LONG-TERM PERFORMANCE OF GLASSES FOR HANFORD LOW-LEVEL WASTE

A. J. Bakel, W. L. Ebert, and J. S. Luo

ARGONNE NATIONAL LABORATORY
Chemical Technology Division
9700 South Cass Avenue
Argonne, IL 60439-4837

Submitted to the
1995 American Ceramics Society Meeting
Cincinnati, Ohio
April 30-May 4, 1995

Work supported by Pacific Northwest Laboratory, which is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
LONG-TERM PERFORMANCE OF GLASSES FOR HANFORD LOW-LEVEL WASTE

A.J. Bakel, W.L. Ebert, and J.S. Luo
Chemical Technology Division
Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

The long-term performance of glasses developed for stabilizing Hanford low-level radioactive waste is being assessed using static leach tests conducted for up to one year and under conditions that accelerate corrosion. These tests support development of durable waste-form compositions and application of performance assessment models. Static leach tests were run with crushed glass at glass surface area/solution volume ratios of 2000 and 20,000 m⁻¹ and temperatures of 20, 40, 70, and 90°C. All tests showed sodium to be released from the glass faster than boron or silicon. These results are interpreted in terms of the glass structure, the corrosion mechanism, and the effects of time, glass surface area/leachant volume ratio, and temperature. Vapor hydration tests were conducted at elevated temperatures (70-200°C) using glasses containing various amounts of SiO₂, Na₂O, B₂O₃, CaO, and Al₂O₃. The response of a glass in these tests is relevant to its durability over very long disposal times. Different responses were observed in the tests: some glasses completely corroded within a few days while others were only slightly corroded. Corrosion led to the formation of analcime and gobbinsite; the corrosion rate increased significantly after these phases formed. Implications of these test results for the long-term glass durability are discussed.

INTRODUCTION

Glass waste forms are being developed to stabilize low-level radioactive wastes currently stored at the Hanford site. Argonne National Laboratory (ANL) is conducting laboratory tests to assess the long-term durability of a reference glass developed at Pacific Northwest Laboratory (PNL) and several compositional variants. Tests with long reaction times and tests that accelerate glass corrosion are being conducted to gain insight into the corrosion mechanism and the effects of time, temperature, and composition on the long-term corrosion rate. The accelerated tests also promote secondary phase formation as the glass corrodes. The identification of secondary phases is required to predict glass performance over long disposal times.

Radioactive wastes currently stored in tanks at the Hanford site will be chemically separated into high- and low-level waste streams to be stabilized by vitrification,
and glass waste forms are being developed for each. Sodium will be the dominant component in most low-level waste streams, and glasses having high sodium contents and acceptable chemical durabilities are being developed. An aggressive testing program is being conducted to evaluate candidate glasses and to assess their long-term durabilities.

EXPERIMENTAL

Eleven glasses were supplied for testing by PNL. The compositions of the glasses tested are given in Table I. All glasses contain 20 wt% Na₂O. Glass A was used in the most-detailed test matrix. The other ten glasses (B-K) were tested to assess the effects of small composition variations in vapor hydration tests. Monolithic samples of all eleven glasses were prepared at ANL for use in the vapor hydration tests. Glass A was also crushed and sieved to isolate the -100+200 mesh size fraction for use in static leach tests. Monoliths and crushed glass were washed to remove fines and were surveyed using a scanning electron microscope to assure acceptability and to characterize the glasses.

Static leach tests were conducted by reacting crushed Glass A with deionized water at massglass:masswater ratios of 1:10 and 1:1 to achieve glass surface area/solution volume (S/V) ratios of 2000 and 20,000 m⁻¹, respectively. The test procedure is similar to the Product Consistency Test (PCT) [1]. Tests are being performed at 20, 40, 70, and 90°C for reaction times between 28 and 364 days. Tests are conducted at two S/V ratios to measure the corrosion rate in solutions at different pH values, since the S/V is known to affect the solution pH [2]. At the end of a test, the leachate solution was analyzed for cations, anions, carbon, and pH. The surface of the corroded glass was analyzed using scanning electron microscopy (SEM) with associated x-ray spectroscopy (EDS). Reacted glass was also fixed in epoxy and cross-sectioned. Cross-sectioned samples were analyzed using SEM/EDS and analytical electron microscopy (AEM) with associated EDS and selected area electron diffraction (SAED).

Vapor hydration tests were conducted following the procedure developed at ANL in which monolithic samples are corroded in water vapor at elevated temperatures [3]. Vapor hydration tests are being conducted at 70, 120, 150, 175, and 200°C for reaction times between one day and one year using Glass A and at 150°C for 7, 14, and 28 days using Glasses B-K. Tests with Glass A were conducted to assess how the temperature affects secondary phases formation, which phases are formed, and how secondary phase formation affects the glass corrosion rate. Tests with the other glasses were conducted to determine the effect of composition on glass corrosion. Upon completion of the test, the surface and cross sections of the reacted solids were analyzed by SEM/EDS, AEM, and x-ray diffraction (XRD) to characterize the alteration of the surface and to identify secondary phases. The extent of corrosion was determined by the thickness of the crust of secondary phases formed on the glass or the amount of glass transformed into secondary phases.
Table I. Compositions of Glasses Tested.

<table>
<thead>
<tr>
<th></th>
<th>Glass A</th>
<th>Glass B</th>
<th>Glass C</th>
<th>Glass D</th>
<th>Glass E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al_{2}O_{3}</td>
<td>12</td>
<td>6</td>
<td>9</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>B_{2}O_{3}</td>
<td>5</td>
<td>9</td>
<td>9</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>CaO</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K_{2}O</td>
<td>1.46</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Na_{2}O</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>P_{2}O_{5}</td>
<td>0.19</td>
<td>1.18</td>
<td>1.18</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>SiO_{2}</td>
<td>55.91</td>
<td>62.78</td>
<td>59.78</td>
<td>59.78</td>
<td>56.78</td>
</tr>
<tr>
<td>Others*</td>
<td>0.57</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Glass F</th>
<th>Glass G</th>
<th>Glass H</th>
<th>Glass I</th>
<th>Glass J</th>
<th>Glass K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al_{2}O_{3}</td>
<td>12</td>
<td>6</td>
<td>12</td>
<td>6</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>B_{2}O_{3}</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CaO</td>
<td>0</td>
<td>9</td>
<td>9</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>K_{2}O</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Na_{2}O</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>P_{2}O_{5}</td>
<td>1.18</td>
<td>1.18</td>
<td>1.18</td>
<td>1.18</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>SiO_{2}</td>
<td>53.78</td>
<td>62.78</td>
<td>56.78</td>
<td>59.78</td>
<td>56.78</td>
<td>56.78</td>
</tr>
<tr>
<td>Others*</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
</tr>
</tbody>
</table>

*others include 0.2 wt % Bi_{2}O_{3}, Cl, Cr_{2}O_{3}, F, Fe_{2}O_{3}, MnO, Nd_{2}O_{3}, P_{2}O_{5}, SO_{3}, and ZrO_{2}.

RESULTS

Tests have been completed through 182 days; tests with longer scheduled reaction times are in progress. Figure 1 shows the normalized mass loss obtained for B, Na, and Si vs. time for Glass A reacted at 20,000 m^{-1} and 70°C. The normalized sodium mass loss is much higher than that of boron or silicon at all reaction times. The greatest release occurs over the first 28 days, and the solution composition does not change much at longer reaction times. Tests at other S/V ratios and other temperatures also show sodium to be released faster than boron or silicon and the greatest release to occur initially.

Figure 2 shows the normalized mass loss values for sodium in 30-day tests at 2000 m^{-1} and in 28-day tests at 20,000 m^{-1} vs. temperature. These data show that the corrosion rate increases with temperature, the corrosion rate is higher in tests at 2000 m^{-1} than 20,000 m^{-1}, and the effect of the S/V on the rate is greater at higher temperatures. Also, the solution pH values for 28-day tests at 2000 m^{-1} were about one pH unit lower than those for 30-day tests at 20,000 m^{-1}. This is due to the greater dilution in the tests at 2000 m^{-1}.

Examination of the reacted grains by SEM showed them to retain a smooth surface finish that is indistinguishable from the unreacted glass. The only
difference is a noticeable rounding of sharp fracture edges. A sodium-depleted layer is expected to form at the surface, based on the solution results. The thickness of this layer can be predicted from the difference in the normalized mass losses of sodium and silicon. The layers for all tests completed to date are predicted to be less than 100-nm thick. However, examination of the corroded glass from static leach tests by AEM showed no detectable surface alteration. This suggests that dealkalization does not alter the structure or composition of the glass surface enough to be detected.

Sodium-depleted layers were detected in vapor hydration tests, however. Figure 3 shows a cross-section of Glass A reacted 14 days at 150°C. A layer of sodium-depleted glass (SDG) is seen surrounding a core of unreacted glass. The sodium content of the layer was measured by EDS to be about half that of the sodium content in the unreacted glass. Other components were present in the layer at levels similar to those in the glass. Secondary phases precipitated onto the surface of the SDG. By using EDS, SAED, and XRD, these phases have been identified as analcime [Na[Al(Si2O6)].H2O] and gobbinsite [Na5(Al5Si11O32).11H2O] with partial substitution of potassium for sodium. An unidentified phase (or mixture of phases) was also present and has a stoichiometry of Na4.7Ca3K0.5Si7.5O24. Notice in Fig. 3 that the SDG is thinner beneath the secondary phases. The secondary phases may restrict the transport of material into or out of the layer. The morphology of these phases on the glass surface is shown in Fig. 4.

At reaction times less than 14 days, only the sodium-depleted layer forms, and the corrosion rate is relatively low. Analcime, gobbinsite, and the other phase(s) form a crust surrounding the glass after reaction times of about 10 days and the corrosion rate increases significantly. The entire glass is devitrified after about 18 days. Figure 5 gives the measured thickness of the alteration layer in tests with Glass A at 150°C vs. the reaction time in the vapor hydration tests. Scatter in the data is due to variations in the nucleation of the secondary phases and variations in the thickness of the crust of phases surrounding each sample. The line in Fig. 5 gives a corrosion rate of about 40 μm/d, equivalent to about 16 g/m²/d.

Samples of Glass A in vapor hydration tests conducted at 200 and 175°C had completely devitrified within about 3 and 7 days, respectively. Secondary phases had formed within one day at each temperature. Based on the initial thickness of the samples, the corresponding corrosion rates are about 80 μm/d at 175°C and >170 μm/d at 200°C (i.e., about 32 and 68 g/m²/d, respectively). Secondary phases did not form on Glass A until after about 100 days in vapor hydration tests conducted at 120°C. The glass corrosion rate after that was about 5 μm/d (equivalent to about 2 g/m²/d). Secondary phases did not form on samples reacted at 70°C through 182 days.

Table 2 summarizes the measured thicknesses of secondary phase crusts in vapor hydration tests conducted at 150°C for 7, 14, and 28 days. Glasses A, G, H, I, J,
Table 2. Measured Alteration Layers in Vapor Hydration Tests at 150°C, in µm.

<table>
<thead>
<tr>
<th>Glass</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>Glass</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0</td>
<td>300</td>
<td>0</td>
<td>G</td>
<td>30</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>H</td>
<td>40</td>
<td>50</td>
<td>&gt;</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>0</td>
<td>300</td>
<td>I</td>
<td>50</td>
<td>&gt;</td>
<td>&gt;</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>J</td>
<td>300</td>
<td>&gt;</td>
<td>&gt;</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>K</td>
<td>0</td>
<td>400</td>
<td>&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>200</td>
<td>&gt;</td>
</tr>
</tbody>
</table>

* ">" indicates sample was completely corroded.

and K, which contain calcium and 5 wt% or less B₂O₃, are highly corroded. Analcime, gobbinsite, and the unidentified calcium-bearing phase(s) had formed on all corroded glasses. It is not surprising that the same secondary phases formed on these glasses, based on the similarities of their compositions. Glasses B, C, D, E, and F, which do not contain calcium and all contain 6 wt% or more B₂O₃, are not corroded. One test each with glasses B and D had a physically altered layer, but the layer was compositionally indistinguishable from the unreacted glass, and no secondary phases were formed. This may be due to water diffusion into the glass without corrosion, as observed in tests with obsidian [4].

DISCUSSION

The trend observed in all the static leach tests is a rapid initial release followed by a leveling off at longer times. The leveling off is due to the influence of glass corrosion products in the solution (primarily silicic acid) on the glass corrosion rate. The glass corrosion rate is known to depend on the glass composition, temperature, pH, and silicic acid concentration in the solution. While the temperature (and glass composition) remains constant throughout the test, the solution pH and silicic acid concentration vary as the glass corrodes. The effects of changes in the solution chemistry on the glass corrosion rate must be accounted for to determine the effect of temperature on the corrosion rate. The effects of the solution chemistry will be nearly constant when the solution is highly dilute and when it is highly concentrated with glass components (prior to secondary phase precipitation). The leachate solutions have the smallest effect at the shortest times tested. The effects of temperature will also be determined when long-term tests are completed. The results of 30-day tests at 2000 m⁻¹ and 28-day tests at 20,000 m⁻¹ provide the best indication of the effect of temperature on the corrosion rate. Arrhenius plots of these test results (at 20, 40, 70, and 90°C) are linear ($r^2 = 0.986$ for 30-day tests at 2000 m⁻¹ and $r^2 = 0.996$ for 28-day tests at 20,000 m⁻¹), and both yield activation energies of about 130 kJ/mol. These are in the range common for surface reactions [5].
The test results available to date reveal the corrosion mechanism of Glass A. Static leach tests show sodium to be preferentially leached at all temperatures and S/V ratios. This can be explained on the basis of relationship between the glass composition and glass structure. Sodium in the glass may associate with trivalent glass components (such as aluminum and boron) to form units that are readily incorporated into the silicate structure. Sodium bonded to silica terminates the network structure and destabilizes the glass. Formation of Na-O-Al and Na-O-B bonds stabilizes the Na, Al, and B in the glass, while Na-O-Si bonds are easily hydrolyzed during corrosion [6]. Based on the composition of Glass A, up to about 70% of the sodium may be stabilized in Na-O-Al and Na-O-B bonds while the remaining sodium forms Na-O-Si bonds. The sodium is readily released from Na-O-Si bonds during corrosion, while Al, B, and the Na that is associated with Al and B are released stoichiometrically with Si. The depletion of sodium from the surface of glass reacted in static leach tests cannot be detected in tests terminated to date because the layer is too thin to be detected using SEM, dealkalization does not sufficiently alter the structure to permit visual identification and differences in the the sodium concentration cannot be measured due to migration of sodium under the electron beam during AEM analysis. However, a sodium-depleted layer is detected during SEM/EDS analyses of samples corroded in vapor hydration tests. In fact, EDS analyses show the depleted layers in vapor hydration tests to retain about half the original sodium, in good agreement with the amount of sodium expected to be associated with Al or B. The structural roles of Na, B, and Ca in Glasses A-K are likely responsible for the range of behavior observed in the vapor hydration tests at 150°C.

The vapor hydration tests show that Glass A can devitrify to form analcime and gobbinsite at elevated temperatures. Long-term static leach tests are in progress and will be used to determine if these or other secondary phases eventually form under more dilute conditions and at lower temperatures than in the vapor hydration tests. Secondary phases are known to form during the corrosion of glasses more durable than Glass A in static leach tests at 90°C after about six months [7]. The long-term static tests in progress will be used to determine if secondary phases form during corrosion of Glass A.

IMPLICATION TO LONG-TERM DURABILITY OF GLASS A

Results available to date indicate that the corrosion mechanism of Glass A is similar to that of other borosilicate glasses. Glass A (as well as Glasses G-K) are unstable with respect to zeolites (analcime and gobbinsite) and other phases. If provided a pathway, these glasses will devitrify to form these phases. (Glasses B-F will also devitrify, although they are more stable than Glass A.) Devitrification of all glasses is kinetically limited by the need for the glass to dissolve prior to forming secondary phases, and in the absence of secondary phases, all glass dissolves at a relatively low rate. When secondary phases form, however, the driving force for glass dissolution increases, as demonstrated in the vapor hydration tests.
The high sodium content of these glasses results in high solution pH values, which are favorable to zeolite formation. These tests indicate that changes in the glass composition to increase the stability of sodium in the glass structure will improve the glass durability. Calcium may compete with sodium for association with B and Al in the glass and so increase its number of Na-O-Si bonds. As discussed earlier, because boron stabilizes sodium via Na-O-B bonds, a decrease in the boron concentration (or likewise the aluminum concentration) at a constant sodium concentration will decrease the glass durability. These effects on the long-term glass behavior, namely devitrification, are clearly demonstrated in vapor hydration tests of only a few days duration.

CONCLUSIONS

Laboratory tests have been used to investigate the corrosion mechanism of glasses being developed to stabilize wastes with high sodium contents. Test results show:
1. Excess sodium is rapidly leached from the glass,
2. leachates quickly approach saturation at near-ambient temperatures,
3. leaching follows Arrhenius behavior between 20 and 90°C (activation energy is 130 kJ/mol),
4. calcium-bearing and boron-poor glasses devitrify to form analcime and gobbinsite at elevated temperatures, and
5. calcium-free and boron-rich glasses are more durable than calcium-bearing glasses in vapor hydration tests at 150°C.

ACKNOWLEDGMENTS

Solution analyses performed by S.F. Wolf; AEM sample preparation by J.K. Bates and N.L. Dietz; XRD analysis performed by B.S. Tani. Work supported by Pacific Northwest Laboratory, which is operated for the U.S. Department of Energy by Battelle Memorial Institute, under Contract DE-AC06-76RLO 1830.

REFERENCES

Figure 1. Normalized Mass Loss vs. Reaction Time in Tests with Glass A at 70°C and 20,000 m$^{-1}$: (▲) B, (■) Na, and (◇) Si

Figure 2. Normalized Mass Loss for Sodium in (◆) 30-day Tests at 2000 m$^{-1}$ and for (■) 28-day Tests at 20,000 m$^{-1}$ vs. Temperature

Figure 3. Photomicrograph of Cross Section of Glass A Reacted 14 days at 150°C in Vapor Hydration Test

Secondary Phases
Sodium-Depleted Glass
Unreacted Glass

100 µm

Figure 4. Photomicrograph of Phases Formed on Glass A Reacted 14 days at 150°C

Unidentified Phases
Gobbitsite
Analcime

100 µm

Figure 5. Measured Thickness of Secondary Phases vs. Reaction Time for Glass A Reacted at 150°C