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MEASUREMENT OF THE GLASS DISSOLUTION RATE IN THE PRESENCE OF ALTERATION PHASES

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ABSTRACT

The dissolution rate of LD6-5412 glass was measured at 90°C in the presence of its alteration phases with the Product Consistency Test (PCT) Method B, the Vapor Hydration Test (VHT), and the Accelerated Dissolution Test (ADT). Alteration phases formed during the PCTs and VHTs, but variations in the time required for their nucleation resulted in large uncertainties in the measured rates. The alteration phases are generated separately for use in the ADTs, so the measured rates are not affected by the kinetics of alteration phase nucleation. The rates measured in the PCTs, VHTs, and ADTs were 0.4 $g/(m^2 \bullet d)$ (a lower bound), 2 $g/(m^2 \bullet d)$ (extrapolated from the results of tests run at high temperatures), and 1.4 $g/(m^2 \bullet d)$, respectively. The solution pHs were about 12 in all the tests.

INTRODUCTION

Laboratory tests are being conducted to measure corrosion characteristics needed to calculate the long-term performance of glass in a disposal site. The corrosion rates of borosilicate glasses such as those that may be used to stabilize low-level radioactive waste are known to depend on the glass composition, the temperature, and the chemistry of the solution contacting the glass, particularly the pH and the silicic acid concentration [1,2]. A decrease in the dissolution rate of a glass with increased reaction time is generally observed in static dissolution tests as the concentrations of dissolved glass components increase. This decrease is usually attributed to a backreaction involving silicic acid [3-5]. The dissolution rate may decrease to near zero as the solution approaches apparent saturation. However, the dissolution rates of some glasses increase significantly upon the formation of certain alteration phases. This increase has been observed in hydrothermal tests at or near 90°C [6-9] and in tests conducted in water vapor at elevated temperatures (typically 120 to 200°C) [10-12]. The mechanism by which the formation of alteration phases leads to an increase in the glass dissolution rate is not yet understood, but is probably related to the relative stabilities of the glass and the alteration phases. For example, calculations by Van Iseghem and Grambow [13] indicate that some glass compositions are unstable with respect to analcime, which is formed during the corrosion of many waste glasses.

To evaluate glass behavior over long disposal times, both the identity of the alteration phases that form and their effect on the glass corrosion rate must be determined. Laboratory tests must be conducted under conditions that accelerate glass corrosion to generate alteration phases, but account must be taken of the accelerating conditions when determining the corrosion rate relevant to a disposal environment. For example, low-level waste glasses are likely to experience temperatures near 20°C in a disposal site. However, most tests are conducted at higher temperatures to promote a measurable extent of corrosion within a relatively short test duration. Testing and modeling is in progress at lower temperatures.

In this paper, we discuss and compare the corrosion rates of a sodium borosilicate glass at 90°C in the presence of its alteration phases that were measured with three experimental methods: the Product Consistency Test (PCT) Method B, the Vapor Hydration Test (VHT), and the Accelerated Dissolution Test (ADT). Similar tests at lower temperatures are in progress.

EXPERIMENTAL METHODS & RESULTS

The glass that was tested was made at Pacific Northwest National Laboratory and is referred to as LD6-5412. It contains, in mass %, about 56 SiO_2, 20 Na_2O, 12 Al_2O_3, 5 B_2O_3, 4 CaO, 1.5 K_2O, and a total of 1.5 other components. The dissolution rates were measured at 90°C with PCTs and ADTs and calculated from the VHT results by extrapolating the rates measured in tests conducted at higher temperatures to 90°C.

The glass dissolution rates were calculated based on solution and solids analyses. Solutions were analyzed for pH with a combination electrode and for dissolved constituents with inductively coupled plasma mass spectrometry (ICP-MS). Reacted solids were examined with optical microscopy and scanning electron microscopy (SEM). Alteration phases were identified with X-ray diffraction (XRD) and analytical electron microscopy (AEM). The test methods and test results are discussed below.

Product Consistency Test (PCT) Method B: Static dissolution tests were conducted in deionized water following PCT Method B [14] with crushed glass in deionized water at 90°C and a glass surface area/solution volume (S/V) ratio of 20,000 m^{-1} for up to 223 days. The corrosion rate was computed from the normalized mass losses based on boron, NL(B), after different reaction times. The values of NL(B) are plotted vs. the reaction time in Fig. 1. While the values of NL(B) increased with the reaction time, very high values were measured in tests conducted for 98, 182, and 195 days. The high NL(B) in tests conducted for 98 days and longer were correlated with the formation of analcime [$Na(AlSi_2O_6)\cdot H_2O$] and gobbinsite [$Na_5(Al_5Si_{11})O_{32}\cdot 11H_2O$]. The reacted glass from duplicate 98-day tests was examined with SEM. Trace amounts of these alteration phases were detected in one test, but not in the other. The NL(B) in the 98-day test in which alteration phases had formed was 0.26 g/m^2. It was 0.065 g/m^2 in the 98-day test in which these alteration phases had not formed.

Alteration phases formed in all tests conducted for 182 days and longer, although different amounts formed in different tests. The largest amount of alteration phases had formed in the test conducted 195 days. Based on the measured B concentration in the leachate solution from that test, almost 90% of the glass had been converted to alteration phases. Glass in the other tests had not reacted to as great an extent as that in the 195-day test.

The measured pH values are included in Fig. 1. These were measured at room temperature and have not been adjusted to account for the effects of either temperature or Na. The pH values do not appear to be correlated with the reaction time, the increase in the extent of corrosion, or the formation of alteration phases.

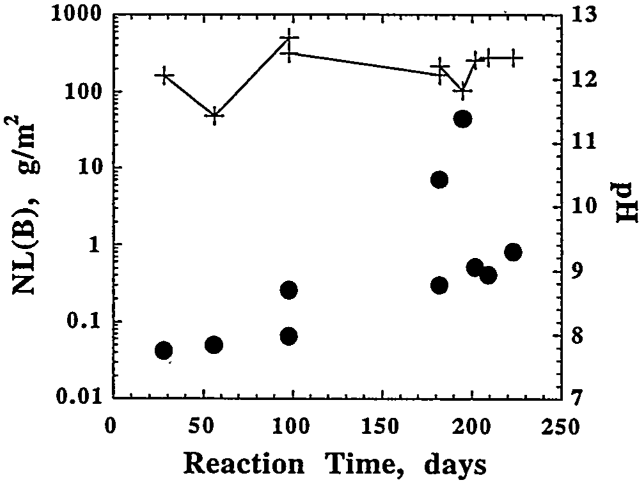

Figure 1. Results of PCTs, NL(B) (●) and pH (+) vs. Reaction Time.

Notice that the values of NL(B) in duplicate tests appear to define two different trends, one with a steeper upward curvature than the other. The tests for which the NL(B) values show the steeper curvature contained greater amounts of alteration phases than the other tests reacted for the same or similar durations. The large differences between the NL(B) values in duplicate tests conducted for 98, 182, and 223 days reflects the differences in the reaction times required for alteration phases to form in each test. That is, since the dissolution rate increases significantly upon the formation of certain alteration phases, the extent of corrosion measured in each test is highly dependent on when those phases formed. Therefore, alteration phases are assumed to have formed earlier in the tests with the high NL(B) values than in the tests with the low NL(B) values.

The dissolution rate is calculated by dividing the difference in NL(B) between tests of two different durations by the difference in the reaction times. The average dissolution rate over the initial 28 days of corrosion is 1×10^{-3} $g/(m^2 \cdot d)$. From the results of tests conducted for 28 and 98 days (the 98-day test without alteration phases), the dissolution rate prior to formation of the alteration phases was calculated to be 2×10^{-4} $g/(m^2 \cdot d)$. The dissolution rate in the presence of the alteration phases was calculated to be about 0.4 $g/(m^2 \cdot d)$, based on the results of the 98-test in which alteration phases had formed and 195-day test. Determination of the rate from the results of batch tests is complicated by the fact that alteration phases are likely to form after different reaction times in different tests. The actual rate would be higher if the alteration phases formed later than after 98 days or lower if they formed before 98 days. A minimum value of the rate can be calculated by assuming that the alteration phases had formed and the pH increased to 12 immediately after the test was initiated. In that case, the minimum value of the dissolution rate in the 195-day test is 0.23 $g/(m^2 \cdot d)$.

The values of NL(B) and the dissolution rates were calculated based on the initial surface area of the glass used in each test. Dissolution of the glass will result in a nonlinear decrease in the surface area, so that the instantaneous dissolution rate after alteration phases have formed will be significantly higher than the rate calculated using the initial surface area. Unfortunately, not enough data are available to adjust the calculated rate to take into account the loss of surface area. Therefore, the rate calculated from these data provides a lower bound to the dissolution rate in the presence of alteration phases.

Vapor Hydration Test (VHT): In the VHT, monolithic samples are reacted in saturated water vapor at elevated temperatures [12]. While the VHT is important for identifying alteration phases and providing a qualitative measure of their effect on the dissolution rate, test results can also be used to estimate the corrosion rate after the alteration phases form. Because the solution evaporates from the sample when a VHT is completed, the extent of corrosion must be measured based on alteration of the glass surface. The pH values of small drops of water remaining on some samples were measured to be about 12 with pH paper. The extent of corrosion can be monitored by measuring the thickness of the crust of alteration phases that forms on the surface or the thickness of the glass core that remains beneath the crust. Tests were conducted with LD6-5412 glass in saturated water vapor at 120, 150, 175, and 200°C. The extent of glass corrosion was measured on cross-sectioned samples with an SEM.

The extent of corrosion was negligible prior to the formation of alteration phases, but increased quickly after they formed. Corrosion resulted in dissolution of the glass and the formation of a crust of alteration phases. A Na-depleted layer formed after short test durations at the glass surface in tests at 120 and 150°C, but was consumed by the formation of alteration phases at longer times. Analcime and gobbinsite were the predominant alteration phases formed at all temperatures. A poorly crystallized calcium-bearing phase was also formed. It is probably composed of residual material that was not incorporated into the zeolite phases.

Corrosion occurred at a very low rate prior to the formation of alteration phases, but at high rates after the alteration phases formed, such that the monolithic sample was completely

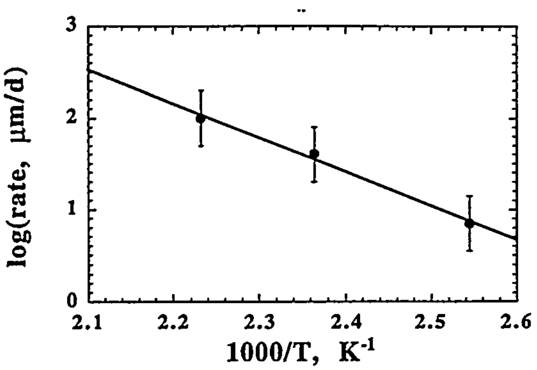

Figure 2. Results of VHTs at 120, 150, and 175°C. Line shows regression fit to mean rates at each temperature.

altered after a few days. The formation of alteration phases and complete alteration of the glass occurred between about 90 and 170 days at 120°C, between about 3 and 14 days at 150°C, and between about 0 and 2 days at 175°C. As in the PCTs, the formation of the alteration phases and the increase in the corrosion rate occurred after different reaction times in different tests. The corrosion rates were calculated using tests having the greatest extent of corrosion in the shortest reaction times.

Corrosion of the glass in the VHTs was not uniform and the thickness of the crust of alteration phases varied. The rates measured in tests at 120, 150, and 175°C are plotted vs. the inverse of the absolute temperature in Fig. 2. The variation in the thickness of the crust was used to calculate the uncertainty bars for the plotted rates, where the upper and lower rates were calculated from the minimum and maximum thicknesses. Since the glass had completely reacted within the shortest test duration at 200°C, only a lower limit of about 300 μm/d could be calculated by assuming the entire sample had corroded after 3 days. This rate agrees well with the value determined by extrapolation of the fitted line in Fig. 2 to 200°C (2.16 on the x-axis), which is about 500 μm/d. At this rate, the entire sample would have reacted in about 2 days.

The rate at which the thickness of the crust increased was converted to a dissolution rate by multiplying that rate by 2.5 g/cm^3. This value is the density of the glass, which is assumed to be similar to the density of the collection of alteration phases. The glass dissolution rate is estimated to be about 1 g/(m^2•d) at 90°C. The apparent activation energy for corrosion in VHTs calculated from the Arrhenius slope in Fig. 2 is about 80 kJ/mol. The activation energy measured for the same glass with tests in which the solution was maintained highly dilute was about 93 kJ/mol [15]. The similarity of the activation energies suggests that the same process controls glass dissolution under both test conditions.

Accelerated Dissolution Test (ADT): This new test method, developed at ANL, combines aspects of the MCC-1 Static Leach Test [16], the PCT, and the VHT to measure the dissolution rate of a glass in the presence of its alteration phases. Tests were conducted by combining (1) a monolithic test sample of unreacted LD6-5412 glass that had been polished to a 600-grit finish, (2) a monolithic sample of LD6-5412 glass that had been vapor-hydrated at 150°C to generate alteration phases, and (3) a preconditioned solution that was prepared by reacting crushed LD6-5412 glass in deionized water at 90°C and an S/V ratio of 20,000 m^{-1} for about 21 days. The ADT exposes fresh glass to a solution that is nearly saturated with respect to its alteration phases in the presence of those alteration phases. That the solution was nearly saturated is known by comparison to the solutions in PCTs in which alteration phases had formed.

Three ADTs were conducted at 90°C. The vapor-hydrated disks were examined with optical microscopy to ensure that similar amounts of the same phases were present on the disks used in the three tests. Three control tests were also conducted by placing a monolith sample in the preconditioned solution without a vapor-hydrated disk. Aliquots from the same preconditioned solution were used in all tests. Test samples from both the ADT and control tests were periodically removed from the test vessels, air dried, weighed, then placed back in the vessels to continue the tests. The glass corrosion rate was calculated from the mass loss of the test sample.

The dissolution rate of the LD6-5412 glass is known to depend on the pH of the solution [15]. The pH of the preconditioned solution was about 12, as were the solution pH values measured in the ADTs and control test solutions at the end of the tests. Therefore, the dissolution rates were measured at a nearly constant solution pH value.

The mass losses of the test samples in the control tests were all negligible at all test times. The mass loss results of three ADTs at test times through 64 days are shown in Fig. 3. The lines drawn in Fig. 3 were used to calculate the dissolution rate in the units mg/d. The measured dissolution rates are 0.17 mg/d (circles), 0.28 mg/d (squares), and 0.28 mg/d (diamonds). The differences in the rates in may be due to the different amounts of alteration phases present in each test. The normalized dissolution rate was calculated by dividing the rate as mg/d by the surface area of the test sample, which was about 1.7 x 10^{-4} m^2 for the samples in all three tests. The average rate calculated from the three replicate tests was 1.4±0.4 $g/(m^2 \cdot d)$.

Examination of the test samples with optical microscopy and SEM at the end of the tests confirmed that alteration phases had not formed on the test samples. The vapor-hydrated disks were also examined with SEM. Small crystallites were observed to have precipitated on the larger analcime crystals of the vapor-hydrated glass. Notice in Fig. 3 that extrapolation of the fit lines of the test results to zero mass loss suggests that glass dissolution was affected by the alteration phases after about 2, 14, and 42 days. This apparent "inoculation time" may be required for the alteration phases to equilibrate with the solution or may result from a systematic error not yet controlled.

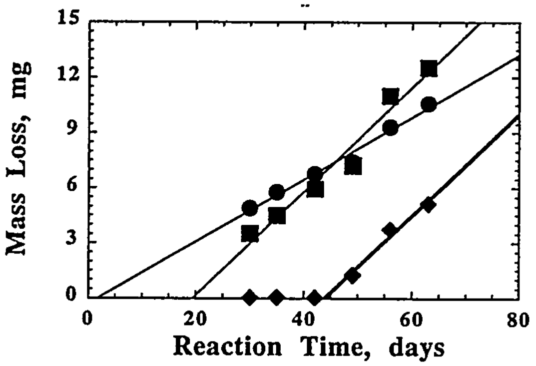

Figure 3. Results of ADTs at 90°C. Circles, squares, and diamonds indicate three replicate tests. Lines show regression fits.

DISCUSSION

Uncertainties and limitations exist in the measurement of the dissolution rate in the presence of alteration phases with all three test methods. However, greater uncertainties are associated with the PCT and VHT than with the ADT. An important uncertainty of the PCT and VHT results from their being conducted as batch tests, in which a separate test is used to generate each data point. Because the time required for alteration phases to nucleate is usually variable, alteration phases may form at different times in the different tests. The uncertainty associated with the reaction time required for phases to form and the time at which the glass is completely reacted compounds with other testing uncertainties (e.g., in solution analyses) to result in a large uncertainty in the measured rates. We believe that differences of when the alteration phases form and the corrosion rate increases is the cause of most of the scatter seen in the PCT results in Fig. 1.

There is also uncertainty in the rate calculated from PCT results because the true surface area of crushed glass used in a PCT is difficult to measure. The surface area is usually estimated based on the sieve sizes used to isolate the fraction used in a test [14]. The uncertainty in the surface area results in a corresponding uncertainty in the dissolution rate. The rates measured in tests conducted with crushed glass are also strongly affected by the loss of surface area as the glass dissolves. If the crushed glass is modeled to be spherical grains, then dissolution of about 25% of -100 +200 mesh crushed glass will result in a decrease in the surface area of about 20%. This amount exceeds the analytical uncertainty for solution analysis, and is expected to have a measurable effect on the dissolution rate. The dissolution of smaller grains will result in a more rapid decrease in the surface area. Calculation of NL(B) based on the initial surface area after a large fraction of glass has reacted will result in values that are too low. The rates calculated from those NL(B) will also be too low.

The VHTs must be conducted at elevated temperatures to generate alteration phases within a reasonable time. Extrapolation of the rates measured at high temperatures to lower temperatures is based on the assumptions that (1) the same phases form in tests at high and low temperatures, and (2) that the dissolution mechanism is the same at both temperatures. Quantification of the corrosion rate based on alteration of the glass surface is also complicated by the nonuniform corrosion that is often observed.

The ADTs avoid some of the uncertainties that are inherent in PCT and VHTs. The ADTs use monolithic samples for which the surface area can be measured directly and are not affected by the loss of surface area during the test to a significant degree. They are not conducted as batch tests and are not affected by the nucleation kinetics of the alteration phases, since the alteration phases are present throughout the test. The ADTs can be conducted at the temperature of interest, so rates measured at elevated temperatures do not have to be extrapolated to lower temperatures, as in the VHTs. However, in both the VHTs and ADTs, it must be verified that the same alteration phases are formed at elevated temperatures and at the temperatures of interest. In the case of LD6-5412 glass, analcime and gobbinsite are the most abundant alteration phases that are observed to form in both the high-temperature VHTs and low-temperature PCTs.

All three test methods provide information needed to calculate the glass corrosion behavior over long times. The PCT is needed to characterize glass dissolution in the nearly saturated solutions before the formation of alteration phases and to confirm that the same phases form at the test temperature and at elevated temperatures; the VHT is needed to generate alteration phases within a reasonable time for identification; and the ADT provides a reliable measure of the dissolution rate in the presence of alteration phases.

CONCLUSION

The dissolution rate of LD6-5412 glass in the presence of its alteration phases has been measured with the PCT, the VHT, and the newly developed ADT. Given the uncertainties and limitations associated with each test, the rates measured after the formation of alteration phases in the three tests are in good agreement. The ADT probably provides the best measure of the dissolution rate because (1) it is not affected by nucleation kinetics of the alteration phases and (2) the surface area remains nearly constant as the glass dissolves. The rate measured in triplicate ADTs was 1.4±0.38 $g/(m^2 \bullet d)$. The rates measured using PCTs and VHTs were 0.4 and 2 $g/(m^2 \bullet d)$, respectively. The average dissolution rate at 90°C from the three test methods is 1.3±0.8 $g/(m^2 \bullet d)$ in the presence of alteration phases.

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