keeping the grain size to 1 μm .

Criticality Safety

The immobilization of plutonium in solid form raises concerns about possible future criticality events. To avoid criticality, one can reduce the amount of plutonium in the solid, add neutron absorbers that will take free neutrons out

Table 5: LLNL Synroc phase compositions and element ratios.

Synroc formulation	Phase	Composition
Synroc-1	Pyrochlore	$(Ca_{0.89}Gd_{0.11})(Hf_{0.23}Ce_{0.22}U_{0.44}Gd_{0.11})Ti_2O_7^a$
	Hollandite	$Ba_{1.14}Al_{2.29}Ti_{5.71}O_{16}$
	Rutile	TiO_2
	Other	HfO_2
Synroc-2	Pyrochlore	$(Ca_{0.89}Gd_{0.11})(Hf_{0.23}Pu_{0.22}U_{0.44}Gd_{0.11})Ti_2O_7^a$
	Rutile	TiO_2
	Other	HfO_2
	Waste & neutron absorbers	Ratio
	U:Ce (or Pu)	2:1
	Neutron absorber: Pu analog	
	Gd:Ce	1:1
	Hf:Ce	1:1

a. Ce is used as a plutonium-equivalent in the first Synroc formulation; 0.22 Ce or Pu corresponds to a weight loading of 10 wt percent PuO_2 .¹⁶⁸

ofreside in the United States, circulation, and seek to ensure homogeneity of plutonium distribution in the waste form. The Department of Energy intends waste loadings for glass and ceramic to be approximately 10 wt percent PuO_2 .¹⁶⁷ Neutron absorbers isotopes with large neutron capture cross-sections) such as Hf, Gd, and other rare earth elements will be added to the basic compositions of the LaBS glass and Synroc (or other crystalline forms). Table 1 one shows the most recent LaBS composition at the Savannah River Site Laboratory, in which Gd acts as neutron absorber. Although B and Li have been considered neutron absorbers in some HLW borosilicate glass compositions, corrosion tests show that they leach rapidly and would not remain with plutonium.¹⁶⁹

Table 5 shows representative experimental compositions for pyrochlore and hollandite for two possible formulations of Synroc, one with hollandite and one without. Substitution of Ce for Pu (at 10 wt percent PuO_2) was done for one formulation. Pyrochlore is the only phase that will contain fissile material, and it has one-to-one ratios of Pu (Ce) to both Gd and Hf. In terms of crystal chemistry, the Gd is split between two structural sites, the Ca and the U

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(Zr site in zirconolite) sites, and the Hf is located entirely on the U site. In single phase ceramics, such as zircon and monazite, Hf and Gd are also added as neutron absorbers. In zircon, Hf substitutes easily for Zr^{170} and in monazite, Gd and Eu easily substitute for La.¹⁷¹

A future criticality concern for the immobilized plutonium is that of fissile U-235, the alpha decay product of Pu-239. Although accumulation of U-235 will be slow (the half life of Pu-239 is 24,100 years), U-235 is a more mobile element than Pu-239 because it is more soluble than plutonium in water,¹⁷² and consequently the risk of criticality from it is higher due to selective transport and elemental concentration during repository evolution. One way to handle this problem is to add U-238 (depleted U) to dilute the U-235, thereby avoiding criticality. For example, Forsberg and others¹⁷³ have suggested adding depleted U from the large U.S. stockpiles¹⁷⁴ to the spent nuclear fuel package in a geologic repository. Another way to increase the volume of U-238 would be to make it an integral part of the waste form so that as the waste form corrodes, depleted U will travel with U-235.

Savannah River Site scientists are planning to add Pu to U in a ratio of 60:40 in LaBS glass, so that for 9.6 wt percent PuO_2 , 6.4 wt percent UO_2 will be added.¹⁷⁵ Plodinec and others¹⁷⁶ have shown that for borosilicate glasses only 10–12 wt percent UO_2 can be added, indicating that the solubility of U in borosilicate glass is low, but they received better results for their Löffler-type glass, in which they achieved a solubility of 20 wt percent UO_2 .¹⁷⁷ In contrast, U has a relatively high solubility in ceramics. Natural samples of zircon, monazite, zirconolite, and pyrochlore all contain U and Th in amounts that range from a few ppm to 30 wt percent to pure end-member phases such as $USiO_4$ (coffinite) and $ThSiO_4$ (thorite).¹⁷⁸ Table 5 shows a pyrochlore composition with a 2:1 ratio of (depleted) U:Pu for the purpose of addressing the decay problem.

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By the late 1970s, a number of scientists, particularly in Australia, had developed several promising alternative waste forms. Although some of these waste forms were evaluated in the late 1970s and early 1980s for the immobilization of high-level waste,¹⁸¹ glass again won out.¹⁸² In fact, the basis for the decision to use borosilicate glass to contain high-level nuclear waste (HLW) at the Savannah River Site was due to its alleged advantages over other forms, such as low temperature processability.¹⁸³ These studies calculated the "risk to man" or "dose-to-man" based on the assumption that the transport of radionuclides to the environment from the repository was a more important factor than the waste form.¹⁸⁴ Such analysis disregarded significant differences in the chemical durability, radiation effects, fracture quantity and transmutation effects of the waste forms, and consequently detected no great differences between the forms. It should be noted that although borosilicate glass was selected as the top waste form for high-level waste, the DOE listed Synroc as the second choice.¹⁸⁵ Although these comparative studies essentially halted the funding for alternative high-level waste forms in the early 1980s,¹⁸⁶ research on alternative waste forms for excess weapons plutonium is now being conducted by the Department of Energy (DOE).

Early work on polyphase ceramics as a waste form for defense high-level waste indicated potential problems due to formation of intergranular glass phases that concentrated radioactive Cs.¹⁸⁷ This situation led to concerns about leaching of Cs from the glass phase, due to the lower chemical durability of glass. Because this phase was glass, ceramics appeared to have no advantages over glass as far as Cs retention, and therefore chemical durability was concerned. These glass phases formed due to the presence of high concentrations of silica and sodium in the Savannah River high-level waste.¹⁸⁸ These species are much less abundant in the weapons plutonium to be immobilized, and plutonium and uranium do not tend to enter the glass phase.¹⁸⁹

19. In applying thermodynamics (or a systematic description of material properties, etc.) to chemical reactions, it is convenient to represent a chemical reaction as a molar balance equation with reactants on one side and products on the other. The number placed before each reactant and product so that the total number of moles of material on each side of the equation is the same is called the "stoichiometric number." These are often normalized so that their sum (on both sides) is equal to 1. Because glass, by its very nature, is a poorly structured material, a mole of glass is usually described by an "average" composition. This is just an approximation. It is therefore difficult to assign a precise (or accurate) stoichiometric number to a mole of glass when writing a chemical reaction.
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