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**Results of Testing the Grambow Rate Law for
Use in HWVP Glass Durability Correlations**

W. L. Kuhn
L. R. Bunnell

March 1996

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

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SUMMARY

A theory based on work by Grambow describing the hydration of glass as a known, linear function of solution composition has been evaluated experimentally; the evaluation is the subject of this report. Use of the Grambow's linear rate law to facilitate correlation of durability with glass composition is not recommended.

The linear rate law was tested by determining the dissolution rate at constant pH of a single glass as a function of silicic acid concentration in solution. The dissolution rate of the glass was determined using a recently developed experimental technique: determining the rate of release of sodium using an ion selective electrode.

The experimental technique itself was first tested by applying it to the determination of the initial dissolution rate of several glasses at several temperatures with a zero initial concentration of silicic acid. The glasses HW39-2, HW39-4, and SRL-202 (obtained from Savannah River) were tested. We found significant scatter in the data and found the dissolution rate of the HW39 glasses and the SRL glass to be comparable within this scatter.

The principal objective of the experiment described herein was to determine the rate of dissolution of SRL-202 glass (used in lieu of a "reference" glass for the HWVP project) at 80 C and pH 7 for concentrations of silicic acid that were 0%, 25%, 50%, and 100% of the saturation concentration. The dissolution rate was found to decrease dramatically at only 25% of the saturated silicic acid concentration, which does not conform to the linear theory.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the indispensable contribution of B. P. (Pete) McGrail and R. W. (Ron) Stephens, who conducted the experimental work described herein, reduced and presented the data, and collaborated in its interpretation. As far as we know, their work was the first application of the pH stat/ion-selective electrode technique to measuring directly the effect of silicic acid concentration on the rate of dissolution of a complex-glass. We particularly appreciate their persistence in providing a useful experimental result within limited funding.

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1.0 INTRODUCTION

Glass produced by the Hanford Waste Vitrification Plant (HWVP) Project must meet acceptance standards in order to be shipped to a high-level waste geologic repository for permanent disposal. The acceptance standards have been defined that are expected to apply to the HWVP. The specifications include minimum standards for the durability of the glass as defined by standardized laboratory tests, such as the product consistency test (PCT). The specifications allow methods to be used to characterize the durability that are equivalent to subjecting the product glass to the standard tests.

The current strategy for the HWVP to characterize the durability of glass is to correlate the durability in terms of the composition of the glass. This is desirable to minimize actual testing of radioactive glass and to control the process based on measured compositions of slurries in tanks without requiring direct testing of the product. Direct testing of the product glass is impractical as a basis for controlling the process since there is a substantial time delay involved in passing the slurry along from the control point (the slurry mix-evaporator tank) through the melter feed tank and the melter and finally pouring the glass.

Therefore, it is important for the HWVP to be able to predict the durability of glass from the composition. The current approach is empirically-based and is being developed as part of a study determining the qualified composition region (QCR). Glasses of compositions chosen in accordance with a statistical designed test matrix are subjected to MCC-1 and PCT tests, and the resulting range of test results is correlated statistically against the domain of glass compositions tested. Linear or quadratic regression over composition space (nine independent components) is being used to develop the correlation. Work has been conducted in the Waste Form Qualification task (1.2.2.05) to seek an improved (compared to an empirical statistical fit) technical approach to correlating durability data.

The durability of a glass is judged in terms of the depth of glass dissolved during a standard test, where the depth is calculated from the quantity of soluble components released from the glass and found in solution at the end of the test. The performance of a glass in a standard test depends

on several processes: "unlocking" components from the glass through hydration of the glass structure; accumulation of components in solution in accordance with various equilibration processes; and modification of the rate of hydration by species in solution, notably that portion of dissolved silica existing as silicic acid (H_4SiO_4). Before significant accumulation of glass components in solution, the rate of hydration is expected to be a function of temperature, solution pH, and the bulk composition of the glass. The subsequent concentration of glass components in solution depends on the glass composition (since this determines the relative amounts of components mobilized and thereby made available to the solution) and on various processes (i.e. equilibration among species, precipitation) acting on components in solution.

An attempt to account for the effects of processes in solution was described in milestone report PHTD-C91-05.01A, "Interpretation of Glass Durability Results from the Composition Variability Study." A theory based on work by Grambow describing the effect of species in solution on the rate of hydration of the glass has been evaluated experimentally and is discussed in this report.

2.0 BACKGROUND

During the last ten years important advances have been made in predicting the behavior of complex nuclear waste glasses during dissolution in standard tests. In particular, Bernd Grambow of the Federal Republic of Germany developed an interpretation (Grambow, 1984) of a rate law for the dissolution of minerals (Aagaard and Helgeson, 1982) that could be applied to nuclear waste glasses. According to Grambow's interpretation, the rate of dissolution depends on pH and on the chemical activity of silicic acid in solution. Then, *in principle*, the rate of dissolution of the glass, and in particular the amount of glass dissolved during a standard durability test, could be predicted from the composition of the glass. However, it remains to be demonstrated that the rate can be predicted *in practice*, and in particular that a rate law is available describing the functional dependence of the rate

on the chemical activity of dissolved silica (i.e. silicic acid) and on the pH.

Since the pH occurring during a durability test is buffered by the ionization of silicic acid and boric acid released from borosilicate glasses, thereby causing the pH to remain approximately constant over much of a test, it was hoped that the effect of glass composition on the functional dependence on pH might be unimportant. Then the remaining principle issue would be whether the functional dependence of hydration rate on the chemical activity of silicic acid is understood sufficiently to serve as an aid in correlating the durability with the composition of the glass. This latter issue has been investigated through the experiments described herein.

3.0 TECHNICAL APPROACH

Grambow's interpretation of the rate law for the rate of hydration (reaction with water) of a glass was

$$rate = \frac{d\xi}{dt} = f(glass, temperature, pH) g(a_{Si}, K) \quad (1)$$

where f is a function of glass composition, temperature, and solution pH, a_{Si} is the chemical activity of silicic acid in solution, and K is an equilibrium constant corresponding to the reaction

where H_4SiO_4 is silicic acid, and g is a known function of a_{Si} and K . The constant K was originally taken to be the saturation activity of amorphous silica, and hence would not be a function of the composition of the glass.

The rate is expressed as $d\xi/dt$, where ξ is the extent of reaction, here defined as the depth of glass dissolved. The concentration of a soluble component of the glass, such as boron, is related to the extent of reaction by

$$[B] = \frac{A}{V} c_B \xi \quad (3)$$

where $[B]$ is the concentration of boron in solution, c_B is the concentration of boron in the glass, A is the surface area over which dissolution occurs,

and V is the volume of solution into which dissolution occurs. Since A , V , and c_B are known for a particular glass in a particular test, then from the boron concentration at the end of a test we can infer the extent of reaction.

For a particular glass composition, Equations (1) and (3) combine to give

$$rate = \frac{d\xi}{dt} = \frac{1}{(A/V) c_B} \left(\frac{d[B]}{dt} \right) = k_+(pH) g(a_{Si}, K) \quad (4)$$

where k_+ , the forward reaction rate, is a function of the pH of the solution contacting the glass. If the activity of silicic acid, a_{Si} , is known as a function of ξ and hence as a function of $[B]$, and if the pH of the solution contacting the glass is sufficiently constant over ξ , then the boron concentration reached after some specified time can be predicted (by integration) as a function of k_+ . In other words, the performance of the glass in a standard test can be predicted as a function of glass composition, which is our objective.

Since we do not know k_+ a priori as a function of glass composition, but do know $[B]$ for a number of compositions from the qualified composition region (QCR) testing, then alternately we could attempt to extract k_+ as a function of glass composition from the QCR data. If this could be done, the value of k_+ obtained should correlate more directly with the composition of the glass than would the amount of glass dissolved during a test, since k_+ would not depend on the processes, e.g. precipitation, occurring in solution during a test.

Obtaining the value of k_+ would be possible only if bufferring of pH during tests establishes a nearly constant pH during a test on a given glass, and this pH is nearly the same for different glasses tested. Furthermore, if both conditions are met, the value of k_+ extracted from the data would be associated with the pH characteristic of such tests.

The issue of whether pH effects can in fact be addressed adequately is not addressed in this report. Therefore, this report addresses necessary *but not sufficient* circumstances that must be confirmed before the use of a theory of the rate of hydration can be used to facilitate the correlation of durability with glass composition.

Assuming that the considerable difficulties relate to pH described above could be overcome, then to extract k_+ from [B] we would need to relate a_{Si} to ξ , as stated above, or equivalently to relate a_{Si} to [B], and to know the function $g(a_{Si}, K)$, where we now assume the effect of pH is constant both over a single test and for different glasses. Then we could use

$$k_+ = \frac{1}{(At/V) c_B} \int_0^{[B]} \frac{d[B]}{g(a_{Si}, pH, K)} \quad (5)$$

to determine k_+ from test data, where t is the time to reach [B] in the test. Software exists, such as PHREEQE (Parkhurst et al., 1980), which in principle can be used to predict the pH and a_{Si} in terms of the extent of reaction (and therefore in terms of [B]). The ability to do this depends on equilibrium among species in solution being maintained as dissolution proceeds, i.e. due to fast precipitation kinetics, and on providing a thermodynamic database adequate for the purpose. Some of these issues are discussed in the report "Interpretation of Glass Durability Results from the Composition Durability Study," milestone PHTD-C91-05.01A.

According to transition state theory, the function g is

$$g(a_{Si}, K) = 1 - \frac{Q(a_{Si})}{K} \quad (6)$$

where Grambow interpreted Q as corresponding to the chemical activity (a_{Si}) of silicic acid and K as its solubility at the surface of contact of the solution with the glass. Precipitation processes prevent the value of a_{Si} from reaching that of K , resulting in a residual rate of hydration (dissolution) of the glass (i.e. $a_{Si} < K$, therefore $g > 0$).

One important issue relative to the usefulness of this interpretation is whether a reliable prediction of the value of K is available, and in particular whether it depends significantly on the composition of the glass. A second issue is whether the predicted linear dependence of hydration rate or a_{Si} is correct. If a reliable value of K is not known or depends significantly on the composition of the glass, or if the predicted linear dependence is incorrect, then it would be inappropriate to try to apply Equation (5) in correlating HWVP glass durability data.

The predicted linear dependence of the rate law and the availability of an appropriate value of K can be tested by determining the dissolution rate at constant pH of a single glass as a function of silicic acid concentration in solution. (In dilute solutions, the chemical activity is essentially the molal concentration). Based on the above interpretation of the rate law, the rate should decrease linearly with silicic acid activity and approach a minimum as the silicic acid activity increases toward the solubility of amorphous silica.

4.0 EXPERIMENTAL PROCEDURE

In typical tests of glass durability, glass is contacted with a solution for a period of time, after which the concentration of glass components found in solution are measured. Those elements that are not sequestered in secondary solid phases can be used to determine the average rate of dissolution of the glass. A principal difficulty associated with this approach is that to attain solution concentrations large enough to provide reasonably precise measurements, the amount of silica accumulated in solution is large enough to affect the rate of dissolution of the glass. Therefore, standard tests are inappropriate for evaluating a rate law for the effect of silicic acid in solution, since the silicic acid concentration varies continuously during such tests and the pH is not actually constant.

To circumvent this problem, and more generally to provide a high density of solution concentration data for determining the "forward" rate of dissolution (the rate when the concentration of silicic acid is zero) of a glass, McGrail (1991) developed a pH stat/ion-selective electrode test method. This method was applied by McGrail in our tests. The pH was held constant at 7 using the pH stat to eliminate effects of changing pH on the dissolution rate. The initial, or "forward" dissolution rate was determined for several initial concentrations of silicic acid in solution.

Samples of crushed glass (-140 +200 mesh) were dissolved in water while holding the pH constant by titrating the solution with HCl as dissolution proceeded. The glass surface area was $1.3 \times 10^{-2} \text{ m}^2$ and the liquid volume was 150 ml.

The temperature was held at 80 C. Higher temperatures cannot be maintained using this test method as damage to the reference junction of the ion-selective electrode would occur. The concentration (strictly, the chemical activity) of sodium ions in solution was determined as a function of time using an ion selective electrode. The salt bridge that forms part of the electrochemical circuit between the pH electrode and the instrumentation was found to leak potassium ions to the solution. Since the electrode is sensitive to both sodium and potassium ions, the resulting accumulation of potassium in solution cannot be distinguished from the accumulation due to release of sodium from the glass as it dissolves. The rate of accumulation of potassium in solution was measured prior to a test and then subtracted from the apparent rate of accumulation of sodium found while testing a glass. The correction amounted to roughly 10% of the smallest rates reported in this report.

The concentration of sodium in solution was inferred as a function of time from the voltage signal from the ion-selective electrode. The electrode responds essentially instantaneously to changes in concentration of sodium ions in solution. The sodium released into solution from the glass is highly soluble; therefore, the concentration of sodium in solution is directly indicative of the amount of sodium released from the glass.

When a glass first contacts water, the composition of the surface of the glass changes as hydration occurs. A steady-state surface composition is attained rapidly, which, being the part of the glass contacting water, thereafter determines the durability of the glass. The transient release of sodium ions that occurs during the alteration of the surface must be taken into account when inferring the rate of congruent dissolution (according to theory) of the glass from the changing sodium concentration in solution. The concentration of sodium in solution due to the combined effects of surface alteration and dissolution of the glass is found to approximately follow the following functional form:

$$C = a(1 - e^{-bt}) + mt \quad (7)$$

where C is the concentration, t is time, and a , b , and m are statistically fitted constants. Note that the first term in Equation (7) is important only

for sufficiently small times, and in fact becomes unimportant after 12 hours or so. The constant m is the rate of release of sodium that continues after alteration of the surface has abated, and corresponds to the dissolution rate of the glass. To determine the rate of congruent dissolution of the glass, the above functional form is fit to the sodium concentration as a function of time, and the fitted coefficient m is taken to be the sodium release rate due to dissolution of the glass. The rate of congruent dissolution of the glass is then determined from the rate of release of sodium and the known concentration of sodium in the glass.

Samples of glass were subjected to this procedure for differing concentrations of silicic acid in the water contacting the glass. The rate of dissolution of the glass is determined within a day, during which time the dissolution of the glass does not appreciably affect the concentration of silicic acid. Therefore, by using this experimental method, the dissolution rate of the glass is determined as a function of the concentration of silicic acid in solution.

5.0 EXPERIMENTAL RESULTS

The experimental technique itself was first tested by applying it to the determination of the initial dissolution rate of several glasses at several temperatures with a zero initial concentration of silicic acid and maintaining a pH value of 8. The glasses HW39-2, HW39-4, and SRL-202 (obtained from Savannah River) were tested. A typical plot of sodium release as a function of time and the fitted value of the forward reaction rate, denoted k_+ , is shown in Figure 1. Thiourea was added to provide a correct electrode response to sodium concentration. The need for this has been discussed by McGrail (1991). The results for all the glasses are shown in Table 1.

Although there is significant scatter in the data, the dissolution rates of the HW39 glasses and the SRL glass are comparable within this scatter.

Figure 1. Typical plot of sodium release shown as a function of time. Measurements made using ion-selective electrode for sodium.

This technique for determining the dissolution rate was developed recently, and, as experimentalists gain more experience, it will become more precise.

The objective of the principal experiment was to determine the rate of dissolution of SRL-202 glass at 80 C and pH 7 with initial concentrations of silicic acid that were 0%, 25%, 50%, and 100% of the saturation concentration. The results are shown in Figure 2, Figure 3, and Table 2.

Note that the dissolution rate decreases dramatically at only 25% of the saturated silicic acid concentration and does not decrease significantly as the concentration is increased further. This is in marked contradiction to expectations based on Grambow's interpretation, i.e. that the rate should decrease linearly as the silicic acid activity increases from 0% to 100% of

Figure 2. Normalized sodium concentration (release) shown as a function of time for SRL-202 glass for various initial percent saturation in solution.

saturation (shown by the dotted line in Figure 2). Apparently, the dependence on silicic acid activity is distinctly non-linear, or parameter K is substantially smaller than the saturation activity of silica. The chemical activity and concentration of silicic acid are essentially interchangeable at the small concentrations (up to molal) attained in this study.

Our data should be compared only qualitatively to Grambré's interpretation of the rate law, since this is the first attempt to use McGrail's experimental technique to determine the rate of release of silicic acid from defense waste glass when silicic acid concentration is varied. Various experimental complications have been encountered. For example, potassium ions leaked from the glass at a measurable rate, which adds to the apparent rate of release.

Table 1. Trial application of experimental method to several glasses.

Glass ID	Temperature (°C)	pH	Rate [g/m ² /d]
HW39-2	23	8	6.4×10^{-3}
	50	8	7.2×10^{-2}
	80	8	5.5×10^{-1}
	80	8	4.0×10^{-1}
HW39-4	80	8	6.4×10^{-1}
SRL-202	80	8	9.7×10^{-1}
	80	8	8.9×10^{-1}
	50	8	3.9×10^{-1}
	50	8	2.3×10^{-1}

Table 2. Rate of dissolution of SRL-202 glass for various initial silicic acid concentrations.

Initial Silicic Acid Concentration (Percent Saturation)	Temperature (C)	pH	Initial Rate of Dissolution (g/m ² /s)	Initial Rate of Dissolution (g/m ² /d)
0%	80	7	3.2×10^{-6}	0.28
25%	80	7	4.8×10^{-7}	0.04
50%	80	7	4.6×10^{-7}	0.04
100%	80	7	2.7×10^{-7}	0.02

sodium from the glass and which must be compensated for by subtracting a background rate. In general, the scope of the activity was too limited to thoroughly investigate the experimental technique as it was applied to our particular problem. Nevertheless, the qualitative results are meaningful relative to our objective, which is to evaluate Grambow's interpretation of the rate law as a predictive theory that can be used to extract an inherent, initial dissolution rate to be correlated against glass composition. We find

Figure 3. Initial dissolution rate vs. silicic acid concentration expressed as percent saturation relative to precipitation of amorphous silica.

our data do not conform to Equation (6).

One possible explanation can be found in an extension to Grambow's work provided by Bill Bourcier of Lawrence Livermore National Laboratory (LLNL) (Bourcier et al., 1989). Bourcier proposed a modified rate law, where the function "g" of Equation (6) is replaced by

$$g(\text{glass surface, solution composition}) = \left(1 - \frac{Q(\text{surface})}{K(\text{surface})} \right) \quad (8)$$

where Q is interpreted to be an ion activity product for dissolved species in equilibrium with a virtual solid representing the composition of the surface of the glass, and K is the saturation constant for the virtual solid. Since

the composition of the surface of the glass depends on the composition of the bulk glass, then both K and the functional form of Q depend on the composition of the bulk glass, and g is predicted to be a function of both the composition of the bulk glass and composition of the solution contacting the glass.

If Bourcier's theory is correct, the dependence of g on the chemical activity of silicic acid is no longer predicted to be linear. The dependence depends on the mole fraction of silica in the surface of the glass. Similarly, the constant K is not based on saturation with respect to amorphous silica, but instead on saturation with respect to a virtual mineral that is only partly composed of silica. Then, since we do not know (at least from QCR testing) the composition of the surface, the value of K , or the form of Q , then we cannot correctly construct a plot of rate as a function of Q/K and no longer expect to find a simple relationship between the initial rate observed in our tests and the initial concentration of silicic acid.

6.0 CONCLUSIONS

The forward rate of dissolution of a simulated nuclear waste glass has been investigated experimentally by contacting the glass with aqueous solutions of silicic acid over a range of concentrations. The result expected from Grambow's interpretation of the hydration rate law is a linear dependence of initial dissolution rate on the initial silicic acid concentration with the rate approaching zero as the concentration approaches saturation with respect to precipitation of amorphous silica. The expected result was not observed. Instead, the initial rate of dissolution decreased dramatically at the lowest silicic acid concentration tested and did not decrease significantly as the concentration was increased further.

At least one alternative theory has been proposed that is consistent with our experimental results. However, the theory predicts that the hydration rate law depends intrinsically on the composition of the bulk glass, in which case the rate law would not reduce the difficulty in correlating durability with glass composition. We conclude that a simple, linear rate law cannot be used to assist in correlating HWVP durability data by extracting initial dissolution rates as a function of glass composition.

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