REACTIVITY OF HIGH PLUTONIUM-CONTAINING GLASSES FOR THE IMMOBILIZATION OF SURPLUS FISSION MATERIALS


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ABSTRACT

Experiments have been performed on glasses doped with 2 and 7 wt% plutonium to evaluate factors that may be important in the performance of these high-Pu-loaded glasses for repository storage. The high Pu loadings result from the need to dispose of excess Pu from weapons dismantling. The glasses were reacted in water vapor to simulate aging that may occur under unsaturated storage conditions prior to contact with liquid water. They were also reacted with liquid water under standard static leach test conditions. The results were compared with similar tests of a reference glass (202 glass) containing only 0.01 wt% Pu.

In vapor hydration testing to date, at 2 wt% loading, the Pu was incorporated into the glass without phase separation, and reaction in water vapor proceeded at a rate comparable with that of the 202 glass. At 7 wt% loading, a Pu phase separated and was not uniformly incorporated into the glass. The vapor reaction of this glass proceeded at a more rapid rate. This phase separation was manifested in the static leach tests, where colloidal phases of Pu-rich material remained suspended in solution, thereby increasing the absolute Pu release when compared to the 202 glass.

I. INTRODUCTION

The United States is evaluating several options for disposal of excess plutonium being produced from the dismantling of nuclear weapons. Disposal of the material in underground storage at the Yucca Mountain Site is one option under consideration. While a final waste form has not been chosen, borosilicate glass is one of the waste forms being evaluated. Because the amount of Pu in the glass will be greater than that currently found in the high-level waste glass to be produced by the Defense Waste Processing Facility (DWPF), there is a need to evaluate the performance of a range of glasses with high Pu content. While the composition of the glass used for Pu immobilization has not been finalized, an initial evaluation of the effect of Pu loading on reactivity provides insight into issues that will be important when evaluating the performance of a high concentration Pu glass. For purposes of comparison, a substantial data base on the reactivity of the reference DWPF glass (frit 202 based glass) exists.¹

Because the proposed site for storage of high-level waste in the United States is located in an unsaturated environment, tests have been conducted in water vapor to simulate reactions that will occur prior to contact of the waste glass with liquid water. The reaction under such conditions is termed vapor hydration.² Of interest in these tests is the extent of reaction and the distribution of Pu between the reacted glass and the secondary phases. Tests have also been conducted by the static leach test method designated as the Product Consistency Test, version B (PCT-B). In these tests the reactivity and release of Pu to solution have been measured and compared to the standard glass.
II. APPROACH

The reference 202 glass contains about 0.01 wt% Pu (see reference 3 for the composition). Four new glasses were made by using 202 glass as the starting composition and doping with 2 and 7 wt% PuO₂, and also with PuO₂ plus an equal mole percent of gadolinium. The Gd is added as a neutron poison to address concerns related to criticality during production and in the repository. The four glasses are being reacted by test methods that accelerate the glass reaction but also account for the conditions that will likely be present in an unsaturated repository. One test is PCT-B, which is a static test performed at 90°C with a glass surface area (SA) to leachant volume (V) of 20,000 m⁻¹. The leachant is water taken from well J-13 and equilibrated with tuff at 90°C. This water is a standard reference water used in glass testing for the Yucca Mountain Project, but the water that contacts the glass may be of slightly different composition due to interaction with waste package components. Because of the relatively high SA/V, this test procedure accelerates the glass reaction and can be used to measure the reactivity of the glass and the release of Pu to solution.

The glasses are also being tested by the Argonne Vapor Hydration Test (VHT). This test accelerates the glass reactivity by using evaluated temperatures and an extremely high SA/V, defined by a layer of condensed water that forms on the glass. This test can determine the reaction rate of the glass under vapor conditions and also identifies the secondary phases that will likely form under leach test conditions. The formation of secondary phases is important because they control the silicic acid concentration in solution and, thus, the long-term reaction rate of the glass. These phases may also incorporate Pu into their structure, thereby making the Pu less likely to be transported from the waste form as a dissolved species. The results of the tests with 2 and 7 wt% PuO₂ glasses are compared to the reference 202 glass.

III. RESULTS AND DISCUSSION

A. Vapor Hydration Tests

Vapor hydration tests were conducted at 200°C for 7, 14, and 21 days. Additional tests through 56 days will be completed for comparison with tests performed on the 202 glass. The reacted glass surfaces were analyzed by optical microscopy and scanning electron microscopy (SEM) to characterize the secondary phases that formed and by SEM in cross-section to measure the extent of reaction. After 7 days, all glasses showed initial evidence of reaction and secondary phase formation. By 21 days the extent of reaction was such that the surface was nearly completely covered with secondary phases (Fig. 1). These phases (ideal formula) consisted primarily of analcime (NaAlSi₄O₆·H₂O), tobermorite [Ca₆(OH)₂Si₄O₁₁·4H₂O], an unidentified Ca-Si rosette, weeksite [Na₉(UO₂)₂(Si₄O₁₁)·4H₂O], phillipsite [(K,Na)₉(Al₆Si₆O₂₄)·20H₂O], and apatite [(Ca₅PO₄)₃(OH,F,Cl)]. The extent of coverage of the surface by secondary phases and the type of phases varied with the Pu loading. Generally, analcime and the calcium silicate phases were found on all glasses. However,

Figure 1. Optical micrograph of the reacted surface of the 7 wt% Pu glass showing coverage of secondary phases on the glass surface. Magnification 8x.
Figure 2. SEM micrographs of polished cross sections of vapor hydrated glass showing the thickness of the reacted layer and secondary phases that form on the top of the layer. (a) 2 wt% Pu glass, (b) 7 wt% Pu glass, and (c) 2 wt% Pu glass with Gd. The images are taken using backscattered electrons, and the brighter regions contain heavier elements such as U and Pu.

apatite was the only phase found on the 2 wt% Pu glass containing Gd (Fig. 2c). This is the only phase that shows any concentration of Pu higher than that observed in the glass itself. In the other glasses, the Pu remains distributed in the reacted layer to the same extent as in the unreacted glass (Figs. 2a and 2b).

The reaction progress after 21 days is shown in Fig. 2 for the vapor tests. The secondary phases and reacted layer are clearly evident in Figs. 2a and 2b, where the secondary phases are seen forming on the surface of the layer. The layer itself is an iron-rich clay, while the secondary phases include weeksite, analcime and calcium silicates. The 7 wt% Pu sample (Fig. 2b) shows that the Pu has segregated into a discrete Pu phase (PuO2) in the glass, with the individual PuO2 particles being submicron size. As the glass hydrates, the PuO2 phase remains intact and is dispersed throughout the reacted layer in the same manner as in the unreacted glass. For the 2 and 7 wt% Pu glasses, none of the secondary phases contained a measurable amount (<1 wt% using energy dispersive spectroscopy, EDS) of Pu, while for the Gd-doped glass, the apatite phase contained a small but measurable amount of Pu.

The extent of reaction is determined by measuring the thickness of the treated layer. The layer thicknesses for the Pu-rich glasses for the 14- and 21-day periods are given in Table I, together with layer thicknesses of the reference glass reacted under the same conditions. The layer thicknesses were more consistent for the Pu-doped glasses compared with the reference glass, and the Gd-doped glass showed the smallest reaction of all the Pu-loaded glasses. After 21 days, the 2 and 7 wt% Pu glasses
TABLE I
Extent of Vapor Hydration of Pu Glasses

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>Layer Thickness (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(days)</td>
<td>202 P2 P7 G2</td>
</tr>
<tr>
<td>14</td>
<td>18.7 9.2 15 9.5</td>
</tr>
<tr>
<td>21</td>
<td>19.4 26.7 78 13.4</td>
</tr>
</tbody>
</table>

*202 is the reference DWPF glass; P2 is 202 plus 2 wt% Pu; P7 is 202 plus 7 wt% Pu; and G2 is 202 plus 2 wt% Pu and 2 wt% Gd.

showed greater reaction than the reference glass, with the 7 wt% Pu glass having a dramatically increased layer thickness. The reason for the difference in rates will be more fully explored by analyzing the remaining samples in the test matrix.

B. Solution Tests

The solution results available are from 3- and 28-day tests. Analyses measured the cations, anions, pH, radionuclides, and colloidal content in solution. These results can be compared to those from reference glass reacted under the same conditions but slightly different periods. Table II shows the pH and Pu release to solution for the different glasses. (Other analysis will be presented in the future.) The pH is a rough measure of the extent of glass reaction, with a higher pH generally indicating a greater extent of reaction. These data indicate that the reference glass is reacting at these early time periods slightly faster than the Pu-doped glasses.

More importantly, from a glass performance standpoint, is the amount of Pu released and the form in which it is released. In these tests, an aliquot of the unfiltered leachate was taken for Pu determination by alpha spectroscopy, and a sample was wicked through a holey carbon grid to trap colloids that are suspended in solution. The material on the holey carbon grid was analyzed by analytical electron microscopy (AEM). The leachate was then passed through a 0.45 um filter to separate the glass particles, and an aliquot taken for Pu analysis. After the glass was removed from the test vessel, the vessel was stripped with acid to determine the amount of Pu that had sorbed to the vessel walls. This combination of analyses allows the distribution of Pu released from the glass to be determined.

The release values in Table II have not been normalized to the amount of Pu in the glass, but represent the absolute amount of Pu actually released from each glass. Generally, for the Pu-doped glasses, the amount of Pu sorbed on the vessel walls was about 20% of the total. The remaining Pu was either dissolved in solution or existed in solution as colloidal material. The Pu-doped glasses had greater Pu release than the reference 202 glass by factors ranging from 27 to 187. The release from the Gd-containing glass was slightly less than from the 2 and 7 wt% Pu glasses, and the release from the 7 wt% Pu glass was slightly less than from the 2 wt% Pu glass.

TABLE II
Selected Solution Results from Leach Tests with Pu Glasses

<table>
<thead>
<tr>
<th>Glass Type</th>
<th>pH</th>
<th>Total Pu Release*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 Days</td>
<td>14 Days</td>
</tr>
<tr>
<td>202</td>
<td>11.01</td>
<td>11.26</td>
</tr>
<tr>
<td>P2</td>
<td>10.66</td>
<td>10.91</td>
</tr>
<tr>
<td>P7</td>
<td>10.77</td>
<td>10.91</td>
</tr>
<tr>
<td>G2</td>
<td>11.02</td>
<td>11.15</td>
</tr>
</tbody>
</table>

*Total release in μg. Includes Pu in solution and that stripped from the test vessel walls.
The form by which the Pu is released to solution is shown in Fig. 3a. The colloid trapped on the grid is an Fe-rich clay, the same type that is formed during the vapor phase reaction. The clay is likely forming in solution as a result of the dissolution of the glass. As shown in Fig. 3a, attached to the clay is a small discrete Pu oxide particle. This particle is of the same size as the Pu-rich inclusions found in the unreacted glass (Fig. 2b) and likely was released from the glass during the dissolution process and was trapped as part of the clay colloid. The EDS spectrum shown in Fig. 3b indicates that Pu is also dispersed uniformly in the clay. The amount of Pu in the clay varies and is inversely proportional to the amount of Fe in the clay, as shown in Fig. 3c. These results indicate that the Pu is released to solution in the early stages of glass reaction and is suspended in solution mainly as colloidal material. While the same general observations were made with the reference glass, the EDS spectrum did not indicate Pu in the clays. This result is not surprising given the low starting Pu concentration in the reference glass. Additionally, with the reference glass, the amount of Pu that was suspended in solution decreased with time, as the ionic strength of the solution increased. The longer term tests with the doped-Pu glasses will determine whether the same trend is observed.

IV. CONCLUSIONS

Glasses based on the reference 202 composition have been doped with 2 and 7 wt% Pu and reacted to simulate conditions that are expected to be found in an unsaturated repository environment. Tests in water vapor were done at 200°C to accelerate the reaction and to be comparable with tests done on the 202 reference glass. These preliminary results from the vapor hydration tests indicate that the 7 wt% Pu glass hydrates more rapidly than the other glasses, and that except for the Gd-containing glass, the Pu is not concentrated in secondary phases that form during the hydration process.

In the Product Consistency Tests, all the glasses showed similar reaction rates based on pH measurements, but the doped glasses released between 27 and 187 times the amount of Pu than the reference 202 glass. The majority of this Pu is associated with material suspended

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Figure 3. (a) AEM micrograph of a clay colloid with a trapped Pu oxide particle. (b) EDS spectrum of the clay showing dispersed Pu. (c) Plot showing the displacement of Pu by Fe in the clay.
in solution as colloids, and the Pu exists either as Pu oxide particles embedded in clay or as Pu dispersed throughout the clay. While the amount of Pu in solution is greater for the doped glasses than the reference 202 glass, if the release is normalized to reflect the amount of Pu in the starting glass, the normalized release from the doped glasses is less than from the reference glass since the amount of Pu in the doped glasses is 200 to 700 times greater than in the reference glass.

Experience with the reference glass indicates that changes in both the rate of glass reaction and the disposition of Pu between the solution and the test vessel changes with time. Therefore, before a full comparison can be made between the reaction of the doped glasses and the reference glass, the longer-term tests in both the VHT and PCT matrices must be completed.

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REFERENCES


