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PERFORMANCE TESTING OF WEST VALLEY REFERENCE 6 GLASS

W. L. Ebert and J. K. Bates

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

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William L. Ebert and John K. Bates
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439-4837
(708) 252-6103

ABSTRACT

The chemical durability of West Valley Reference 6 glass is being evaluated by using a suite of laboratory tests which highlight the early, interim, and long-term stages of corrosion. The test results are being used to describe the glass corrosion path and its long-term durability. The long-term durability of the SRL Environmental Assessment glass is being evaluated for comparison. Test results also provide parameter values for an analytical corrosion model that can be used in performance assessments of specific disposal sites.

I. INTRODUCTION

The West Valley Demonstration Project will vitrify radioactive wastes that were generated during the reprocessing of spent fuel for eventual disposal in a federal high-level waste repository. Acceptance of the waste form for disposal requires, in part, that its long-term chemical durability be demonstrated. Because the waste form must stabilize radioactive waste components for a period that is much longer than can be tested directly, demonstration of the long-term durability must be based on an understanding of the glass corrosion mechanism and the effects of the storage environment to project glass behavior by using computer simulations. The West Valley Reference 6 (WV6) glass is a nonradioactive homologue of the waste glasses that are to be produced and is being evaluated by a suite of laboratory tests. The SRL Environmental Assessment (SRL EA) glass has been identified as a standard for high-level waste glasses.[1] Its long-term durability is being evaluated for comparison.

The glass corrosion rate is modeled analytically as a product of (1) a forward rate term and (2) a reaction affinity term.[2] The forward rate term gives the corrosion rate in the absence of corrosion products and depends on the glass composition, reaction temperature, and solution pH. The reaction affinity term accounts for the effects of corrosion products in the leachate and is generally expressed in terms of the silicic acid concentration in the leachate and a "saturation" silicic acid concentration. Under conditions where the silicic acid concentration is far from saturation and the reaction affinity term has a value near one, the glass corrosion rate is determined primarily by the glass composition, the temperature, and the solution pH. As the glass corrodes and the silicic acid concentration approaches its "saturation" value, the reaction affinity term and the corrosion rate approach zero. Secondary phases that are formed as the fluid becomes more concentrated may prevent the reaction affinity from becoming zero by establishing a solubility limit for silicic acid that is lower than the "saturation" value. The glass corrosion rate will then be determined by the effects of secondary phases on the solution chemistry, and the corrosion rate may increase significantly. Determination of how the secondary phases affect the corrosion rate is necessary to project the long-term durability of the waste form.

According to this model, corrosion can be described as occurring in three stages. Stage I occurs when the leachant fluid is initially highly dilute and only the pH affects the corrosion rate, and the affinity term is one. Stage II occurs when the glass corrosion products build up in the leachate and slow the corrosion as the affinity term approaches zero. Stage III appears when secondary phases form and control the solubility limits of important glass components, and the affinity term becomes nonzero.

Three information needs exist for modeling the long-term durability of a waste glass: (1) the forward rate as a function of temperature and pH, (2) the "saturation" silicic acid concentration, and (3) identification of the assemblage of secondary phases formed as the glass corrodes. Characterization of glass corrosion behavior requires tests which subject the waste glass to three reaction environments: highly dilute conditions in Stage I (to measure the forward rate), saturated conditions prior to formation of secondary phases in Stage II (to measure the silicic acid concentration under saturated conditions), and saturated conditions that result in secondary phase formation in Stage III (to permit phase identification). While experiments which drive corrosion into Stage III provide qualitative insight into the effects of secondary phase formation, computer modeling is required to account for the effects of other materials and processes that affect the solution chemistry during actual disposal. This paper describes the use of laboratory tests (MCC-1, Product Consistency Test, and the ANL Vapor Hydration Test) to determine values of modeling parameters for WV6 and SRL EA glasses.

II. EXPERIMENTAL

The MCC-1 tests were performed at 90°C with WV6 glass in a J-13 tuff groundwater solution (referred to as EJ-13) or deionized water. The major dissolved ions measured in the EJ-13 before testing were 48 ppm Na, 41 ppm Si, and 120 ppm HCO_3^-. These MCC-1 tests were conducted in EJ-13 for 3, 7, and 14 days to measure the forward reaction rate. They are conducted at an S/V (glass surface area to leachant volume) ratio of 10 m^{-1} and use a monolithic glass sample in a 304L stainless steel vessel. The test conditions maintain dilute conditions relevant to Stage I. The Product Consistency Tests (PCT) were conducted using crushed WV6 glass in EJ-13 and in deionized water at S/V ratios of 2000 m^{-1} and in EJ-13 at 20,000 m^{-1}. These tests were conducted to characterize corrosion under "saturated" solution conditions relevant to Stage II. Product Consistency Tests were also performed with SRL EA glass for comparison. Tests at 2000 m^{-1} were conducted with the -100+200 mesh size fraction, and tests at 20,000 m^{-1} were conducted with both the -100+200 and -200+325 mesh size fractions to assess the effects of particle size. The ANL Vapor Hydration Test was used to accelerate the corrosion of WV6 glass . In this test, monolithic samples are corroded in saturated water vapor at elevated temperatures to promote secondary phase formation and show the effects of their formation on continued glass corrosion behavior in Stage III. Vapor Hydration Tests were performed at 200°C for between 7 and 55 days.

Solutions from the MCC-1 and PCT tests were analyzed for pH, cations, and anions. The reacted glass samples and secondary phases from all tests were analyzed by using optical microscopy, scanning electron microscopy (with associated X-ray spectroscopy), analytical electron microscopy (with x-ray spectroscopy and electron diffraction), and X-ray diffraction.

III. RESULTS

The rates measured in MCC-1 tests conducted for 3, 7, and 14 days in the EJ-13 solution ranged between 0.001 and 0.025 $g/m^2/d$ (based on the boron release). The scatter in the results is large because of the small amount of glass that has reacted; the boron concentrations were only a few one-hundredths of a ppm above the boron content of the initial leachant. The (boron release) rate measured in duplicate 7-day PCT tests in EJ-13 water is 0.03 $g/m^2/d$, and in triplicate 7-day PCT tests in deionized water, the rate is 0.05 $g/m^2/d$. The rates are higher in the PCT tests because a higher solution pH was attained (about 9.6 in both EJ-13 and deionized water) than in the MCC-1 tests (8.8 after 7 days).

The PCT tests conducted at 2000 m^{-1} showed a nearly linear increase in the amounts of dissolved glass components with the reaction time. The PCT tests conducted at 20,000 m^{-1} attained higher solution pH values and higher solution concentrations than tests at 2000 m^{-1} after the same corrosion time. Tests with both glasses at 20,000 m^{-1} conducted with the -200+325 mesh fraction had slightly lower concentrations of dissolved glass components than tests with the -100+200 mesh fraction. The differences are likely due to the greater decrease in total surface area of the smaller fraction as the glass dissolves. Tests through 182 days with WV6 glass show the solution concentrations of the soluble glass components (including silica) to still be increasing, indicating that the solution has not become saturated. The corrosion rate, based on the release data for 91 and 182 days, is 0.0026 $g/m^2/d$ in tests at 20,000 m^{-1} conducted with the -100+200 mesh fraction (pH 10.1) and 0.0021 $g/m^2/d$ in tests at 20,000 m^{-1} conducted with the -200+325 mesh fraction (pH 10.2). The difference is due to the loss of material in the tests conducted with the -200+325 mesh fraction.

Solutions from tests conducted with SRL EA glass at 2000 m^{-1} did become saturated within 7 days, and nearly constant solution concentrations are maintained through 70 days (the longest time this glass has been tested to date) due to the low corrosion rate. The rate based on the 7-day data is 0.64 $g/m^2/d$ for tests in deionized water (pH 11.9) and 1.36 $g/m^2/d$ for tests in EJ-13 (pH 11.6), but decreases to about 0.01 $g/m^2/d$ in EJ-13 at longer reaction times (pH 12.2). The leachates in PCTs conducted at 20,000 m^{-1} also become saturated, but corrosion continues due to the effects of the secondary phases that have formed. Three sodium-aluminum-silicate phases have formed but have not been characterized yet. The corrosion rate is about 0.11 $g/m^2/d$ in tests with both glass particle fractions (pH 12.2 for both).

Vapor Hydration Tests showed WV6 glass to form several secondary phases during corrosion, including weeksite (a uranium silicate), orthoclase (a potassium feldspar), analcime (a zeolite), and lithium phosphate. The formation of these phases has been observed to affect the corrosion rate of similar glasses.[3] Measurement of the thickness of the alteration layer (excluding phases precipitated on the outer surface) shows the glass to corrode at a rate of about 2 μm/day after these phases form. Assuming both the layer and glass densities are 2.7 g/cm^3, this is equivalent to about 5.4 $g/m^2/d$.

IV. DISCUSSION

The relevance of these data to the glass corrosion behavior of WV6 glass is summarized schematically in Fig. 1a, where the data from the MCC-1, PCT, and Vapor Hydration Tests are included in a plot of the amount of glass reacted against the reaction progress. The data are positioned on the curve to illustrate which stage of corrosion is highlighted by the tests. The relation between the test results and the reaction progress is a complicated function of time, pH, S/V, and other test parameters. The curve in Fig. 1a represents the reaction path, which includes the effects of the changing solution chemistry on the glass corrosion rate. While MCC-1 results generally give the corrosion rate during Stage I, the use of a silicate groundwater leachant clearly reduced the corrosion rate in these tests. Thus, the results fall in Stage II. The results of the PCT tests describe the progress curve during the early part of Stage II, prior to saturation of the solution. The observation that the rate had not become constant within the times tested indicates that the extent of corrosion is still early in Stage II in tests at both 2000 and 20,000 m^{-1}. Vapor hydration tests reacted 7 days and longer have progressed to Stage III, and the glass corrodes at a nearly constant rate.

Figure 1b shows the progress plot and data from PCT tests with SRL EA glass. Tests at 2000 m^{-1} attained nearly constant solution concentrations, and so had progressed into late Stage II. Tests at 20,000 m^{-1} maintained a relatively high corrosion rate and had progressed into Stage III.

The rates measured in MCC-1 or PCT tests will differ from the forward rates due to the effects of the pH and the accumulation of silica in the solution during the test: silica will slow the corrosion rate through the affinity term, and increased pH values will accelerate the reaction through the rate coefficient. The measured rates effectively average the rate over the entire test period, and so provide bounding estimates of the rates relative to the solution pH and the silica concentration. The forward corrosion rate of WV6 glass is probably slightly greater than 0.025 $g/m^2/d$ at pH values less than about 9 (from the MCC-1 tests) and greater than 0.05 $g/m^2/d$ at pH values greater than about 9 (from PCT tests at 2000 m^{-1}). The "saturation" concentration of silica (total silica) is greater than 100 ppm at pH values near 10.2 (from PCT tests at 20,000 m^{-1}). The corrosion rate after secondary phases form is about 5 g/m^2/d at 200°C. Assuming Arrhenius behavior and an activation energy of 60 kJ/mol (that measured for R7T7 glass[4]), the rate at 90°C is predicted to be about 0.06 g/m^2/d. Considering the high pH values that are attained in the Vapor Hydration Tests, the rate after secondary phase formation is similar to the forward reaction rate.

The forward reaction rate of SRL EA glass cannot be determined from these tests, because the reaction has progressed well into Stage II in all tests. The 7-day PCT tests in deionized water at 2000 m^{-1} give an average corrosion rate of about 1.4 g/m^2/d (at pH 11.9), and the forward rate (at pH 11.9) will be greater than this value. (This rate is consistent with that measured by Jantzen et al.,[5] but about 100 times that predicted by Plodinec and Ramsey.[1]) The "saturation" concentration of silica is 646 ± 22 ppm (total silica) at pH 11.7 (average value of PCT tests at 2000 m^{-1} conducted for 56, 98, and 182 days), and the corrosion rate under saturated conditions is about 0.005 g/m^2/d. From the tests at 20,000 m^{-1}, the long-term rate is 0.11 g/m^2/d at 90°C and pH 12.2. The long-term rate is much higher than the rate under saturated conditions but much less than the forward rate at a similar pH.

The performance of a high-level waste glass in a disposal site must be determined by coupling the glass corrosion behavior measured in laboratory tests with the likely disposal environment. Which stage of corrosion behavior represents the long-term glass behavior will depend on the storage conditions. Since contact by groundwater provides the primary mode of escape, repositories will be designed to minimize the amount of water that contacts the waste forms. The likely contact scenario is for water vapor to initially condense on the waste forms and then for liquid water to slowly accumulate in or on waste packages. Tests at high S/V better represent this scenario than do tests at low S/V. The durability of the glass under these conditions depends on whether or not secondary phases form, and on the effect of their formation on the continued glass corrosion rate. The tests reported here show that secondary phases do form during the corrosion of SRL EA and WV 6 glass and increase the corrosion rate. They also show that test conditions will affect whether or not secondary phases form. For example, solutions from tests with SRL EA glass at 2000 m^{-1} have become saturated, but secondary phases have not yet precipitated. It may be that the solution pH values in the tests at 2000 m^{-1}, which were near 11.7, are not high enough to precipitate the phases observed to form in tests at 20,000 m^{-1}, which have pH values near 12.2. Likewise, PCT tests with WV6 glass may never attain the pH values in the Vapor Hydration Tests, and secondary phases may never form in PCT tests at 20,000 m^{-1}. Higher S/V may be required to drive the corrosion into Stage III. Conditions during disposal may well generate effective S/V higher than 20,000 m^{-1}. The Vapor Hydration Tests provide insight into the later stages of glass corrosion behavior that may not be accessible by other laboratory tests but may be very important to the long-term durability of waste glasses.

V. CONCLUSIONS

A suite of three laboratory tests (MCC-1, PCT, and Vapor Hydration Test) has been used to describe the long-term corrosion behavior of two reference high-level waste glasses: WV6 and SRL EA. The WV6 glass is quite durable, and tests completed to date describe the early stages of corrosion. The solutions in PCT tests with WV6 glass at S/V ratios of 20,000 m^{-1} are not saturated after 182 days, and the corrosion rate continues to decrease with the reaction time. Vapor Hydration Tests show that secondary phase formation will eventually increase the long-term corrosion rate. Longer reaction times are needed to demonstrate this behavior in PCT tests.

The SRL EA is much less durable than the WV6 glass, and tests completed to date describe the later stages of corrosion. The solutions in PCT tests at 2000 m^{-1} with SRL EA glass become saturated within 30 days, and corrosion occurs at a low rate. The corrosion rate increases after secondary phases form in tests at 20,000 m^{-1}. The corrosion rate of SRL EA glass relevant to projecting its long-term behavior is that measured after secondary phases form.

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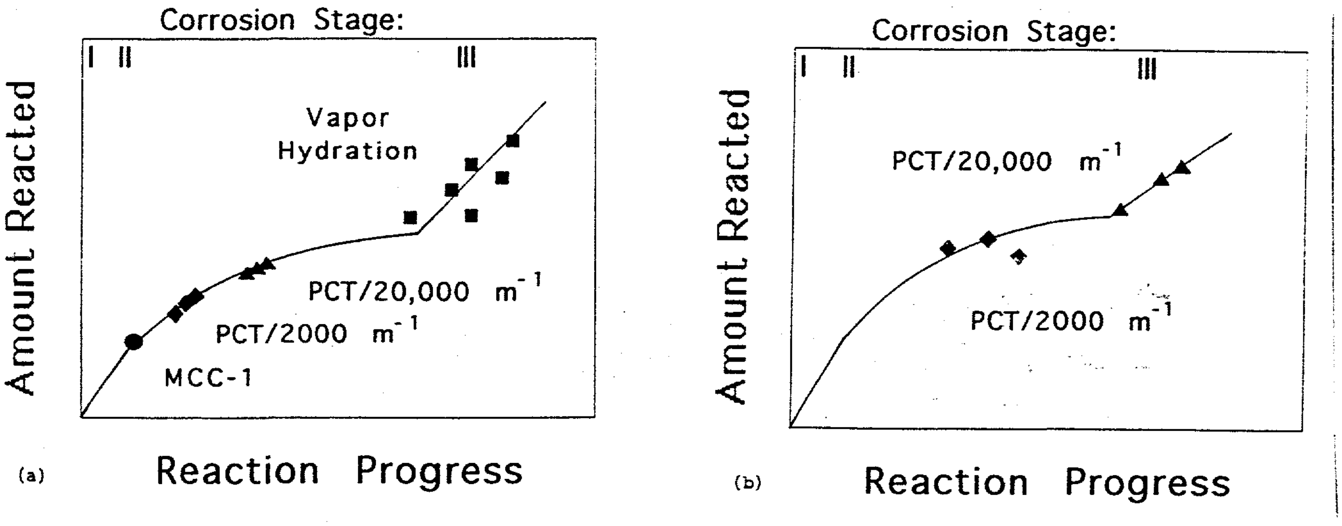

Fig. 1. Schematic Plot of Corrosion Progress and Results for Tests with (a) WV6 Glass and (b) SRL EA Glass.