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ABSTRACT

We measured the dissolution rate of a simple five-component glass at 70°C using static tests and single-pass flow-through (SPFT) tests with pH buffers at pH values of 6.2, 8.3, and 9.6. The two methods yielded similar rates; however, the measured rates are about 10X higher than the rates measured previously for a glass having the same composition using an SPFT test method. Differences are attributed to how the effect of the solution flow rate on the glass dissolution rate was taken into account and how the surface area of crushed glass was estimated. The differences indicate the need to standardize the SPFT test procedure.

I. INTRODUCTION

The dose from radionuclides released from high-level radioactive waste (HLW) glasses as they corrode must be taken into account when assessing the performance of a disposal system. In the performance assessment (PA) calculations conducted for the proposed Yucca Mountain, Nevada, disposal system, the release of radionuclides is conservatively assumed to occur at the same rate at which the glass matrix dissolves. A simple model was developed to calculate the glass

dissolution rate of HLW glasses in these PA calculations [1].

In the model, the glass dissolution rate depends on temperature, pH, and the compositions of the glass and solution [1]. The rate is calculated as:

$$rate = k_0 \cdot 10^{\eta \cdot pH} \cdot e^{-E_a/RT} \cdot (1-Q/K) \quad (1)$$

where k_0 , η , and E_a are the parameters for glass composition, pH, and temperature dependence, respectively, and R is the gas constant. The term $(1-Q/K)$ is the affinity term, where Q is the ion activity product of the solution and K is the pseudo-equilibrium constant for the glass. Values of the parameters k_0 , η , and E_a are determined under test conditions where the value of Q is maintained near zero, so that the value of the affinity term remains near 1. The dissolution rate under conditions in which the value of the affinity term is near 1 is referred to as the forward rate. This is the highest dissolution rate that can occur at a particular pH and temperature. The value of the parameter K is determined from experiments in which the value of the ion activity product approaches the value of K . This results in a decrease in the value of the affinity term and the dissolution rate.

For the PA calculations that were conducted to evaluate the suitability of the Yucca Mountain, Nevada, site, ranges of parameter values were selected to bound the dissolution rates of the wide range of HLW glass compositions that will be disposed. The values and ranges of the model parameters for the pH and temperature dependencies were extracted from the results of single-pass flow-through (SPFT), static leach tests, and Soxhlet tests in the literature [1]. Static tests were conducted with several glasses to measure the range of values for the glass composition parameter.

Additional tests will be conducted to support PA calculations for the license application. The model and parameter values may be modified to provide a “reasonable expectation” dissolution rate for HLW glasses rather than the upper bound rate that was used for Site Recommendation. As part of that effort, we are evaluating test methods used to measure dissolution rates and provide model parameter values.

The highly dilute solutions required to measure the forward rate and extract values for k_0 , η , and E_a can be maintained by conducting dynamic tests in which the test solution is removed from the reaction cell and replaced with fresh solution. In the SPFT test method, this is done by continuously pumping the test solution through the reaction cell. Alternatively, static tests are conducted with sufficient solution volume that the solution concentrations of dissolved glass components do not increase significantly during the test. Both the SPFT and static tests can be conducted for a wide range of pH values and temperatures.

Both static and SPFT tests have shortcomings. The SPFT test requires analysis of several solutions (typically 6-10) at each of several flow rates to determine the glass dissolution rate at each pH and temperature. Also, as will be shown, the rate measured in an SPFT test depends on the solution flow rate. In the case of static tests, the solutions will eventually become concentrated enough to affect the dissolution rate. In both the SPFT and static test methods, a compromise is required between the need to minimize the effects of dissolved components on the dissolution rate and the need to attain solutions concentrated enough to analyze.

In this paper, we compare the results of static leach tests and SPFT tests conducted with a simple five-component glass to evaluate the equivalence of the test methods. Tests were conducted over the pH range 6 to 10, which is most relevant for waste glass dissolution in a disposal system. The glass and temperature used in the tests were selected to allow direct comparison with SPFT tests conducted previously [2]. The ability to measure parameter values with more than one test method and an understanding of how the rate measured in each test is affected by various test parameters provides added confidence to the measured values.

II. TEST DESCRIPTION

Static Leach Test

The static leach tests were conducted following the American Society for Testing and Materials (ASTM) method C 1220 [3]. Tests were run by immersing monolithic samples of known geometric surface area in dilute buffer solutions for short durations. The increase in the solution concentration of silicon with test duration was used to calculate the dissolution rate. Although

boron is usually used to track the dissolution of borosilicate glasses, our use of borate buffers required that silicon be used for these tests. A sufficiently low glass surface area-to-solution volume (S/V) ratio, about 10 m^{-1} , and sufficiently short test durations, up to 10 days, were used so that the silicon that accumulated in the solution over the test period would not measurably affect the dissolution rate.

Tests were conducted in Teflon vessels. Samples were set on perforated Teflon support stands so that most of the glass surface was contacted by solution. The test vessels were placed in a constant-temperature oven at 70°C for up to 10 days. At the end of the test, aliquots of the test solution were taken for pH measurement and for analysis with inductively coupled plasma mass spectrometry (ICP-MS). The extent of dissolution was calculated as the normalized mass loss by dividing the concentration of Si in solution by the S/V ratio used in the test and by the mass fraction of Si in the glass:

$$NL(Si) = C(Si) / [(S/V) \cdot f(Si)] \quad (2)$$

where $NL(Si)$ is the normalized mass loss, $C(Si)$ is the concentration of element i in the test solution, and $f(Si)$ is the mass fraction of Si in the glass. The normalized dissolution rate, $NR(Si)$, was determined as the slope of a plot of $NL(Si)$ versus the test duration, t , as

$$NR(Si) = \Delta NL(Si) / \Delta t \quad (3)$$

The solution was presumed not to affect the dissolution rate as long as $NR(Si)$ was constant. A decrease in the value of $NR(Si)$ as the test duration increases indicates that solution feedback is slowing glass dissolution.

Single-Pass Flow-Through Test

The SPFT tests were conducted by pumping a solution through a reaction cell that contained the glass and by collecting the effluent for analysis. The glass dissolution rate was calculated from the steady-state Si concentration and solution flow rate by using Eq. 4:

$$NR(Si) = [C^{ss}(Si) \cdot (F/S^\circ)] / f(Si) \quad (4)$$

where $C^{ss}(Si)$ is the background-corrected steady-state concentration of Si, F is the solution flow rate, and S° is the initial surface area of the glass sample. Different steady-state concentrations were attained at different solution flow rates. This resulted in different values of the affinity term and different dissolution rates, so the dependence of the rate measured in SPFT tests on the solution flow rate had to be taken into account.

The SPFT apparatus was constructed using a variable-speed peristaltic pump with polyethylene tubing. Various pump speeds and tubing diameters were used to achieve a range of flow rates and different amounts of glass were used to vary the surface area and achieve a range of F/S° values. A modified polyethylene pipette tip was used as a reaction cell. Polyethylene wool was placed in the syringe to prevent sample from being flushed from the cell during the test. Tests were conducted with 1 - 3 g of glass. The glass was not constrained within the reaction cell, and the solution flowed freely upward through the glass. Channeling was not suspected to occur, though flow rates were not sufficient to fluidize the glass.

The reaction cell and was housed in a constant-temperature oven set at 70°C . Buffer solution was pumped from a large reservoir and through about 1 m of tubing

that was coiled in the oven ahead of the reaction cell to heat the solution to 70°C. The tubing exiting the reaction cell was kept short so that the effluent solution could be collected soon after it left the reaction cell to minimize the time lag.

Effluent solution was collected periodically in polyethylene solution bottles for analysis. The mass of each sample aliquot and the time it was collected were used to calculate the flow rate. The solutions were analyzed with ICP-MS. All solutions collected at a particular pH, temperature, and flow rate were analyzed in the same group to eliminate effects of the day-to-day variability of the ICP-MS. Control tests were conducted without glass to verify that interactions between the buffers and the apparatus were negligible.

Glass

Tests were conducted with a glass made at Argonne with the same composition as the CSG glass (Celia's simple glass). This is a five-component glass (B_2O_3 - Na_2O - CaO - Al_2O_3 - SiO_2) that was formulated to represent glass from the Defense Waste Processing Facility (DWPF) [2]. The mass fractions of Al, B, Ca, Na, and Si were 0.039, 0.024, 0.049, 0.139, and 0.277, respectively. The glass was crushed and sieved to isolate the -40 +60 mesh (425 μ m to 250 μ m) size fraction. The crushed glass was washed repeatedly with absolute ethanol in an ultrasonic bath to remove fines. Some of the glass was examined with a scanning electron microscope to verify all fines had been removed and the particles were the expected size. The specific surface area of the crushed glass was calculated to be 0.0071 m²/g by assuming the particles were spheres having a diameter equal to 338 μ m, which is the

arithmetic average of the sieve sizes. This is the ASTM method recommended for tests conducted with crushed glass [4]

Monolithic samples were prepared for static tests by cutting 1-cm cores from a block of annealed glass and then cutting the cores into wafers approximately 1.5 mm thick. The faces of the monoliths were polished with silicon carbide paper with water lubrication to a final finish of 600-grit. The samples were ultrasonicated in absolute ethanol to remove fines. The dimensions of the monoliths were measured with calipers and the surface area was calculated geometrically by modeling the samples to be right square cylinders.

Buffer Solutions

All tests were conducted using the following pH buffer solutions:

pH at 70°C	Buffer Composition
6.2	0.0038 m KHphthalate + 0.0031 m LiOH•H ₂ O
8.2	0.064 m H ₃ BO ₃ + 0.010 m LiOH•H ₂ O
9.5	0.012 m H ₃ BO ₃ + 0.010 m LiOH•H ₂ O

III. RESULTS

Static Tests

Figure 1 shows the results of static tests conducted with CSG glass at 70 °C in buffer solutions at pH 6.2, 8.2, and 9.5. Each point represents the results of a separate test, and the uncertainty bars are drawn at 15% of the measured value to account for analytical uncertainty. The regression lines drawn through the data give the dissolution rates at the three pH values. As discussed in Section IV,

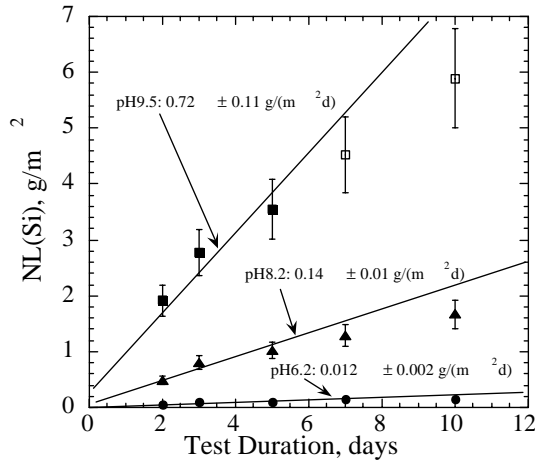


Figure 1. Static Tests with CSG glass at 70 °C: NL(Si) vs. Test Duration.

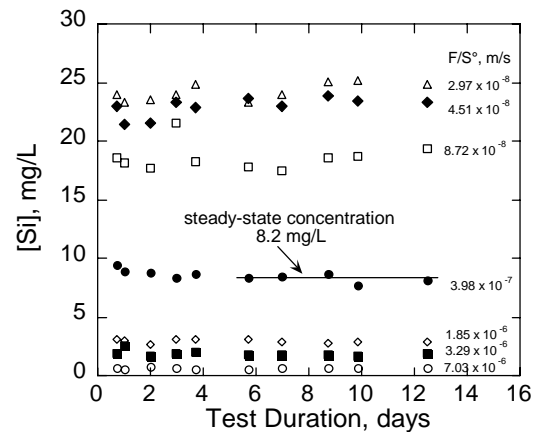
dissolution in the pH 9.5 tests beyond about 5 days is suspected to be slowed by the buildup of Si in the solution, and those results were excluded from the regression fit. The regression lines in Fig. 1 all have positive y-intercepts. This is probably a result of the slight surface roughness.

Single-Pass Flow-Through Tests

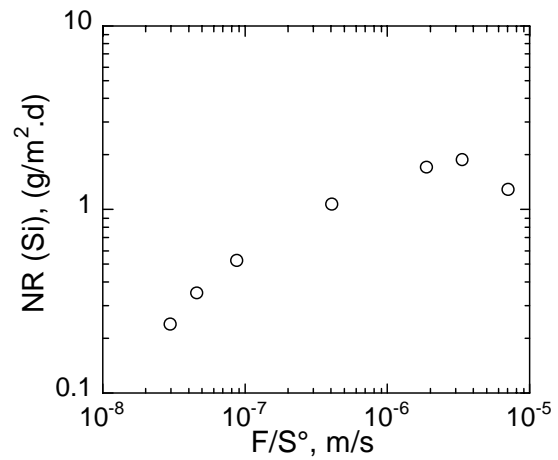
Figure 2a shows Si concentrations in the aliquots from SPFT tests conducted at pH 9.5 and seven different F/S° values. The data at each F/S° represent the aliquots of effluent solution collected sequentially during the test. The average flow rate for each set of aliquots in a test was used to calculate the value of F/S° for that test. The steady-state Si concentration for each test was determined as the average of the last five aliquots. Higher concentrations were sometimes measured in the first several samples due to the dissolution of high-energy sites (e.g., sharp ends of glass shards). The dissolution rate for each test was calculated using Eq. 4. For example, the steady-state Si concentration for the test conducted at pH 9.5 and $F/S^\circ = 3.98 \times 10^{-7}$ m/s was $C^{ss}(Si) = 8.2$ mg/L and the

mass fraction of Si in the CSG glass is $f(Si) = 0.277$. The dissolution rate is 1.04 g/m².

Figure 2b shows the measured rate plotted against the value of F/S° . The rate initially increases with the value of F/S° and then levels off at an F/S° value of about 1×10^{-6} m/s. The size of the symbol corresponds to the uncertainty in the steady-state Si concentration extracted from Fig. 1a. The change in the glass dissolution rate with the value of F/S° is due to the increase in the value of the affinity term as F/S° increases. The dissolution rate is



(a)



(b)

Figure 2. Results of SPFT Tests with CSG Glass at pH 9.5 and 70 °C: (a) Si Concentration vs. Test Duration and (b) NR(Si) vs. F/S° .

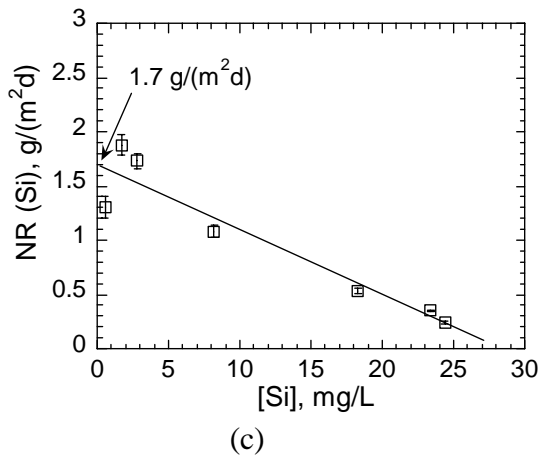
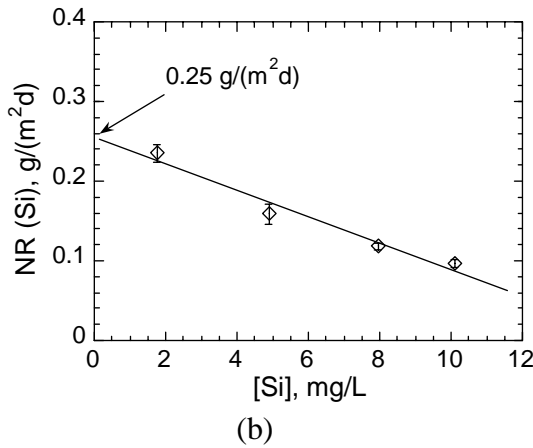
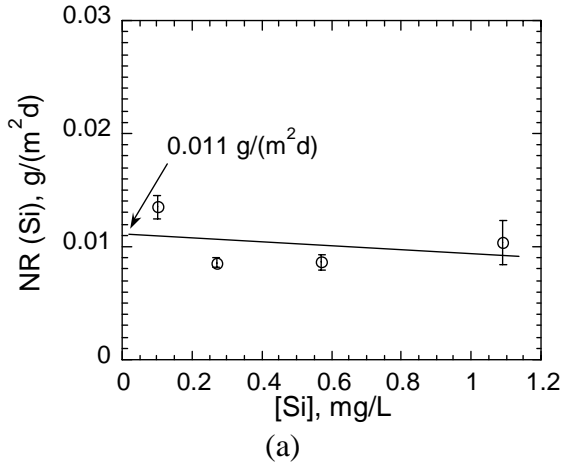


Figure 3. $NR(Si)$ vs. $C^{ss}(Si)$ for SPFT Tests at $70^\circ C$ and (a) pH 6.2, (b) pH 8.2, and (c) pH 9.5.

expected to reach a maximum rate (i.e., the forward rate) when the affinity term becomes 1. The dissolution rate is not expected to increase with further increases in F/S° . This appears to occur in Fig. 2b between about 1 and 2 $g/(m^2 \cdot d)$.

Because of scatter in the data and experimental uncertainty with the dilute solutions resulting from tests at high F/S° , it is difficult to determine the forward rate from the plot in Fig. 2b. Instead, we have plotted the rates against the steady-state Si concentrations in Fig. 3. The measured rates are linearly regressed and the y-intercept (at a Si concentration of 0) gives the forward rate. The scatter in the experimental results at low Si concentrations has only a minor impact on determination of the rate.

IV. DISCUSSION

The dissolution rates measured using static leach tests and SPFT tests are compared in Fig. 4. The rates are the same at pH 6.2, but differ at higher pH values. Comparison of Figs. 2a and 2b indicates that Si concentrations greater than about 8 mg/L are sufficient to slow the glass dissolution rate at $70^\circ C$ and pH 9.5. In the static tests, a Si concentration of 8 mg/L would result in a $NL(Si)$ value of about $3 g/m^2$. Static tests at pH 9.5 conducted for 5 days and longer resulted in Si concentrations that were greater than 8 mg/L and $NL(Si)$ that were greater than $3 g/m^2$. This suggests that the results of static tests conducted for 7 and 10 days at pH 9.5 should not be used to determine the forward rate. This is the reason that the 8- and 10-day data were excluded from the regression fit for the pH 9.5 tests. The concentrations in all tests at pH 8.2 and 6.2 are less than 8 mg/L.

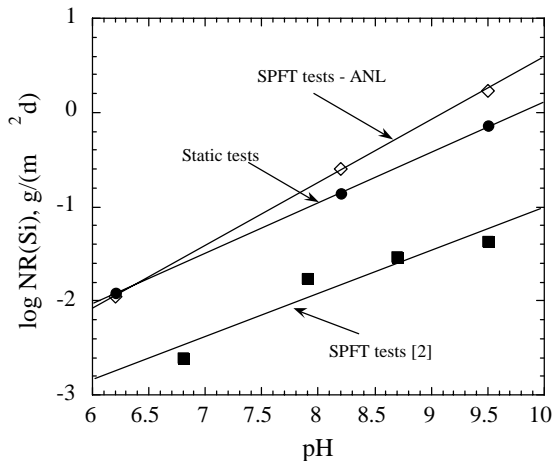


Figure 4. NR(Si) vs. pH for Static and SPFT Tests at Argonne and from Ref. [2].

Part of the difference between the static and SPFT test results may be due to errors in estimating the surface areas of the glass monoliths used in the static tests and the crushed glass used in the SPFT tests. A small error in the surface area of the monoliths is due to neglect of the initial surface roughness. This is estimated to be less than a factor of 1.5X for samples with a 600 grit finish. Higher uncertainties are expected for the crushed glass.

The results of SPFT tests with CSG glass conducted by Knauss et al. [2] are included in Fig. 4. Their measured rates are significantly lower than what we measured with either the static or the SPFT test method. Differences in the SPFT test results may be due to differences in how the tests were conducted and how the data were analyzed. Knauss et al. measured the surface area of crushed CSG glass to be 485 cm²/g by gas adsorption and used that value to calculate the dissolution rate [2]. For comparison, the geometric surface area calculated from the average particle size (which was 100 μm) is 234 cm²/g. From Eq. 4, the calculated rate is inversely proportional to the surface area.

The rates measured by Knauss et al. would be about 2X higher if they were calculated using the specific surface area based on sieve sizes. Nevertheless, the rates would still be about 10X lower than the rates we measured.

Additional experimental details regarding the test method used by Knauss et al. were provided in a subsequent paper [5]. Those conditions are compared with our tests to evaluate possible contribution of test conditions to the difference in the results. The SPFT tests of Knauss et al. were run with about 1 g of glass at flow rates up to 60 mL/day. Using the geometric surface area of 234 cm²/g, the typical F/S^o value for those tests is about 3 x 10⁻⁸ m/s. At pH 10, the steady-state Si concentration was about 13 mg/L (from Table 9 in reference [5]). Our tests at pH 9.5 and F/S^o 3.0 x 10⁻⁸ m/s gave a steady-state Si concentration of about 24 mg/L (see Fig. 2a). The results in Fig. 2b indicate that Si concentrations greater than about 8 mg/L are expected to decrease the glass dissolution rate. This suggests that the dissolution rates measured by Knauss et al. were slowed by feedback effects. However, it is stated in Ref. [5] that doubling the flow rate after steady state was reached did not measurably affect the dissolution rate. It is uncertain how much of the differences in SPFT test results are due to experimental design, test execution, and data interpretation.

The ASTM Nuclear Fuel Cycle subcommittee C26.13 on repository waste form testing is working to standardize the SPFT test method so that results obtained in different laboratories can be compared directly. The SPFT tests discussed in this paper were conducted, in part, to help develop a standard test procedure, identify the test conditions that need to be tracked

and reported, and develop a standard method for data analysis and determination of the dissolution rate. An interlaboratory study will be conducted in the near future to measure the precision of SPFT tests. This will support development of an ASTM standard method for SPFT tests and provide a measure of the test precision.

V. CONCLUSIONS

Static tests are suitable for measuring the dissolution rates of borosilicate glasses in the absence of significant solution feedback effects for the purpose of extracting model parameter values. Comparison of the results of static tests with SPFT tests shows that solution feedback effects can be avoided by conducting static tests at low S/V ratios and for short durations. The results of SPFT tests provide insight regarding the Si concentrations at which feedback effects become significant. The results of SPFT tests are sensitive to the F/S° value used in the test because different steady-state Si concentrations are attained. Tests must be conducted at several F/S° values to verify that feedback is not affecting the dissolution rate. In addition, the rate determined from SPFT tests depends on how the surface area of crushed glass is estimated. The SPFT test procedure should be standardized to provide confidence in its use.

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