GLASS CORROSION AND IRRADIATION DAMAGE PERFORMANCE

by

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GLASS CORROSION AND IRRADIATION DAMAGE BEHAVIOR

by


INTRODUCTION

Several options are under consideration for the disposition of surplus Pu resulting from weapons dismantling and site remediation. One option is immobilization of the Pu and scrap metal in glass, followed by repository disposal. However, the final composition of glass has not been selected, and the information regarding the long-term behavior of high Pu-loaded glasses under potential unsaturated repository conditions is limited. Additionally, several issues exist that are relevant to the feasibility of using glass as a waste form. In this paper, we discuss (1) the general behavior of Pu-loaded glasses when corroded by water; (2) the distribution of Pu, $^{235}$U, together with neutron absorbers during corrosion; (3) the effect of irradiation damage on glass corrosion behavior; and (4) the role of glass modeling in the calculation of long-term performance.

The high-level waste glass compositions that are currently under consideration in the United States are based on wastes that result from the reprocessing of used reactor fuel [1]. In general, the feed streams contain a range of components that are either glass formers or modifiers, but very little Pu. The resulting glass contains about 0.01 wt% Pu and considerable Al, Fe, Na, Ca, and Mg. These glasses, therefore, have been optimized to accommodate high loadings of compositionally complex wastes. Adaptation of the existing glasses to incorporate high concentrations of Pu has not been required and thus only a limited data base is available for evaluating precisely how much Pu can be dissolved in glass. However, the work that has been done on Pu solubility in glasses [2-5] suggests that fairly high Pu loadings (2-13 wt%) should be achievable. This work also suggests compositional adaptations based on glass chemistry that can be used to ensure high Pu loadings. Additional work regarding the development of high Pu-loaded glasses is reported elsewhere in these proceedings [6].

While past compositional studies have not focused on Pu, considerable emphasis has been placed on the behavior of Pu and other actinides during exposure of glass to water [7]. This focus exists because the actinide elements are of concern from a regulatory standpoint. This previous work has resulted in the derivation of Figure 1 which provides a schematic of the reaction pathway by which glass reacts. In a thermodynamic sense, the reaction of glass with water proceeds in a manner that minimizes the free energy of the system and also minimizes the chemical potential gradients between the solution and the glass. When the gradients are steep, particularly for major glass-forming components such as SiO$_2$, the rate of reaction will be relatively high, whereas when the gradients are comparatively shallow, the rate of reaction will be relatively low. The slope of the chemical potential gradients and the energy required to extract the rate-limiting component from the surface of the glass are controlling factors in determining the rate of glass corrosion. For silicate-based glasses, the rate controlling step is the hydrolysis of the last Si-O-Si bond and the formation of H$_4$SiO$_4$ (silicic acid). The chemical potential gradients between the glass and water are initially large (Stage I) because the leachant is dilute, and the reaction proceeds at the forward rate. As the silicic acid concentration in solution increases, the chemical potential gradient decreases (Stage II). Glass reaction during Stages I and II usually results in the formation of a reacted layer, which may or may not be crystalline, but this change does not increase the glass reaction rate. However, certain alteration phases
that nucleate during glass corrosion can serve as a sink for silicic acid. When this occurs, the rate of glass corrosion is controlled not by the chemical potential gradient between the glass and solution, but by the gradient between the glass and alteration phases. This, in turn, may accelerate the rate of glass corrosion (Stage III). This increased rate may be controlled by the precipitation of the silicic acid consuming phases, or by the forward rate of the glass at the conditions of temperature and pH of Stage III.

The reaction pathway is useful in conceptualizing glass behavior, but to calculate glass behavior over a range of conditions, modeling must be performed. This activity requires that the reaction mechanism be elucidated through the results from well-designed experiments and expressed as a mathematical kinetic rate equation. This rate equation can then be used in concert with a number of computer codes to calculate the long-term behavior of glass under disposal conditions. Typically, the kinetic expression contains all the chemical and physical parameters that are important to the rate-limiting step in the kinetic mechanism. For glass, the important parameters appear to be the silicic acid concentration \([H_2SiO_3]\), the temperature, and the pH of the surrounding solution. A glass dissolution model, therefore, is a well-defined mathematical expression of the kinetics by which glass interacts with water and for which the kinetic parameters are known. While testing provides valuable information about the distribution of actinides and neutron absorbers and about glass reaction during each stage of the reaction pathway, no single test can provide all the information that is required to calculate glass behavior. Thus, the development of a predictive model, as opposed to an empirical extrapolation, is necessary to complete a performance assessment of Pu glass in a repository setting.

Testing is required to provide data with which to develop and validate such predictive models. Long-term testing of actinide doped and fully radioactive glasses that are within the compositional envelope of potential glasses to be produced at the Defense Waste Processing Facility (DWPF), indicates that the behavior of Pu is dependent on the test conditions. Static tests with a large ratio of the surface area of the glass to the volume of solution (S/V) result in the initial release of Pu being dominated by a colloidal fraction in
which the Pu is associated with clay phases [8,9]. Ultimately, however, the majority of the Pu released from the glass is sorbed to the metal test vessel. Uranium in these tests initially is released more rapidly than Pu. As the reaction proceeds into Stage III, the U forms alteration phases that precipitate from solution and are found on the glass surface. Of potential neutron absorbers, B is released rapidly to solution and is not incorporated into alteration phases. Transition metals and rare earth elements have a release pattern similar to that of Pu, although most studies have not evaluated the release characteristics of these elements in detail. Thus, tests to evaluate the behavior of high Pu-loaded glasses must be designed specifically to evaluate the distribution of the neutron absorbers and of Pu and U in solution, in the alteration products, and in the reacted glass.

Other tests with DWPF-type glasses have evaluated the reaction of glass with water vapor under conditions that accelerate the reaction into Stage III. The goals of these tests are to determine which alteration phases form and which of these phases contain actinide elements. In general, U forms alteration phases, such as weesite \( \text{K}_2\text{(UO}_2\text{)}_2\text{(Si}_2\text{O}_5\text{)}_3\cdot4\text{H}_2\text{O} \), while Pu remains associated with the clay layer that forms as the glass reacts.

Considerable testing has also been done to determine whether the corrosion behavior of glass would be affected by irradiation damage that may accumulate during disposal. Studies have considered all aspects of irradiation damage, including alpha decay that would result from the decay of Pu. In these studies irradiation damage has been accelerated by using a variety of techniques. For standard borosilicate waste glasses, the indication is that any increase in the reactivity of the glass will be within errors associated with performance calculations [10-12].

Each of the above points must be reconsidered when evaluating the behavior of a high Pu-loaded glass for repository disposal. In this paper, available information on information related to the behavior of high Pu loaded glasses is reviewed.

COMPOSITION AND BEHAVIOR OF HIGH PU-LOADED GLASSES

High Pu DWPF Glass

The reference composition to be produced in the DWPF is termed the blend glass. This composition will not be used as the high Pu-loaded glass; however, there is a large data base on its reactivity under potential disposal conditions [7], and these data are being used in initial performance assessments to determine whether a high Pu-loaded glass raises issues different from those identified for the blend glass. To assist the Yucca Mountain Project (YMP) in evaluating issues unique to high Pu-loaded glass, a set of preliminary experiments is in progress with the blend glasses that contains 2 and 7 wt% Pu (P2 and P7 glass) and 2 wt% Pu plus an equal mole percent Gd (G2 glass). The Gd is added as a neutron absorber and its behavior during reaction is largely unknown. The blend glass was chosen because of the ongoing YMP preliminary performance assessment efforts and because the results can be analyzed within the context of the reaction pathway.

To establish the corrosion behavior of the glass, samples were reacted using the product consistency test, version B (PCT-B) and the Argonne vapor hydration test (VHT). The PCT-B test conditions include a temperature of 90°C, an S/V of 20,000 m⁻³, and concentrated ground water as the leachant [13]. The VHT tests were conducted at 200°C under saturated vapor conditions. It has been found that there is a correlation between the formation of alteration phases in the VHT and the reactivity of glass under PCT-B conditions [9]. Additionally, the distribution of radioelements in the alteration phases can provide information regarding the eventual release of these elements to solution. It is not
anticipated that waste glasses will be exposed to a temperature of 200°C under repository conditions, but previous results [14] have indicated that this temperature can be used to accelerated glass reaction without altering the mechanism, thereby providing insight into potential reactions that may occur under long-term storage conditions.

The results of PCT-B tests on the P2, P7, and G2 glasses have been reported through 215 days [4]. The test solutions were analyzed extensively [e.g., 13], but for comparison with other glasses, only the results for B, Pu and Gd are given (Table I). Boron provides an upper bound of the glass reaction, and information on Pu and Gd are required for criticality calculations. The values in Table I include a contribution from the leachate and the acid strip of the test vessel. These data indicate that the reaction of the P2 and P7 glasses remains in Stage II of the reaction pathway. Glass G2 shows a seven-fold increase in normalized release of B, \((NL)_B\), at the 215-day period, while the releases of Pu and Gd are within a limited range for the entire test period. The normalized releases of Pu and Gd are equivalent. However, there is evidence from the P7 test results that as the glass reacts it forms clay colloids that entrain PuO\(_x\) crystals from the glass (Fig. 3a). These results suggest that glass compositions should be designed to dissolve completely the Pu and to react with water without the formation of clays.

<table>
<thead>
<tr>
<th>Waste Form</th>
<th>Test Conditions</th>
<th>Duration (days)</th>
<th>Normalized Release, ((g/m^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
</tr>
<tr>
<td>P2 [13]</td>
<td>PCT-B</td>
<td>215</td>
<td>0.5</td>
</tr>
<tr>
<td>G2 [13]</td>
<td>PCT-B</td>
<td>215</td>
<td>6.0</td>
</tr>
<tr>
<td>P7 [13]</td>
<td>PCT-B</td>
<td>215</td>
<td>0.5</td>
</tr>
<tr>
<td>ATS(^c) [4]</td>
<td>PCT-B</td>
<td>98</td>
<td>0.7</td>
</tr>
<tr>
<td>Lanthanide 15 wt%</td>
<td>PCT-A</td>
<td>7</td>
<td>0.003</td>
</tr>
<tr>
<td>SRL 165 Frit [20]</td>
<td>MCC-1</td>
<td>28</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\(^a\) Neutron absorber. 
\(^b\) Th replaces Pu. 
\(^c\) ATS = alkali-tin-silicate glass.

In the VHT, the glasses reacted to reach Stage III (Fig. 2a), and the distribution of Pu, Gd, and U between the reacted glass, and alteration phases was determined. Plutonium and Gd remain associated with the reacted glass as smectite clay. To the extent measurable with energy dispersive spectroscopy (~0.2 wt%), Pu was not observed in any of the alteration products that formed on the surface of the reacted glass. However, U is readily incorporated into weissite, which is seen as the bright regions in Fig. 2a. Gadolinium remains with the Pu, in the clay layer.
From the results of the VHT, Pu and Gd remain closely associated with the reacted glass, and these elements have little tendency to concentrate to a significant degree in alteration phases. However, U is readily immobilized as an alteration phase that is dispersed among other phases on the surface of the reacted glass. Information from these tests is being used in the YMP criticality studies.

**Lanthanide Glass**

Based on the general chemistry of commercial optical borosilicate glasses with high lanthanide oxide contents, two Pu-loaded glasses were produced [15]. This general composition was chosen because actinides and lanthanides often have similar chemistries in glasses, thus a high Pu loading was likely. Additionally, this glass contains no Na so the durability should be greater, and Pb is known to form a layer on the glass surface during corrosion tests in solution and vapor that appears to cause a decrease in the corrosion rate. Both glasses were processed at 1450°C, with the first having batched concentrations of PuO₂ and Sm₂O₃ of 15 and 6.1 wt% respectively and the second with 13 and 17.1 wt%, respectively. For the first glass, the Pu was added as the oxide that did not all dissolve in the glass. For the second glass PuO₂ dissolved in HNO₃ was the feed, and the Pu was completely dissolved in the glass. In both cases Sm₂O₃ was added as a neutron absorber.

Both glasses were tested by using the standard PCT version A (PCT-A) (ASTM C-12850) [15]. The glasses were reacted in triplicate at 90°C in DIW for a period of 56 days using the VHT (a) P7 glass and (b) ATS glass.
7 days. While the PCT-A does not specify an S/V ratio, a value of ~1100 m$^{-1}$ was calculated by approximating the density of the glass to be 5 g/m$^3$. At this time, only leachate analyses are available, because an acid strip of the test vessel is not required in the procedure. However, acid strips are now being performed to make the data comparable with the other results given in Table I. The main points noted from the 7-day tests for the 15wt% glass are the minimal pH rise from 6.3 to 7.8, the low release of Pu compared to B, and the equivalency of the releases of Pu and Sm. In comparing the results of Pu and Sm from these tests, it should be noted that some of the Pu is in the undissolved PuO$_2$ crystals in the original glass and unlikely to dissolve in aqueous solution. Thus, the normalization procedure yields (NL)$_p$ values that are slightly lower than if the Pu were completely dissolved in the glass. For the 13 wt% Pu glass, in which the Pu is totally dissolved, the (NL)$_p$ values are the same as for the 15 wt% Pu glass. No Sm release data are available for the 13 wt% Pu glass. It was suggested that the small rise in pH (compared to that observed for DWPF glasses) favors increased durability and is due to the absence of Na in the glass [3,15]. The short-term reactivity of these glasses is better that the standard DWPF glass by about a factor of 25. The long-term corrosion behavior of these lanthanide glasses has not been determined.

Alkali-Tin-Silicate Glass

An alkali-tin-silicate glass (ATS) was specifically formulated to take advantage of glass chemistry and information contained in the reaction pathway to increase Pu loading and glass durability. In a borosilicate glass structure, Pu competes with Al, Fe, and Ca to stabilize alkali non-bridging oxygen atoms. The Pu solubility can be increased by reducing the concentration of these elements that compete more effectively than Pu and replacing them with Sn, Zr, and Ti [4,13]. Tin, Zr, and Ti also have the advantage of not forming major silicate alteration phases in natural hydrothermal systems. The resulting glass should be less likely to reach Stage III in the reaction pathway.

This ATS glass was produced and is being tested [13]. It was thought initially that 10 wt% Pu could be dissolved into this glass. However, the initial formulation dissolved 7.2 ± 0.3 wt% Pu, with the undissolved fraction remaining as PuO$_2$. This level of Pu meets the 5 wt% requirement for the Greenfield and adjunct melter processing options [1] and the composition is being refined to achieve a higher Pu loading.

This glass was reacted using the same matrix as the high Pu-loaded blend glasses described previously, but deionized water (DIW) was used instead of ground water. While the pH values for the P2, P7, and G2 glasses exceed 11 by 98 days and increase to 11.7 by 215 days, the pH for the ATS glass increased only slightly from its initial value of 10.3 at three days. The initial B release from the ATS glass is slightly greater than for the other glasses. For short time periods, the release in DIW is usually greater by a factor of 2-5 than in ground water [7]. The release of Pu from the ATS glass is slightly less than that of Gd, and the values for both elements are less than those measured for the Pu-loaded DWPF glasses. The manner by which the glass reacts was examined with transmission electron microscopy (TEM). Figure 3b shows a section of the reacted surface of the glass after 98 days. There is no evidence of a clay layer forming on the glass, and it appears that the early stages of the reaction are controlled by dissolution of the glass matrix. These results, though preliminary, suggest that the short-term reactivity of the ATS glass is similar to that of the blend glass, the long-term behavior may result in slower reaction with minimal release of Pu.
In the VHT, the tendency of a glass to undergo reaction to form alteration phases is accelerated, and the distribution of actinide elements between the reacted glass and the phases can be determined. The reacted glass samples were analyzed with optical microscopy, scanning electron microscopy (SEM), and TEM. A thin reacted layer forms on the ATS glass and is detectable after 56 days. The layer is about 1.5 μm thick, compared to ~250 μm for the P7 glass reacted under the same conditions (Fig. 2). No alteration phases are found on the surface of the layer, indicating the glass has not reached Stage III in the reaction pathway. The Gd and Pu remain in the reacted layer, which itself appears to be hydrated, without any of the restructuring that is often seen in vapor-reacted glasses [4]. The rate of reaction of the glass, as measured by the thickness of the hydrated layer, is similar to that observed for the natural glass obsidian reacted under the same conditions [16]. These results suggest that the glass will not undergo reaction to form rate-accelerating alteration phases, and that only a very minimal clay layer will form. Additionally, the Pu and Gd remain in the reacted glass without apparent segregation.

Other Waste Glasses

Other compositions that have been evaluated for high Pu loadings include two phosphate glasses [3,17] and two early European Community borosilicate glasses [5,18]. Phosphate glasses in general have the advantages of low processing temperature and high durability [19], but they are limited in their Pu loading to about 3 wt% for a homogeneous
glass. The durability of the high Pu-loaded glasses has not been quantitatively reported. The early borosilicate glasses also dissolved about 3 wt% Pu and 5 wt% U. The glasses were reacted at 200°C in DIW and NaCl solution at an S/V of about 10 m⁻¹. Analysis of the reacted glasses indicated that the actinide elements were retained within the altered layer. No results for potential neutron absorbers were given.

**Simple Glass Analogs**

The issue of the behavior of Pu and neutron absorbers during reaction and in the reacted glass is important for the entire immobilization concept. The plutonium group at the Massachusetts Institute of Technology [20] has examined the corrosion behavior of simple DWPF glass analogs using the MCC-1P test method. The glasses tested were a SRL 165 frit and the reference glass ARM-1. Both glasses were doped with 2 wt% each of Th, Eu, Gd, and Sm. Thorium was used as a stand-in for Pu, and the rare earth elements were used as neutron absorbers. The ARM-1 glass is similar to SRL waste-containing 165 glass, except that it does not contain Fe. For each glass, each of the dopants was completely dissolved in the glass. The MCC-1P tests were run in DIW at 90°C for up to 28 days with an S/V ratio of 10 m⁻¹. The (NL) values are given in Table I. Boron is released more rapidly than Th and Eu, which were below detectable limits in solution. The analyses focused on Eu because criticality calculations using the neutron transport code Monte Carlo Neutron Photon (MCNP) indicate that for corroded SRL 165 glass, Eu is the most effective neutron absorber, of the elements studied. While the results are not definitive because of the low levels of Th and Eu in solution, the general trend observed for the glasses described above is followed: that is, B is released most rapidly, while the actinide and rare earth elements are released at a much lower rate.

**IRRADIATION BEHAVIOR**

There have been many studies on the effect of ionizing radiation on glasses. These studies have ranged from basic research investigating trapped defects induced in the glass by radiation to more practical studies to determine if radiation affects the ability of a glass to immobilize nuclear waste. Results of both types of research have been reviewed several times [11,12]. Nearly all of the practical studies have been directed toward investigating glasses for immobilization of defense high-level wastes. These wastes contain radioactive fission products and actinides. The glass is thus exposed to gamma, beta, alpha, and alpha recoil radiation. Properties studied include radiation-induced volume changes, stored energy, changes in microstructure and mechanical properties, and the effect of radiation on radionuclide release and radiolytic decomposition. Also, helium accumulation has been investigated. Most of these results were from studies performed between 1970 and 1990. Several effects were observed. For example, it was observed that alpha radiation and its associated alpha recoil radiation could increase radionuclide release from glass by up a to factor of three. It was also observed that ionizing gamma and beta radiation could increase radionuclide releases by up to a factor of four, but a later study using the leach PCT-A showed no effects from the radiation. Examination of the irradiated glass by TEM also indicated no radiolytic decomposition of the glass. New data for the blend glass frit also indicated no effect of gamma radiation on radionuclide release through a total dose of 4 x 10⁸ rads, and while possible increases in glass corrosion were observed in short-term tests, no data are available on the effect of radiation on Pu release under long-term conditions. It has been concluded that all of the effects that were observed in the various studies were not great enough to cause glass to be unsatisfactory as a matrix to immobilize nuclear waste. Thus the United States, Great Britain, Russia, France, and other countries are using or will use glass to immobilize their nuclear waste.
The Savannah River Site (SRS) has initiated a study of the effects of radiation on the lanthanide glasses for immobilization of Pu. A glass doped with Cm-244 to accelerated alpha decay events in the glass has already been fabricated. Initial TEM studies of nonradioactive lanthanide glasses in which Ce is substituted for Pu have shown that the glass does not decompose in the intense electron beam of the microscope. This suggests that these glasses may have good radiation stability. (Glasses with DWPF type compositions are very sensitive to beam damage, primarily because of the presence of Na in the glass [21].) Gamma irradiation studies to investigate possible bubble formation have been initiated. The durability of these glasses will also be measured by the ASTM test. In addition, SRS has Cm-244 and Pu-238 doped DWPF-type glasses that have accumulated very large doses of alpha radiation. In the near future, these will be examined by SEM for damage and leached according to the standard PCT method to determine if the alpha/alpha recoil radiation has affected the durability of the glass.

MODELING

There are basically two models for glass dissolution. In the first model, developed at the SRS [22,23], the glass is treated as an ideal mechanical mixture of mineral phases. The interaction of these phases with water is expressed as a “free energy of hydration.” This is a thermodynamic construct, not a kinetic mechanism. The outcome of the calculation is a thermodynamic driving force that can be translated into a kinetic rate. The second model was first developed by Grambow [24] and is based on the work of Aagaard and Helgeson [25]. In this model, the kinetic driving force is based on nonequilibrium thermodynamics, and the minimum reaction rate is provided by the “residual affinity” or the inability of the dissolving phase to equilibrate with solution. The original mathematical kinetic expression by Grambow was modified by McGrail and Olson [26], but only to refine its mathematical underpinnings. Typically, this model (kinetic rate law) is used in conjunction with a geochemical computer code to account for all the other reactions that take place in solution as the glass dissolves, i.e., as the glass dissolves. For example, the model can account for the fact that as the glass dissolves, Al^{3+} increases in solution until the solubility of a mineral phase, such as gibbsite [Al(OH)]_3, is reached, at which time the phase precipitates. Grambow’s model is the basis for the models used by Bourcier [27], and Delage and Dussossoy [28]. For a more complete review of the state of modeling see Bourcier [29] and Strachan, Bourcier, and McGrail [30] and the references therein.

The available data from various glass/water experiments suggest that the rate-limiting species is H_2SiO_4. Glass, when first placed in water, dissolves at an initial fast rate known as the forward rate. As H_2SiO_4 builds in solution, the dissolution rate of the glass begins to slow, until, at some long time, depending on experimental conditions, the rate reaches a minimum value. Any event along the reaction pathway that causes a decrease in the [H_2SiO_4] causes an increase in the dissolution rate of the glass. For example, Van Iseghem and Grambow [31] noted that the dissolution rate increased for a glass for which the mineral analcime was calculated to precipitate. Ebert [8] and Bates and coworkers [9] noted similar results but were able to identify analcime and other mineral phases on the surface of glasses. The increase in dissolution rate, however, was found to be coincident with the formation of the analcime phase.

As noted above, however, the solubilities of various mineral phases are exceeded during the course of glass dissolution. As these solubilities are exceeded, the mineral phases precipitate. This is reflected in the apparent incongruent nature of the dissolution process as monitored in the solution composition. This behavior is shown in Fig. 4, where congruent dissolution is shown as a straight line of unit slope, typical of the behavior of boron. Other elements are shown to depart from congruent behavior as the minerals that
control their solution concentrations precipitate. The release of plutonium and any neutron absorbers is expected to be controlled by solid phases to which the glass alters during its reaction with water.

Plutonium, as such, in the glass is not expected to change the dissolution rate significantly, nor are the neutron absorbers. However, the research community's experience with glasses containing large quantities of these elements is very limited. Still, it is expected that any deleterious effects on the glass dissolution rate may be ameliorated by a change in the composition of the glass. The important aspect of the problem is the behavior of the Pu and neutron absorbers. It is likely that plutonium will be controlled by the precipitation of an oxide phase (such as PuO₂) or a hydrated form, or a hydroxide phase (such as PuO₂(OH)₃), or by adsorption on a clay material that forms during glass dissolution. The type of Pu-bearing or neutron absorber-bearing phase that forms is strongly dependent on the solution composition and redox properties. Similarly, the neutron absorbers will precipitate as oxides, phosphates, or hydroxides, depending on the solution chemistry from which they precipitate. Thus, the behavior of the Pu and neutron absorbers is dependent on the solution chemistry, which is dominated by the glass/water interaction close to the glass, by the engineered barrier system components a short distance from the glass, and by the host rock at some distance from the engineered barrier system.

Transport of the dissolved Pu and neutron absorbers is controlled by the solubility of the precipitated mineral phase, the ground water, and the rate at which that ground water flows through the host rock. However, these elements may also be transported if colloids form. Sorption of Pu on colloids has been the subject of many papers [e.g., 32]. Colloids

Figure 4. Calculated behavior of 200 frit-based glass
can form as a result of the corrosion of the glass [6] or the engineered barrier components. The phenomenon of colloid formation is not part of the current waste form modeling.

The remaining issue with respect to high loadings of Pu in glass is the effects of radiation damage and transmutation of the Pu to U. Currently, these effects are evaluated experimentally and to date have not been incorporated into models. However, the result of nitric acid formation and its effect on glass reaction can be added to models by adding acid to solution based on the acid formation rate. The need to incorporate radiation damage and transmutation effects on glass corrosion behavior into current models will have to be evaluated.

CONCLUSIONS

Much of the data on which the behavior of a high Pu loaded glass will be evaluated with respect to disposal in a high-level waste repository are preliminary, short term, and incomplete. Other data are based on glass compositions that will not be used for high Pu loading. However, the results from testing indicate that it is important to dissolve the Pu fully in the glass and to formulate the glass to limit the formation of alteration phases. If these two goals are met, it is unlikely (1) that the glass will reach Stage III in the reaction pathway, thereby limiting the long-term reaction rate and (2) that Pu will be released at the same rate as the glass dissolves. Under these circumstances, the Pu release will be solubility-limited and therefore quite low. The results also indicate that B is released more rapidly than Pu and thus will act as a neutron moderator for the solution, while Pu and rare earth elements are released at nearly equivalent rates, suggesting that Pu remaining in the glass will also remain in the presence of a moderator.

Preliminary testing of glasses specifically formulated to accommodate high loading of Pu show an improvement in corrosion behavior compared to the standard DWPF glass. Accelerated vapor tests done with the alkali-tin-silicate glass show no tendency to reach Stage III in the reaction pathway, while short-term batch tests with both the high lanthanide and alkali-tin-silicate glasses show performance better than or equal to the standard DWPF glass. While these results are encouraging, longer-term tests must be completed with both glasses to fully describe their behavior and provide input for modeling.

Limited modeling has been done for Pu loaded glasses. However, the reaction of the P2, P7, and G2 glasses suggests that Pu loaded glasses will follow the general outlines of current glass corrosion models. This means that the models currently have the correct basis for describing glass reaction but need additional development to account for compositional differences, the manner by which Pu and neutron absorbers are released from the glass, and radiation damage effects.

Finally, while no radiation damage studies have been completed on the high Pu compositions under development, work on other nuclear waste glasses indicates that the production of acids will have little effect on the rate of glass reaction or Pu release. This work also indicates radiation damage may be of some concern, the increase in reaction rate may not translate into an increase in the release of Pu, and that any effect probably is within the ability to do a reliable performance assessment of the near-field repository environment.

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