SURVEY OF GLASS PLUTONIUM CONTENTS AND POISON SELECTION

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ABSTRACT

If plutonium and other actinides are to be immobilized in glass, then achieving high concentrations in the glass is desirable. This will lead to reduced costs and more rapid immobilization. However, glasses with high actinide conconentrations also bring with them undesirable characteristics, especially a greater concern about nuclear criticality, particularly in a geologic repository.

The key to achieving a high concentration of actinide elements in a glass is to formulate the glass so that the solubility of actinides is high. At the same time, the glass must be formulated so that the glass also contains neutron poisons, which will prevent criticality during processing and in a geologic repository.

In this paper, the solubility of actinides, particularly plutonium, in three types of glasses are discussed. Plutonium solubilities are in the 2 - 4 wt% range for borosilicate high-level waste (HLW) glasses of the type which will be produced in the U.S. This type of glass is generally melted at relatively low temperatures, ca. 1150°C. For this melting temperature, the glass can be reformulated to achieve plutonium solubilities of at least 7 wt%. This low melting temperature is desirable if one must retain volatile cesium-137 in the glass. If one is not concerned about cesium volatility, then glasses can be formulated which can contain much larger amounts of plutonium and other actinides. Plutonium concentrations of at least 15 wt% have been achieved. Thus, there is confidence that high (≥ 5 wt%) concentrations of actinides can be achieved under a variety of conditions.

INTRODUCTION

The easing of tensions between the former Soviet Union and the United States has led to consideration of immobilization of the nuclear materials produced for national defense purposes. This work is focused on the actinides, primarily plutonium, which have been used in nuclear devices. An important driver for this is the concern that the material might be diverted, for example by a terrorist group, who could reconstitute the material into a crude weapon. This could constitute an even greater threat than the material does now. Thus, in the United States, the immobilization task within the Materials Disposition program is funding programs to look at glass and crystalline ceramics as hosts for these materials.

The vitrification working group (which includes representatives from Argonne National Laboratory, Battelle-Pacific Northwest Laboratory, Lawrence Livermore National Laboratory, Oak Ridge National Laboratory, and Savannah River Technology Center) is currently performing research and development to support the U.S. NEPA process, and to assist in selection of a reference process and glass composition, for detailed development and design.

Several process and facility options are being considered and are discussed in other papers in this workshop. For all of the options being considered, a high loading of actinide (≥ 5 wt%) in the glass is desirable. High plutonium loadings can mean a more rapid completion of immobilization. As a result, the period of heightened vulnerability for these materials would be shortened. A more rapid completion of immobilization also would lead to a lower total cost of the program. High plutonium loading can also lead to smaller, less expensive, facilities, particularly for storage of the material.

It must also be recognized that glasses containing large amounts of actinides, particularly Pu-239, also have undesirable facets.

- A glass with a high loading of plutonium is a more attractive target for diversion than a less-concentrated form.
- Processing may be complicated by the need to preclude the possiblity of a nuclear criticality in process vessels, and in the offgas system.
- Assuring that the form does not present a significant potential for criticality in a repository may be made more difficult.

For this paper, the options being considered can be consolidated as follows:

- Addition of high-level waste to make the immobilized actinides a less attractive target for diversion. The nuclear material would be immobilized in a heavily shielded facility, such as the Defense Waste Processing Facility at the Savannah River Site. This option has the least technical risk, because the technology is in hand to vitrify HLW.
- Immobilization of the actinides in a glass containing large amounts of radioactive cesium (or other high dose rate material), to achieve the same purpose. This option entails somewhat greater risk than the first option, because it requires development of new glasses, and potentially new types of melters.
- Production of a highly stable interim glass form. If it were decided to dispose of this material, the waste forms could then be interspersed with either HLW glass or another source of radiation, at a later date. This option potentially could be initiated more rapidly than the others (for example using existing remote facilities), and would make retrieval of the actinides unattractive from a processing standpoint. This option also has a larger technical risk than the first.

Thus, the vitrification working group is concentrating much of its efforts on determining how much plutonium can be dissolved by molten glass to support each of these options. As an important part of these efforts, the group is also working with the repository program to identify the potential for nuclear criticality in a repository due to glasses containing large amounts of actinides. In the sections below, the current state of our progress is summarized.

CRITICALITY PREVENTION STRATEGY

Assuring that a glass containing large concentrations of actinides does not have a significant criticality potential in geologic storage is a daunting challenge. Little or no credit can be taken for man-made structures or components during the long period of time during which such a glass might pose a significant criticality hazard. Thus, chemical means - nuclear poisons (neutron absorbers which can prevent nuclear criticality) - must be included in the glass formulation to prevent nuclear criticality.

Another important part of the challenge comes from the solubility of the actinides in repository groundwater. It is well-known that plutonium is only sparingly soluble in aqueous solutions representative of those in a repository. However, depending on the time frame of interest, the daughter of Pu-239 - U-235 - may pose a more significant risk of a nuclear criticality. Uranium is likely to be more soluble in oxidizing aqueous environments, where U(VI) predominates. However, under reducing conditions, UO_2 forms, which is insoluble in groundwater. Thus, the working group is including both water soluble and insoluble nuclear poisons in the glass formulation. Boric oxide is included in all of the glasses which might be used to immobilize actinides. For each of the options below, different species are used as insoluble poisons.

HIGH-LEVEL WASTE GLASS

Vitrification of a high-level waste is best thought of as a dissolution process. Glass-forming chemicals, either as unreacted chemicals, or as premelted glass frit, are mixed with the waste, and heated to 1150°C. At this temperature, the glassforming chemicals form a melt which dissolves the high-level waste (HLW). The melt is then poured into a canister, which is sealed for storage, and, ultimately, disposal. Ideally, the resulting glass is homogeneous - it contains no separate second phases, either crystalline or amorphous. Thus, the glassformer can be thought of as a solvent, which is formulated to maximize waste solubility and other important properties (such as chemical durability).[1]

Glassformer compositions for HLW have been developed to dissolve large amounts of HLW. In general, actinide solubility has not been a consideration. The concentrations of actinides in U.S. HLW glasses are very small. In the case of Savannah River Site's HLW, concentrations of plutonium are on the order of 10^{-2} to 10^{-3} wt% of the waste.[2] Thus, for HLW, the focus has been on developing glassformer compositions which can tolerate the variations in major non-radioactive components in HLW, such as sodium, iron, and aluminum.

As a result, little systematic work has been done on plutonium solubility in HLW glass. In Russia, at least one production facility has produced HLW glasses containing 1 wt% plutonium.[3] In France,[4] Germany, and the United States, glass doping studies, performed to examine radiation effects, have been the primary source of information about actinide solubility. In these studies, plutonium or other actinides have been added to glass batches to achieve concentrations in excess of 1 wt%.[5] Unfortunately, because of the focus of these studies, little effort was made to ensure that the plutonium was completely dissolved. Often, characterization of the amount and distribution of plutonium actually dissolved in the glass was incomplete. However, these studies all lead to the same general conclusions. For HLW glasses,

- The solubility of plutonium is limited to about 2 - 4 wt%.
- The solubility of thorium is approximately the same, or somewhat higher.
- The solubility of uranium is considerably higher, and depends on the redox state of the glass. The solubility of "UO2" is approximately 10 - 12 wt%; the solubility of higher oxides is higher.
- The actual solubility depends on the glass composition.

In perhaps the only study which specifically examined plutonium solubility in HLW glasses, Plodinec was able to dissolve up to 7 wt% PuO_2 in a HLW glassformer composition.[6] Although he could not determine an exact solubility for plutonium in HLW glass, he was able to provide an upper bound through visual examination of glasses produced from batches containing various concentrations of plutonium. At 4 wt% PuO_2, he concluded that the solubility of plutonium had definitely been exceeded. He also explored the effects of glass composition on plutonium solubility. He came to the following conclusions:

- Higher alkali contents in the base glass increased the solubility of plutonium. Higher boron contents also appeared to have the same effect, but he could not rule out a kinetic effect for boron.
- Waste content, and waste type, played a major role in plutonium solubility. It appeared that +3 cations in the waste were competing with plutonium for the same sites.
- Based on the emerald green color of the glasses which contained only glassformer and plutonium, it appeared that the plutonium was incorporated into the glass in the +3 state. If this is, in fact, true, it means that plutonium solubility will be affected by glass redox.

Plodinec also performed similar studies with uranium oxides.[7] In these studies, the solubility of "UO_2" was 10 - 12 wt%, and depended on the glassformer composition in the same way as indicated for plutonium. The solubility of more oxidized uranium oxides was at least 25 wt%. Again, the redox state of the actinide appears to play an important role in the solubility.

A typical American borosilicate HLW glass composition is shown in Table 1. This glass represents a blend of all of the HLW at the Savannah River Site (SRS). Soluble nuclear poisons include both lithium and boron. However, the criticality safety basis for the glass is based on the water-insoluble neutron poisons, iron and manganese.[8] If a HLW glass needed more than these species to prevent criticality, rare earth oxides could be included. The solubility of rare earth oxides, for example Gd_2O_3, in SRS HLW glass is approximately 10 wt%.

Table 1. Projected composition of initial DWPF glass. Minor components not included.

Component	Amount (wt%)
Al_2O_3	4.85
B_2O_3	7.66
$BaSO_4$	0.22
CaO	1.16
$CaSO_4$	0.12
Cr_2O_3	0.10
Cs_2O	0.08
CuO	0.40
Fe_2O_3	12.47
K_2O	3.47
Li_2O	4.40
MgO	1.36
MnO	2.05
Na_2O	8.58
Na_2SO_4	0.10
NaCl	0.31
NiO	0.74
SiO_2	49.61
ThO_2	0.36
TiO_2	0.65
U_3O_8	0.53

An important unresolved issue is whether insoluble poisons actually could be separated from Pu-239 (or U-235) through differential migration or colloidal transport. While there are no definitive data, the work of Bates, et al., is very encouraging.[9] A glass similar to that in Table 1 was doped with 2 wt% Pu, and an equimolar amount of of gadolinium. Longer-term, high surface area, static leach tests are being performed to provide source terms for glass performance under various conditions. Although the data is only preliminary, it appears that the release of plutonium and gadolinium to solution is occurring congruently. The plutonium and gadolinium are apparently both held in the leached layer on the glass surface, and are not involved in formation of any clay layer, which could form colloidal material.[10] If these observations are borne out by subsequent results, it would provide important evidence that an insoluble neutron poison in the glass can be relied upon to stay with the plutonium, and, hence, prevent a nuclear incident in the repository. Clearly, additional work is needed to determine whether differential migration of plutonium and neutron absorbers is likely, or even possible.

LOW TEMPERATURE CESIUM — ACTINIDE GLASS

As noted above, another option for immobilization of actinides from nuclear weapons is to include them in a glass which contains a high concentration of a gamma emitter. The high dose rate from Cs-137, for example, would make it more difficult to process glass forms containing high concentrations of actinides, and thus discourage diversion.

However, it is well-known that cesium readily volatilizes from glass melts. In order to retain it in the glass, the melting temperature should be kept as low as possible. The melting temperature for HLW glasses - 1150°C - represents a practical maximum for cesium retention. However, since the current generation of HLW glasses have not been formulated to contain either actinides or cesium at high concentrations, reformulation to contain both is being pursued. Since current HLW glasses are formulated to tolerate the non-radioactive components (Fe, Al, and Na) which dominate HLW, a new glass, which did not have to tolerate HLW, can be "tailored" to provide improved properties (for example, enhanced durability).

Ellison has formulated an alkali-tin-silicate glass which appears to achieve both goals.[9] It contains nearly 1 wt% Cs_2O, and has been shown to be capable of dissolving up to 7 wt% PuO_2. He used the following strategy to design the glass in Table 2. In order to achieve low melt temperatures, the glass must contain a significant alkali metal oxide concentration (including Cs_2O). As noted above, alkali also enhances the solubility of actinides in the melt.

Table 2. Typical alkali-tin-silicate glass composition for plutonium immobilization.

Component	Amount (wt%)
Al_2O_3	2.6
B_2O_3	13.7
Cs_2O	0.8
Gd_2O_3	3.5
K_2O	5.9
Li_2O	4.6
Na_2O	10.4
SiO_2	47.3
TiO_2	2.3
ZrO_2	6.0

Several studies have established that the corrosion of glass in a repository is highly dependent on the concentration of silicate in the groundwater. The difference between the saturation concentration and the actual concentration acts as a driving force for the dissolution process. The saturation concentration of silicon in solution increases rapidly with increasing pH, for pH values above 9. Glasses with large amounts of alkali tend to push the pH of aqueous solutions in contact with them to high values. Thus, high alkali glasses tend to be non-durable.

In order to suppress the potential high pH due to the alkali metal content, boron is included in the glass. Quadrivalent cations - Ti, Sn, and Zr - are also included in the formulation, to tie up the alkali in the glass. These +4 oxides also have positive free energies of hydration, and thus should render the glass inherently more durable.[11] Based on this reasoning, it is likely that plutonium itself also would enhance the durability of the glass. The concentrations of elements such as aluminum and calcium are minimized, because of the potential for secondary reactions which may precipitate silicon, and thus reduce its concentration in solution. This would result in a large difference between the solution concentration and the silicon saturation concentration, which would drive the reaction betwen glass and water to proceed more rapidly.

The glass in Table 2 has been shown to have a solubility of about 7 wt% for Pu, higher than that of HLW glasses. With further development, this is expected to go higher. Tests similar to those for the plutonium-doped SRS HLW glass have also been performed for this glass. The results indicate that this glass avoids formation of clay minerals usually found as corrosion products of HLW glasses. Again, plutonium and the neutron absorber, gadolinium, are found to behave similarly.

Thus, while short-term releases from the glass are slightly higher than those for the SRS HLW glass, the evidence indicates that this glass may be more durable in the longer-term. Further work is needed, however, before any definitive statement can be made.

The major unknown with this glass formulation is its processing behavior. While it appears to readily form a glass at 1150°C, the viscosity and volatility of cesium are not known. These must be determined before a process can be designed which employs this formulation.

INTERIM GLASS

As noted above, there may be significant cost advantages to begin immobilization of actinides as soon as possible. SRS expects to begin immobilization of unneeded process solutions containing americium and curium in about one year. A small high temperature "bushing" melter will be used to produce the glass. This glass will then be sent to Oak Ridge National Laboratory to be stored until needed as a raw material for production of more exotic isotopes, e.g., Cf-252. This can serve as a model of what might be done with unneeded plutonium.

According to this scenario, the plutonium is mixed with a glass-forming frit, either as a solution or as an oxide. This material is then melted, and poured into small (approximately 10 cm diameter x 40 cm high) canisters, for interim storage. At a later date, the plutonium could either be recovered (for example, to be made into a mixed oxide fuel), or included in a canister of HLW glass. A test is underway to demonstrate the feasibility of the latter process.

The glass type which is being used for development of this concept is based on the commercial "Löffler" glasses.[12] These optical glasses typically contain up to 55 wt% rare earth oxides. Their solubilities for plutonium should also be high, because the chemistry of the actinides and the rare earth oxides often are similar. The boron and the barium provide the "flux" which allows these glasses to be melted. PbO is known to form adherent surface layers during glass leaching, and thus should enhance glass durability.

A typical glassformer (frit) composition is shown in Table 3. Notice that these glasses have almost no alkali content. Thus, reaction of the glass with water generally produces near-neutral pH values. As a result, the saturation concentration of silicon in solution is lower than for typical HLW glasses (e.g., that in Table 1). This implies that these Löffler glasses should be more durable than typical HLW glasses. This is, in fact, observed. A Löffler glass containing 13 wt% Pu was 25 times more durable than the glass in Table 1 using the Product Consistency Test. In these tests, it was also observed that the Sm and Pu were released congruently to solution.[13] This further supports the earlier observations about the likelihood of insoluble neutron poisons remaining with plutonium.

Table 3. Typical Löffler glass composition for plutonium immobilization.

Component	Amount (wt%)
Al_2O_3	11.1
B_2O_3	6.1
BaO	3.6
La_2O_3	9.4
PbO	15.1
SiO_2	35.0
Sm_2O_3	19.7

Solubilities of actinides in this type of glass are currently being determined. Up to 20 wt% ThO_2 or UO_2 can be dissolved in this glass. Melts have been formed containing up to 2 wt% of a mixture of americium and curium, with no evidence that a solubility limit was reached. Up to 15 wt% plutonium has been dissolved into a composition similar to that in Table 3.

For both plutonium and thorium, the apparent solubility when the actinide nitrate is used as the starting material is greater than when the oxide is used. At this time, it is not clear whether this effect is due to the oxidation state of the glass melt, or to the slow kinetics of dissolution of the oxide. Tests are underway to determine the cause.

This family of glasses shows great promise for immobilization of actinides. However, long-term glass / water interaction testing is needed, to develop a better understanding of how these glasses will behave during geologic disposal.

SUMMARY AND PATH FORWARD

From the preceding, it is clear that the solubility of actinide elements in glass varies widely, and depends on both the actinide and the type of glass. Plutonium solubilities are in the 2 - 4 wt% range for borosilicate high-level waste glasses of the type which will be produced in the U.S. This type of glass is generally melted at relatively low temperatures, ca. 1150°C. For this melting temperature, the glass can be reformulated to achieve plutonium solubilities of at least 7 wt%. This low melting temperature is desirable if one must retain volatile cesium-137 in the glass. Plutonium concentrations of at least 15 wt% have been achieved in Löffler glasses, which are melted at high temperatures. Thus, there is confidence that high (≥ 5 wt%) concentrations of actinides can be achieved under a variety of conditions.

For each of the types of glasses discussed here, further work is needed. If actinide contents in excess of 5 wt% are needed, and a decision is made to use an existing HLW vitrification facility, then reformulation of the glass will be necessary. While it appears that there is a family of glasses (the alkali-tin-silicates) which is compatible with existing HLW processing equipment, important processing characteristics of this family of glasses must be determined. The high temperature Löffler glasses have high solubilities for the actinides, but their production is as yet undemonstrated. Use of a "bushing" melter with its long commercial history for production of this glass reduces the degree of technical risk. The campaign to immobilize americium and curium at SRS should eliminate any questions about the viability of this approach.

For all of the glasses, work currently underway is providing important evidence that inclusion of rare earth oxides (e.g., gadolinium or samarium) in the glass formulation may provide the means to eliminate concerns about nuclear criticality in the repository setting. These species, which are insoluble in water, apparently behave similarly to plutonium, and appear to stay with plutonium during interaction of the glass with water. While further testing is needed, these preliminary results are very encouraging.

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