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GLASS DISSOLUTION AT 20, 40, 70 AND 90°C:
SHORT-TERM EFFECTS OF SOLUTION CHEMISTRY AND LONG-TERM NA RELEASE

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ABSTRACT

The corrosion behavior of a borosilicate glass containing 20 mass % Na_2O was assessed using static dissolution tests. This glass (LD6-5412) is representative of high Na glasses that may be used to stabilize Hanford low-level radioactive waste. The normalized mass loss (NL) decreases as $NL(Na) \approx NL(B) > NL(Si)$ in 20 and 40°C for tests conducted at glass surface area to leachant volume (S/V) ratio of 10 m^{-1}, and decreases as $NL(Na) > NL(B) \approx NL(Si)$ in 90°C tests conducted at 10 m^{-1} and in all tests conducted at higher S/V. The difference in the corrosion behavior is probably caused by the influence of dissolved glass components in the leachates. The NL(Na) is greater than the NL(B) or NL(Si) in all the tests conducted. Results from long-term tests at 2000 m^{-1} show that the preferential release of Na persists for longer than one year at all temperatures and indicate that Na is released from this glass by an ion exchange process.

INTRODUCTION

The large volume (60 million gallons) of radioactive waste stored in underground tanks at the Hanford Site will be separated into high and low level fractions prior to immobilization. Vitrification has been specified as the immobilization method for the large volume of Na-rich low level waste. Many Na-rich glass compositions have been tested to develop a waste form that optimizes waste loading, ease of processing, and durability [HRMA-1994, FENG-1996]. We are conducting a series of static dissolution tests to characterize the corrosion behavior of one of these high sodium glasses, LD6-5412, which has the following composition: 56 mass % SiO_2, 20 mass % Na_2O, 5.0 mass % B_2O_3, 4.0 mass % CaO, 12 mass % Al_2O_3, 1.5 mass % K_2O, and 1.5 mass % "others." Tests are being conducted with this glass under conditions that highlight different aspects of its corrosion behavior. Corrosion data from this glass will be useful for calculation of the long-term corrosion behavior of this and other Na-rich glasses.

EXPERIMENTAL

Tests were conducted following the MCC-1 protocol [ASTM-1992] to describe the behavior of the glass in dilute solutions. The MCC-1 tests are conducted at S/V ratios of 1, 10, and 50 m^{-1} by placing one monolith in about 180, 18, and 3.6 ml of deionized water, respectively. Tests at S/V ratios of 1 m^{-1} were conducted in 250-ml LPE vessels, while tests at 10 and 50 m^{-1} were conducted in 22-ml Teflon vessels. Tests were run for 3, 7, and 14 days at 20, 40, and 90°C. The thickness and diameter of each monolith were measured, and the geometric surface area was calculated. The monoliths all had geometric surface areas of about 1.8 x 10^{-4} m^2. At the end of the test period, the leachate was removed from the vessel and analyzed for pH with a combination electrode (all pH measurements were performed at room temperature) and for B, Na, Si, and other cations with inductively coupled plasma-mass spectrometry (ICP-MS). The reacted glass was archived for later analyses. Blank tests were also conducted by adding deionized water to clean reaction vessels and heating the vessels to the test temperatures for 3, 7, or 14 days. The solutions from the blank tests were analyzed identically to the test solutions.

Other tests were conducted following the PCT method B protocol [ASTM-1995] to describe the behavior of the glass in concentrated solutions. Crushed glass (-100+200 mesh U.S. Standard) was reacted with deionized water. A series of tests was conducted at 20 and 40°C and at S/V ratios of 400, 1000, and 2000 m^{-1} for 3 and 7 days. Other tests were conducted at 20, 40, 70, and 90°C and at S/V ratios of 2000m^{-1} for durations of 28 to 364 days. Appropriate masses of glass and water were sealed in Teflon or Type 304L stainless steel vessels and placed in a constant temperature oven for the scheduled test duration. The glass surface area for each test was calculated from the weight of the glass sample and a specific surface area of 2 x 10^{-2} m^2/g for -100+200 glass particles. The glass had a measured density of 2.5 g/cm^3. At completion of a test, the leachate was removed, and aliquots analyzed for pH, B, Na, Si and other cations by ICP-MS. The reacted glass was archived for later analyses.

The concentrations of glass components in test solutions, the S/V ratios of the tests, and the glass composition were used to calculate NL and normalized release rate (NR) for each test using the following equations:

$$\mathrm{NL(i)} = \frac{c_i - c_i^{\circ}}{\left(\frac{S}{V}\right) f_i}, \text{ and } \mathrm{NR(i)} = \frac{\mathrm{NL(i)}}{t} \tag{1}$$

where c_i is the concentration of species i, in mg/L; c_i^{o} is the background concentration of species i, in mg/L; S/V is the glass surface area/solution volume ratio, in m^{-1}; f_i is the mass fraction of element i in the glass; and t is the reaction time in days.

RESULTS AND DISCUSSION

Results from 20 and 40°C tests at 1, 10, and 50 m^{-1} describe the corrosion behavior of the LD6-5412 glass in dilute solutions that are not expected to affect the corrosion rate. The results of 40°C, 10 m^{-1} tests are plotted in Figure 1. The uncertainty in the NL values, primarily due to the uncertainty in the ICP-MS analyses, was determined to be about ±20%. Figure 1 shows that NL(B) and NL(Na) are higher than NL(Si), and that the NL value for all elements increase linearly with time. The release rates of B (0.016 $g/m^2 \cdot d$ at 20°C and 0.031 $g/m^2 \cdot d$ at 40°C), and Na (0.018 $g/m^2 \cdot d$ at 20°C and 0.040 $g/m^2 \cdot d$ at 40°C) are higher than that of Si (0.001 $g/m^2 \cdot d$ at 20°C and 0.006 $g/m^2 \cdot d$ at 40°C). The corrosion rate from these tests is interpreted to be a lower bound for the forward reaction rate.

Results from 90°C 10 m^{-1} tests at show the effects of increased solution concentrations on glass reaction. Figure 2 shows NL(B, Na, and Si) as a function of time in 90°C, 10 m^{-1} tests. The value of NL(Na) is higher than NL(B) or NL(Si). In addition, NL(B) and NL(Si) increase about 0.8 g/m^2 between 7 and 14 days, while NL(Na) increases about 1.2 g/m^2 over the same period. The change in NL(B) and NL(Si) between 7 and 14 days (about 0.8 g/m^2) is less than the change between 3 and 7 days (1.1 and 1.7 g/m^2, respectively) due to the increasing concentration of glass components in solution. Comparison of results from 20, 40, and 90 °C tests at 10 m^{-1} (Table 1) shows that higher temperatures leads to more concentrated solutions over the same test duration, and that this concentrated solution affects the corrosion.

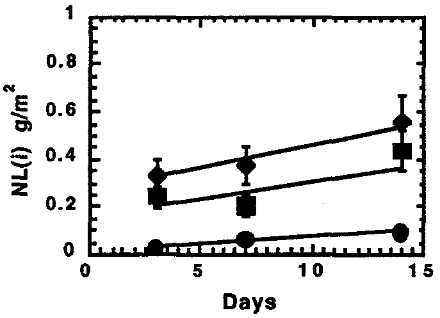

Figure 1. Results from 40°C, 10m^{-1} MCC-1-type tests: NL(B) [■], NL(Na) [♦], and NL(Si) [●]. Error bars are ± 20%, representing the uncertainty of the ICP-MS analyses. Lines are drawn to show general trends only.

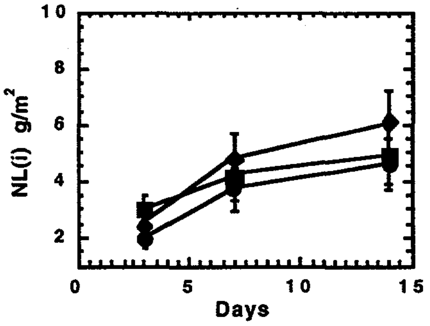

Figure 2. Results from 90°C, 10m^{-1} MCC-1-type tests: NL(B) [■], NL(Na) [♦], and NL(Si) [●]. Error bars are ± 20%, representing the uncertainty of the ICP-MS analyses. Lines are drawn to show general trends only.

Results from long-term tests at 2000 m^{-1} describe the corrosion behavior of the glass in concentrated solutions that are expected to affect the corrosion rate. The NL(B, Na, and Si) values are plotted as a function of test duration in Figure 3 for 40°C 2000 m^{-1} tests. The NL(B) and NL(Si) values are similar and significantly lower than the NL(Na) value. Since no alteration products were observed, we believe that these differences result from the dissolution of the glass. The values of NL(B) and NL(Si) increase only slightly after 28 days, while NL(Na) continues to increase up to 364 days. The behavior of B and Si shows that their release from the glass is inhibited in the relatively concentrated solutions evolved after 28 days. The continued increase in the NL(Na) value suggests that the release of Na is not affected by the solution chemistry in the.

Table 1. Glass Dissolution Rates Measured in MCC-1 Tests and PCT[a].

Time	Temperature	S/V	pH	NR(B)	NR(Na)	NR(Si)
3	20	10	7.62	0.033	0.082	<0.003
3	20	50	7.14	0.019	0.031	0.008
3	20	400	7.93	0.0037	0.018	0.0013
3	20	1000	9.37	0.0035	0.013	0.0017
3	20	2000	9.75	0.0027	0.011	0.0014
7	20	10		0.015	0.024	<0.001
7	20	50	8.67	0.011	0.018	0.001
7	20	400	9.50	0.0022	0.0065	0.0015
7	20	1000	9.93	0.0018	0.0062	0.0012
7	20	2000	10.28	0.0017	0.0062	0.0011
14	20	1	9.49	0.020	0.069	<0.006
14	20	10	8.01	0.016	0.018	0.001
14	20	50	7.35	0.009	0.012	0.002
3	40	1	7.34	0.15	0.41	<0.03
3	40	10	8.37	0.079	0.11	0.008
3	40	50	7.64	0.038	0.058	0.010
3	40	400	9.22	0.0096	0.022	0.010
3	40	1000	9.79	0.0082	0.021	0.0084
3	40	2000	9.69	0.0060	0.019	0.0060
7	40	1	8.37	0.055	0.20	<0.012
7	40	10		0.029	0.053	0.008
7	40	50	8.80	0.027	0.037	0.009
7	40	400	9.78	0.0077	0.014	0.0081
7	40	1000	10.07	0.0046	0.011	0.0049
7	40	2000	10.48	0.0033	0.0096	0.0034
14	40	1	6.57	0.051	0.15	<0.006
14	40	10	6.88	0.031	0.040	0.006
14	40	50	7.24	0.021	0.024	0.005
3	90	10	8.23	0.99	0.80	0.65
7	90	10	9.32	0.59	0.68	0.53
14	90	10	8.95	0.35	0.43	0.33
f(i)[b]				0.0182	0.155	0.246

[a] Temperature in °C, S/V in m^{-1}, NR(i) in $g/(m^2 \bullet d)$.
[b] f(i) is the mass fraction of element i in the glass.

same way as the release of B and Si. Results from these high S/V ratio tests show the effects of leachate concentration on the long-term corrosion behavior of this glass

The mean concentrations of B, Na, and Si in leachates from blank tests increase slightly as a function of temperature. Relatively high concentrations are measured in only a few tests, suggesting that the measured concentrations are due to contamination rather than interaction between the vessel and the water. Contamination might occur when cleaning the vessels, assembling or terminating the tests, or analyzing the solutions. The Si concentration was <0.007 mg/L for all tests conducted in LPE vessels and for 20°C tests conducted in Teflon vessels. The average Si concentrations for 40 and 90°C tests conducted in Teflon vessels were 0.023 and 0.043

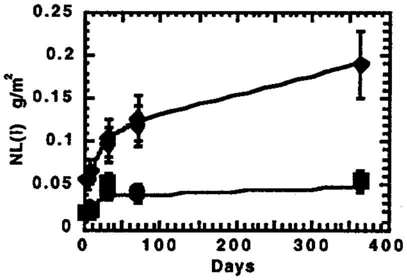

Figure 3. Results from 40°C, 2000m^{-1} PCT-type tests: NL(B) [■], NL(Na) [♦], and NL(Si) [●]. Error bars are ± 20%, representing the uncertainty of the ICP-MS analyses. Lines are drawn to show general trends only.

mg/L, respectively. The average concentrations measured in blank tests at a particular temperature were used as background values for the tests with glass.

To directly compare results from different types of tests and to describe the effects of solution chemistry, we plotted NR(B, Na, and Si) values versus the total Si leachate concentration (mg/L) in Figure 4 for all tests conducted for 3 days at 40°C. The diagonal line in the lower left-hand portion of Figure 4 shows the NR(Si) calculated based on the limit of quantitation (LOQ) for Si. The LOQ is defined as 10 standard deviations of 10 analyses of a blank solution.

The NR(Si) is similar in all tests shown in Figure 4 when [Si] is less than about 8 mg/L, but decreases at higher Si concentrations. Both the [Si] and the pH increase as the glass dissolves (Table 1). An increase in [Si] has been shown to inhibit the corrosion of glass [PEDERSON-1983, GRAMBOW-1985]. On the other hand, an increase in pH is known to increase the corrosion rate of the LD6-5412 glass [McGRAIL-1995]. The observation that NR(Si) decreases at high [Si] and pH indicates that the effect of high [Si] dominates over the pH effect at these conditions.

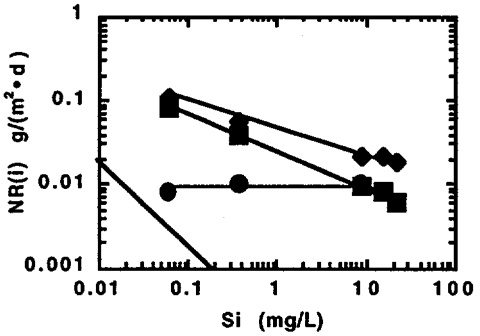

Figure 4. Results from 3 day, 40°C static dissolution tests: NR(B) [■], NR(Na) [♦], and NR(Si) [●]. The line at the lower left of plot represents the NR(Si) at the limit of quantitation. Lines are drawn to show general trends only.

As shown in Figure 4, NR(B) decreases as [Si] (and pH) increases, and is similar to NR(Si) above 8 mg Si/L. The high NR(B) in dilute solutions (<8 mg Si/L) may result from release the of B from the surface and the near surface region of the glass. In more concentrated solutions (≥8 mg Si/L), B is released congruently with Si.

The NL(Na) is higher than the NL(B) and NL(Si) in all the tests conducted in this study (Figures 1-4, Table 1). Ion exchange has been suggested as a process for the release of sodium from simple sodium silicate glasses [RANA-1961, BOKSAY-1967]. The rate of this process is thought to be controlled by the diffusion of water into the glass. If the release of sodium is controlled by a diffusion process, then the Na concentration in solution will be linear as a function of $t^{0.5}$. Figure 5 shows a plot of adjusted Na loss [NL(Na) - NL(Si)] as a function of $t^{0.5}$. The adjusted Na loss is calculated by subtracting the Na release due to glass hydrolysis [NL(Si)] from the total Na release [NL(Na)], and thus represents the Na released by ion exchange in tests where no alteration products were formed. The adjusted Na loss increases linearly as a function of $t^{0.5}$ (regression coefficient >0.95). The diffusion coefficients calculated from the slopes of the lines in Figure 5 are $8x10^{-18}$ cm^2/s at 90°C, $3x10^{-18}$ cm^2/s at 70°C, $3x10^{-19}$ cm^2/s at 40°C and $3x10^{-20}$ cm^2/s at 20°C. Similar values have been reported previously for the diffusion of water into silicate glasses [GRAMBOW-1992]. The diffusion coefficients that we calculated at different temperatures were used to calculate an activation energy of 70 kJ/mol for the diffusion process. This activation energy is similar to those reported in the literature for the diffusion of water into various silicate glasses [GRAMBOW-1992]. Therefore, data from this study are consistent with the rate of Na release from the LD6-5412 glass being controlled by the diffusion of water into the glass.

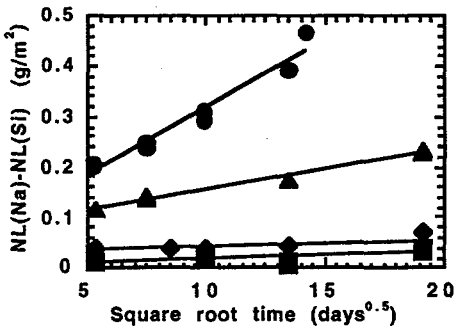

Figure 5. Results from 2000 m^{-1}, corrected NL(Na) vs. $t^{0.5}$: 20°C [■], 40°C [♦], and 70°C [●]. *Lines represent best fits.*

Data presented here show that the NL(Na) is higher than the NL(B) or NL(Si) from LD6-5412 in various static dissolution tests, and that this difference persists in long-term tests. The data in Figures 4 and 5 show that the release of Na from this glass is a diffusion-controlled process. The diffusion of water into the glass is followed by ion exchange of alkali metals. The result that the diffusion-controlled process persists for at least one year indicates that ion exchange can be a long-lived, high-rate process for the release of alkali metals from some glasses.

Therefore, ion exchange reactions must be considered to accurately calculate the long-term corrosion of this glass.

CONCLUSIONS

A series of static dissolution tests was conducted with the Na-rich (20 mass % Na_2O) LD6-5412 glass under conditions that highlight different aspects of its corrosion behavior. Results from these tests show that different test conditions affect the NL(B, Na and Si) in different ways. For example, in 20 and 40°C tests at 10 m^{-1}, the NL decreases as NL(Na)≈NL(B)>NL(Si), while the NL decreases as NL(Na)>NL(B)≈NL(Si) in 90°C, 10 m^{-1} tests and in tests conducted at higher S/V. These patterns reflect changes in the corrosion rates caused by the buildup of silicic acid in the leachate solution. The NL(Na) is higher than the NL(B or Si) in all tests conducted, including tests conducted for more than one year. These data are consistent with a coupled diffusion-ion exchange process for the release of Na. The ion exchange reaction proceeds at a higher rate than the glass hydrolysis reaction and must be considered in calculations of the long-term corrosion of this glass.

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