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GLASS AS A WASTE FORM FOR THE IMMOBILIZATION OF PLUTONIUM

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ABSTRACT

Several alternatives for disposal of surplus plutonium are being considered. One method is incorporating Pu into glass and in this paper we discuss the development and corrosion behavior of an alkali-tin-silicate glass and update results in testing Pu doped Defense Waste Processing Facility (DWPF) reference glasses. The alkali-tin-silicate glass was engineered to accommodate a high Pu loading and to be durable under conditions likely to accelerate glass reaction. The glass dissolves about 7 wt% Pu together with the neutron absorber Gd, and under test conditions expected to accelerate the glass reaction with water, is resistant to corrosion. The Pu and the Gd are released from the glass at nearly the same rate in static corrosion tests in water, and are not segregated into surface alteration phases when the glass is reacted in water vapor. Similar results for the behavior of Pu and Gd are found for the DWPF reference glasses, although the long-term rate of reaction for the reference glasses is more rapid than for the alkali-tin-silicate glass.

INTRODUCTION

The United States has committed to evaluate options for disposing of fissile materials resulting from the dismantlement of nuclear weapons and the cleanup of weapons production sites. One option is to incorporate Pu in glass for long-term disposal in a high-level nuclear waste repository [1]. While glass has been designated as the best available demonstrated technology for the disposal of high-level nuclear waste, the Pu loading in typical high-level waste glass is about 0.01 wt %. Glasses for Pu immobilization are required to contain at least 5 wt % Pu, depending on the option chosen to process the glass. The staff at Lawrence Livermore National Laboratory have the lead responsibility for evaluating the concept of vitrification and geological disposal, and the staff at Argonne are assisting by identifying and evaluating factors that may be important regarding vitrification, including the composition development and corrosion testing of glasses with high Pu loadings.

Two important issues follow from placing high Pu loadings in glass. One is whether reaction under potential long-term storage conditions causes segregation of Pu or its daughter product, ^{235}U, to the extent that criticality becomes an important factor. The second is whether a glass composition can be developed that will dissolve high levels of Pu, yet minimize the known reaction processes that accelerate the corrosion of glass or segregation of actinide elements.

The Yucca Mountain Project (YMP) is addressing the first issue by doing a performance assessment of glass under potential repository conditions using the reference blend glass from the DWPF. While the composition of the blend glass will not be used to formulate the Pu-loaded glass, a considerable data base exists on its corrosion behavior over a wide range of test conditions. A preliminary performance assessment will address the feasibility of a criticality event. As input to the behavior of the Pu loaded blend glass, results of accelerated testing of this glass are reported in this paper.

Also discussed is the compositional development and corrosion testing of a Pu loaded glass that is processed at 1150°C. This glass provides a low-melting-temperature alternative to the high-lanthanide glass, which also has been developed for high Pu loadings [2].

GLASS REACTION BEHAVIOR

The composition of the glass to be used in Pu vitrification has not been identified yet, and very few glasses have been studied with respect to Pu solubility [3-6]. Additionally, little information is available on the long-term repository behavior of Pu-loaded glass. However,

there is enough to describe a general reaction progress pathway for the glass (Fig. 1). 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 magnitude 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. The chemical potential gradients between the glass and water are initially large (Stage I) because the leachant is dilute, and the reaction proceeds at what is defined as 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 does not result in an increase in the glass reaction rate. However, certain alteration phases that nucleate during glass corrosion, can serve as a sink for glass components. When this occurs, the rate of glass corrosion is controlled not by the chemical potential gradient between 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).

BLEND GLASS BEHAVIOR

To assist the YMP in evaluating criticality concerns within the context of the reaction progress pathway, preliminary experiments are ongoing using the blend glass containing 2 and 7 wt% Pu (P2 and P7 glass) and the blend glass containing 2 wt% Pu and an equal mole percent of Gd (G2 glass). The Gd was added as a neutron absorber to address criticality concerns. Unlike boron, which is known to be released rapidly from the glass, the behavior of Gd during reaction is largely unknown. The blend glass was chosen because preliminary performance assessment efforts are in progress and because there is a substantial data base on the reactivity of the glass containing Pu at 0.01 wt% (202A glass) [7]. The data base covers a range of exposure conditions, including reaction with static water at high S/V ratios (ratio of the glass surface area to solution volume), with water vapor, and with dripping water. Each of these exposures is relevant to evaluating glass behavior under conditions that may exist in the unsaturated environment at the proposed high-level waste repository at Yucca Mountain.

The results of PCT-B tests on the P2, P7, and G2 glasses performed at ~20,000 m^{-1}, 90°C, with repository water, have been reported through 182 days [8]. An additional test was terminated at 215 days because, in earlier tests with 202A glass, a sharp increase in the normalized release, $(NL)_i$, due to the formation of alteration phases, was observed shortly after 182 days (Table I). The results for the 215-day tests with P2, P7 and G2 glasses are also shown in Table I. The new data for B release indicate that the P2 and P7 glasses remain in the Stage II of the reaction pathway. Glass G2 shows a seven-fold increase in $(NL)_B$ at the 215-day period, while the releases of Pu and Gd are within the same range for the entire test period. The normalized releases of Pu and Gd are equivalent. The next scheduled sampling period is at 364 days.

The results for the G2 glass suggest that it has reached Stage III, where a particular set of alteration phases control the reaction; and that the releases of Pu and Gd to solution are similar. The P2 and P7 glasses have not reached the stage of accelerated reaction and show a declining $(NL)_{Pu}$ with time. The Pu in the leachate arises from two sources, dissolved and colloidal fractions. Plutonium solubility decreases in more basic solution, while Pu-bearing, clay-based colloids that form as the glass reacts agglomerate and precipitate from solution as the ionic strength increases. Both factors contribute to the decreasing Pu in solution in the present tests. Additional information regarding the Stage III reaction rates of the glasses will be available after the 364 day sampling, but the preliminary information suggests that the Pu and Gd will be released from the glass at the same rate.

Table I. Selected Test Results for PCT-B Tests of Pu-Containing Glasses.
Tests performed at ~20,000 m^{-1}.

Glass	Duration (days)	pH	Normalized Release,[a] g/m^2		
			B	Pu	Gd
202A	3	10.6	0.1	3E-2	—
	28	11.1	0.2	1E-2	—
	98	11.4	0.4	5E-3	—
	182	11.3	6	5E-3	—
	364	11.1	11	8E-3	—
	728	12.0	14	2E-2	
P2	3	10.7	0.2	7E-3	—
	28	10.9	0.2	1E-2	—
	98	11.0	0.3	3E-3	—
	182	11.0	0.5	4E-3	—
	215	11.0	0.5	2E-3	—
P7	3	10.8	0.4	2E-3	—
	28	10.9	0.6	3E-3	—
	98	11.1	0.6	3E-4	—
	182	11.3	0.5	7E-4	—
	215	11.4	0.4	7E-4	—
G2	3	11.0	0.2	3E-3	5E-3
	28	11.2	0.3	6E-3	8E-3
	98	11.2	0.5	2E-3	2E-3
	182		0.9	3E-3	4E-3
	215		6.0	4E-3	6E-3
ATS	3	10.4	0.4	9E-4	3E-3
	28	10.3	0.6	2E-3	7E-3
	98	10.5	NA[b]	NA	NA

[a]Tests performed at 20,000 m^{-1} and 90°C, and (NL)$_i$ values are calculated using the total elemental contribution released from the glass.
[b]NA = Analyses not completed.

ALKALI-TIN-SILICATE GLASS

Glass Design Strategy

The position on the reaction progress pathway (Fig. 1) is controlled the interaction between the solution and the glass. The waste glass producer can only control the composition of the glass. However, it is possible to take advantage of characteristic glass behavior as indicated by the reaction progress pathway. Developing a durable glass for realistic repository conditions requires that, if possible, one design the glass to mitigate against the formation of alteration phases that lead to Stage III reaction. Alternatively, the formation of alteration phases should not result in a substantial acceleration of the glass corrosion rate.

Numerous experimental studies have shown that the factor that most strongly affects the glass corrosion rate in evolved aqueous solutions is the silica concentration of the solution. At fixed temperature, the saturation concentration of silicic acid (H_4SiO_4) does not vary with pH, but the overall silica concentration can be higher than the silicic acid concentration because of the formation of ionized species, e.g., $H_3SiO_4^-$. The relative proportion of silicic acid and ionized
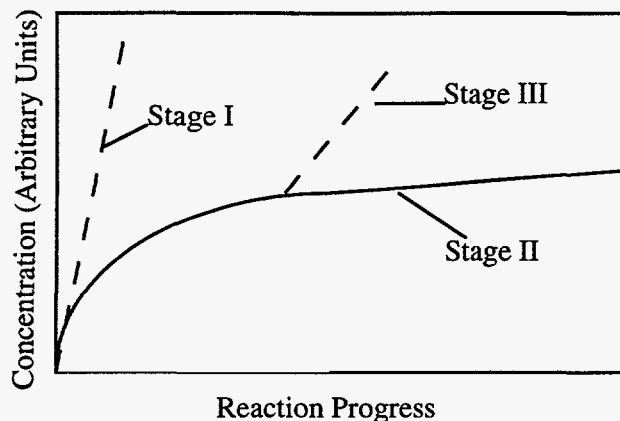
Figure 1.

Schematic description of the reaction progress pathway for glass. The reaction stages are defined in the text.

species is a very strong function of pH in alkaline solutions, with ionized species favored at high pH. Therefore, the first design objective is to keep the pH of any solution in contact with a glass as low as possible. In an alkali borosilicate glass, this can be achieved by including a high concentration of B_2O_3 relative to silica. Alkalis are strong Lewis bases in aqueous solutions, whereas boron behaves as a weak Lewis acid. As long as the rate of B release is comparable to (or exceeds) the rate of alkali release, and the B concentration in solution is comparable to the total alkali concentration in solution, then solution pH will increase very slowly over time. An initial increase in solution pH can be expected due to dealkalization, but once this level is attained, further increases can be suppressed.

Once the solution concentrations of silica and other corrosion products are high enough, then silica-bearing alteration phases can form. It has been repeatedly demonstrated that the phases that have the most profound effect on the rate of glass corrosion are zeolites and calcium silicates. Thus, a second design objective is to reduce or eliminate Al and Ca in the waste glass. Clay minerals do not appear to strongly affect the rate of glass corrosion but can form colloids in solution and thereby serve as inadvertent transport agents for Pu. Therefore, a third design objective is to exclude Mg, Fe, and other oxides that strongly enhance clay formation.

Aluminum, ferric iron, and calcium are important components in commercial glasses and candidate high-level and low-level waste glasses. As discussed by Ellison et al. [9], these components improve the durability of alkali-rich borosilicate glasses by sharing oxygen atoms with alkali atoms. These shared bonding arrangements couple the rate of alkali loss to solution to the rate at which these components dissolve, or the rate at which their bonding arrangements can be reconfigured. Eliminating them from an alkali-rich glass can be expected to increase the rate of alkali release to solution. However, Al, Fe, and Ca are not the only components that form coupled bonding arrangements with alkalis: Ti^{4+} [10], Sn^{4+} [11], and Zr^{4+} [12] also do. While there are a number of alkali zirconosilicates, none is important in igneous rocks or hydrothermal systems in nature. Also, Ti and Sn take part in very few silicate minerals in nature and do not appear to be important in any silicate minerals likely to be found in hydrothermal systems. Thus, even though the alkali-stabilizing capacity of Al is likely greater than that of Zr^{4+}, Ti^{4+}, or Sn^{4+}, this capacity is offset by the much greater tendency of Al to take part in hydrous aluminosilicate minerals in hydrothermal systems. Boron also complexes with alkalis, and due to its very high solubility in basic aqueous solutions, it shows little tendency to form alteration phases. Therefore, B can also be used to stabilize alkalis in the glass.

The complexing of alkalis and large +4 cations such as Zr^{4+}, Sn^{4+}, and Ti^{4+} also suggests a mechanism for incorporating Pu into a waste glass: simply include alkalis in excess of Zr^{4+}, Ti^{4+}, Sn^{4+}, B^{3+}, and any other stabilizing cations, and these will help incorporate Pu in a glass. This mechanism is supported by the plutonium solubility study of Plodinec [3], who found that plutonium solubility is greatest in alkali borosilicate glasses with the highest alkali oxide concentrations. The main merit of this approach is that just as alkalis stabilize Pu in the glass, so

too Pu serves to slow alkali loss to solution. (Taking advantage of this approach requires an assumption about the stoichiometry of the alkali/Pu complex, namely a ratio of 3 alkali atoms per Pu atom.)

Finally, it is desirable to keep the total silica concentration of the glass as low as possible. This is because it is not possible to control the composition of a solution that comes in contact with a glass in a geologic repository. If the solution is comparable to the EJ-13 reference groundwater [7], then it will contain considerable amounts of dissolved alumina and silica, and this could potentially aid in the formation of zeolites or other aluminosilicate phases that might increase the rate of glass corrosion. To the extent that the chemical potential gradient between glass and zeolite drives the rate of glass corrosion in the presence of zeolite, then it is desirable to keep this gradient as small as possible. As noted by Ellison and Navrotsky [13], strong bases (e.g., alkalis) produce large, exothermic free energies of mixing in multicomponent silicate glasses, and thus high concentrations of strong bases are expected to minimize the free energy of the glass with respect to any fixed reference, such as pure SiO_2. Consequently, addition of strong bases to silica is an effective way of reducing the activity of silica [14]. In the composition discussed in this study, the alkali oxide concentration is approximately 25 mol %: if sodium were the only alkali, this would correspond to approximately 25 wt% Na_2O.

Following the above rationale, an initial alkali-tin-silicate (ATS) glass (Table II) was produced by mixing the requisite oxide and carbonate components, followed by ball milling and melting at 1150°C for four hours. The melt was quenched in water and ball milling for final homogenization. To this starting material, Pu was slurried as a plutonium nitrate solution, and Gd (a potential neutron absorber) was added as the oxide. The mixture was then melted for four hours at 1150°C, poured into molds, annealed at 500°C for two hours, then cooled to room temperature.

Characterization

For the initial ATS glass composition, 10 wt% Pu was not fully dissolved into the glass. The dissolved fraction was determined by examining polished thick sections with SEM/EDS and thin sections with TEM/EDS. The Pu concentration in the P2 glass was used as a standard. The average dissolved concentration from multiple measurements using both methods is 7.2 ± 0.3 wt% Pu. The undissolved fraction of Pu is in the form $PuO_{(2-x)}$, its appearance in the glass (Fig. 2), suggests an equilibrium phase. While this level of Pu meets the 5 wt% requirement for the Greenfield processing option [1], further composition refinement that will result in achieving a 10 wt% loading is in progress.

Table II. Composition of ATS Glass[a]

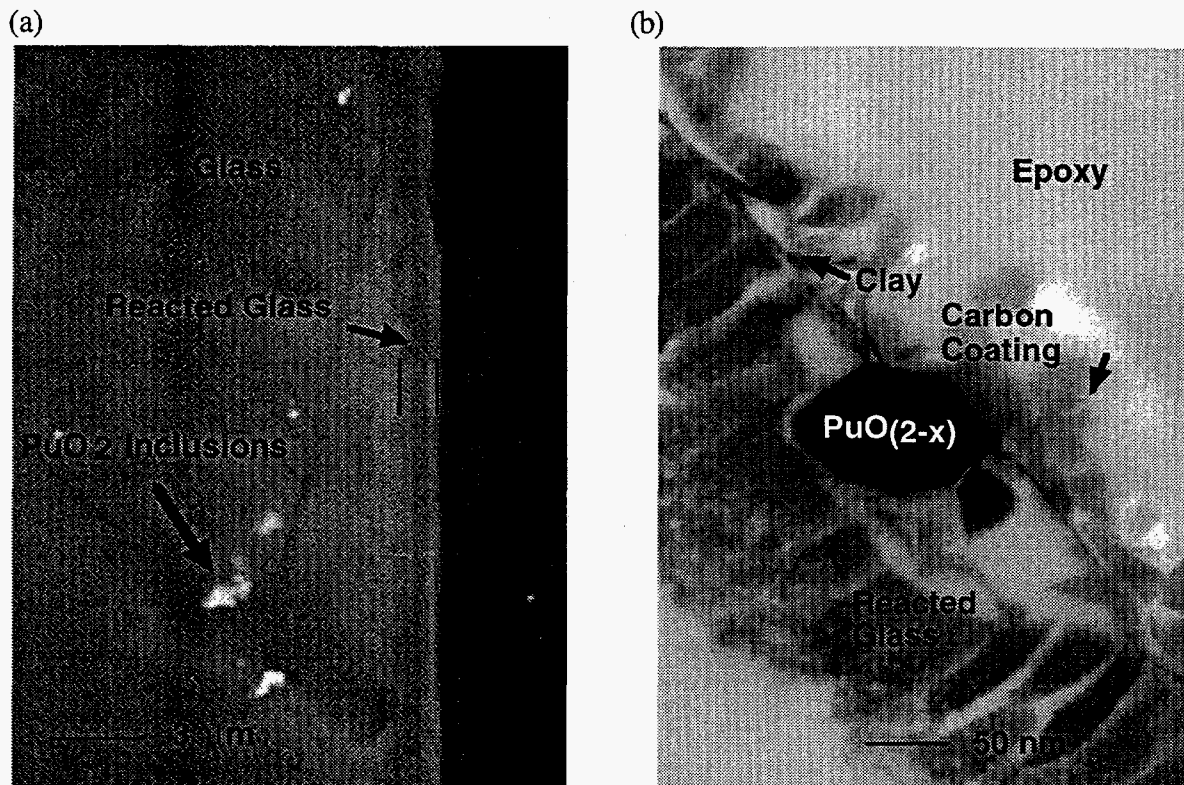| Element	Element wt %
Al	1.22
B	3.74
Cs	0.64
K	4.29
Li	1.86
Na	6.79
Si	19.37
Sn	1.97
Ti	1.21
Zr	3.92
Pu	10.00
Gd	2.77

[a]Oxides are assumed as glass constituents.

Figure 2. (a) SEM micrograph of a thick section of the ATS glass reacted for 56 days at 200°C in saturated water vapor. (b) TEM micrograph of a thin section of the ATS glass reacted for 56 days at 200°C in saturated water vapor.

To establish the corrosion behavior of the glass, samples were reacted using the PCT-B and the Argonne vapor hydration test (VHT). The PCT-B is a static test and the conditions used were 90°C with an S/V ratio of 20,000 m^{-1}. The tests were conducted in Type 304 L stainless steel vessels with a leachant of deionized water (DIW).   Tests with planned duration through two years have been initiated, and partial results are available through 98 days.

The VHT tests were conducted at 200°C under saturated vapor conditions. These tests are used to accelerate glass reaction and indicate the alteration phases that will likely form when the glass reaches Stage III. It has been found that the formation of alteration phases in the VHT is correlated with the reactivity of glass under corrosion conditions [15]. 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 the glasses will be exposed to a temperature of 200°C under repository conditions, but previous results [16] have indicated that this temperature can be used without altering the mechanism of glass reaction, thereby providing insight into potential reactions that may occur under long-term storage conditions. The tests were done for time periods of 7, 14, 21, 35, and 56 days.

PCT-B Tests

The test solutions for the ATS glass underwent extensive analyses [e.g., 8], but here we report only the reactivity of the glass as measured by the pH and the release of B, Pu, and Gd (Table I). Boron provides an upper bound of the glass reaction, and information on Pu and Gd is required for criticality calculations. The values in Table I include a contribution from the leachate and the acid strip of the test vessel. While the pH values for the 202A, P2, P7, and G2 glasses exceed 11 by 98 days and eventually increase to 12.0, the pH for the ATS glass increases

only slightly from its initial (3 day) value of 10.4. The B release from the ATS glass is slightly greater than for the other glasses, but the leachant for the ATS glass is DIW, while it is a silicate groundwater [7] for the other glasses. For short time periods, the release in DIW is usually a factor of 2-5 greater than that in groundwater [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 measured for the other glasses. These results, while preliminary, suggest that the short-term reactivity of the ATS glass has met the design objectives described above.

Vapor Hydration Tests

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 new phases can be determined. The reacted glass samples were analyzed with optical microscopy, SEM, and TEM. The results showed that a thin reacted layer forms on the ATS glass and is detectable after 56 days. The layer is about 1.5 μm in thickness, compared to ~250 μm for the P7 glass reacted under the same conditions [8]. Sections of the reacted layer as analyzed by SEM and TEM are shown in Figs. 2a and 2b. The glass and the layer contain small undissolved Pu inclusions, indicating the incomplete dissolution of Pu. No non-clay alteration phases are found on the surface of the layer, which suggests that the glass has not reached Stage III in the reaction pathway. The TEM image shows that a very thin layer (~5 nm) of a Sn-Ti-Fe-Al-Si bearing clay covers the reacted glass layer. 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 [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.

CONCLUSIONS

Three Pu-containing blend glasses (P2, P7, and G2) have been reacted under accelerated conditions. The reactivity of these high-PU-loaded glasses was compared to that of a well-studied glass (202A), and the behavior of Pu and Gd was monitored during the reaction process. The tests have not proceeded to the point where the long-term behavior of the glasses can be described, as to date only the G2 glass shows any indication of approaching the accelerated Stage III reaction. For each of the glasses, the Pu and Gd are being released at nearly identical rates, which are significantly lower than the glass reaction rate as measured by B release. There is no apparent Pu/Gd segregation.

An alkali-tin-silicate glass was developed, based on principles of glass chemistry and the general glass reaction progress pathway. Four objectives were set in developing the composition of these objectives. Based on initial testing of the glass, progress was achieved in meeting each of the goals. A Pu loading of ~7 wt% was achieved, including the addition of Gd as a neutron absorber; the solution pH in high S/V tests was below that of the standard blend glass, and the pH increase with time was slow; no rate-accelerating alteration phases formed in the VHT so that it is not expected that Stage III in the reaction progress pathway will be reached in the PCT-B; only minor clay formation was observed in the VHT; and the Pu and Gd remained in the reacted glass layer. The latter suggests that Pu/Gd segregation will not occur, and that release of Pu from the glass will be limited mainly by its solubility, and not colloidal pathways.

ACKNOWLEDGMENTS

REFERENCES

1.   Management and Disposition of Excess Weapons Plutonium, Committee on International Security and Arms Control, National Academy Press, Washington, DC (1994).

2.   W. G. Ramsey, N. E. Bibler, and T. F. Meaker, "Compositions and Durabilities of Glasses for Immobilization of Plutonium and Uranium," presented at Waste Management '95, Tucson, AZ, February 27-March 3, 1995.

3.   M. J. Plodinec, Development of Glass Compositions for Immobilization of SRP Waste, Savannah River Laboratory Report DP-1517 (1979).

4.   J. M. McKibben et al., Vitrification of Excess Plutonium, Westinghouse Savannah River Company Report WSRC-RP-755 (1993).

5.   B. W. Veal, J. N. Munday, and D. J. Lam, "Actinides in Silicate Glasses," in Handbook on the Physics and Chemistry of the Actinides, A. J. Freeman and G. H. Lander, eds., pp. 271-309 (1987).

6.   C. T. Walker and U. Riege, "Compatibility of Actinides with HLW Borosilicate Glass: Solubility and Phase Formation," in Ceramics in Nuclear Waste, T. D. Chikalla and J. E. Mendel, eds., CONF-790420, pp. 198-202 (1979).

7.   W. L. Ebert, The Effects of the Glass Surface Area/Solution Volume Ratio on Glass Corrosion: A Critical Review, Argonne National Laboratory Report ANL-94/34 (1995).

8.   J. K. Bates et al., "Performance of High Plutonium-Containing Glasses for the Immobilization of Surplus Fissile Materials," presented at the American Ceramic Society Meeting, Cincinnati, OH, May 1-4, 1995.

9.   A. J. G. Ellison, J. J. Mazer and W. L. Ebert, Effect of Glass Composition on Waste Form Durability: A Critical Review, Argonne National Laboratory Report ANL-94/28 (1994).

10.   J. E. Dickinson, Jr., and P. C. Hess, "Rutile Solubility and Titanium Coordination Number in Silicate Melts," Geochim. Cosmochim. Acta 49, 2289-2296 (1985).

11.   A. J. G. Ellison, P. C. Hess, and G. C. Naski, "Cassiterite Solubility in High-Silica K_2O-Al_2O_3-SiO_2 Liquids," Submitted to J. Am. Ceram. Soc., 8/95.

12.   A. J. G. Ellison and P. C. Hess, "Raman Study of Potassium Silicate Glasses Containing Rb^+, $Sr2^+$, $Y3^+$, and $Zr4^+$: Implications for Cation Solution Mechanisms in Multicomponent Silicate Liquids," Geochim. Cosmochim. Acta 58, 1877-1887 (1994).

13.   A. J. G. Ellison and A. Navrotsky, "Thermochemistry and Structure of Model Waste Glass Compositions," Mat. Res. Soc. Symp. Proc. 176, 193-207 (1991).

14.   F. J. Ryerson, "Oxide Solution Mechanisms in Silicate Melts: Systematic Variations in the Activity Coefficient of SiO_2," Geochim. Cosmochim. Acta 49, 637-649 (1985).

15.   J. K. Bates et al., ANL Technical Support Program for DOE Environmental Restoration and Waste Management: Annual Report October 1993-September 1994, Argonne National Laboratory Report ANL-95/20 (1995).

16.   T. A. Abrajano, J. K. Bates, and J. J. Mazer, "Aqueous Corrosion of Natural and Nuclear Waste Glasses. II. Mechanisms of Vapor Hydration of Nuclear Waste Glasses," J. Non-Crys. Solids, 108, 269-276 (1989).

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