

**LABORATORY TESTING OF WASTE GLASS AQUEOUS
CORROSION; EFFECTS OF EXPERIMENTAL PARAMETERS**

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LABORATORY TESTING OF WASTE GLASS AQUEOUS CORROSION; EFFECTS OF EXPERIMENTAL PARAMETERS W.L. Ebert and J.J. Mazer, Chemical Technology Division, Argonne National Laboratory, Argonne IL 60439

A literature survey has been performed to assess the effects of the temperature, glass surface area/leachate volume ratio, leachant composition, leachant flow rate, and glass composition (actual radioactive vs. simulated glass) used in laboratory tests on the measured glass reaction rate. The effects of these parameters must be accounted for in mechanistic models used to project glass durability over long times. Test parameters can also be utilized to highlight particular processes in laboratory tests. Waste glass corrosion results as water diffusion, ion-exchange, and hydrolysis reactions occur simultaneously to devitrify the glass and release soluble glass components into solution. The rates of these processes are interrelated by the affects of the solution chemistry and glass alteration phases on each process, and the dominant (fastest) process may change as the reaction progresses. Transport of components from the release sites into solution may also affect the observed corrosion rate. The reaction temperature will affect the rate of each process, while other parameters will affect the solution chemistry and which processes are observed during the test. The early stages of corrosion will be observed under test conditions which maintain dilute leachates and the later stages will be observed under conditions that generate more concentrated leachate solutions. Typically, water diffusion and ion-exchange reactions dominate the observed glass corrosion in dilute solutions while hydrolysis reactions dominant in more concentrated solutions. Which process(es) controls the long-term glass corrosion is not fully understood, and the long-term corrosion rate may be either transport- or reaction-limited.

INTRODUCTION

Laboratory testing of high-level nuclear waste glasses is performed to provide insight into the corrosion mechanisms to assist the prediction of the long-term glass performance during geologic disposal. Testing is also important during the vitrification process to determine suitable compositions for glass waste forms and verify that acceptable waste forms are being produced. It may also be necessary to demonstrate that the high-level waste glasses produced can pass site-specific durability tests prior to being accepted for disposal by a repository.

The testing parameters used will affect the response of the glass in any test, and parameters may be selected to simulate likely service conditions, to highlight a particular reaction step, or to accelerate the corrosion reaction in general. The influence of key test parameters on glass corrosion has been reviewed in the document High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics [CLNNANE-1993]. Test parameters were selected for review by considering those that are commonly specified in standardized leach tests or have been studied in other parametric investigations. These include the reaction temperature, the solution composition and chemistry, the reaction

time, and the glass composition, including whether or not radioactive waste materials are present in the glass.

Some test parameters may affect the reaction conditions which then affect the glass corrosion. For example, the glass surface area-to-leachant volume ratio (S/V) used in static tests and the flow rate used in dynamic tests affect the solution composition which then affects the glass corrosion rate. The preparation of the glass sample used in the test also influences the glass response in the test. The surface finish of glass monoliths affects the microfracturing of the glass and the number of high-energy sites on the exposed surface, as well as the area of the glass available for reaction. Powdered samples have fractured surfaces that are quite smooth with sharp points and edges that are more highly reactive. Effects of this nature were considered in the context of other, more general parameters, such as the surface area.

Particular test parameters may affect a single reaction step or all steps. For example, elevated temperatures accelerate most reaction processes, though each process may be accelerated to a different degree. The solution pH may affect different reaction steps differently: high pH values may enhance one reaction step while slowing another. The reaction time is important not only through the time-dependence of individual reaction steps, but may also be important if kinetically-limited secondary phases form, or if the dominant reaction process changes as corrosion proceeds. A brief description of the glass structure and corrosion process is given to facilitate subsequent discussions of the effects of different parameters.

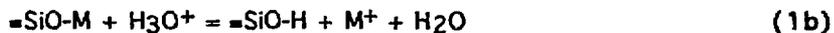
DESCRIPTION OF GLASS STRUCTURE AND CORROSION REACTIONS

Glass is a thermodynamically metastable, highly viscous liquid phase having only short range order corresponding to the hybridization of its component elements. In silicate glasses, the tetrahedral hybridization of silicon generates a three-dimensional polymeric network of $-\text{[Si-O-Si]}-$ bonds where the bond lengths and bond angles are constrained in individual tetrahedra, but long-range order is not maintained. Other elements may be incorporated into the silicate network, but will be disruptive to the silicate network due to their different ionic sizes and charges. The valence of elements added to the glass determines, in part, how they will be incorporated into the glass network. The addition of monovalent and divalent components results in termination of the network structure, while the addition of trivalent components maintains the network structure but requires charge compensation to maintain electric neutrality. Higher valence elements may also be incorporated as network forming groups. Some components have limited solubilities in the glass, and precipitation of phases containing elements not incorporated into the glass

structure, such as noble metals and insoluble spinel phases, may occur within the glass. These phases may be detrimental to the production of high-level waste glasses and the chemical durability of the glass, and HLW glasses can be formulated to minimize the formation of these phases [JANTZEN-1985].

While this model of the glass structure has proven helpful in understanding glass corrosion, it cannot account for some commonly observed aspects of corrosion behavior. For example, boron is typically released from borosilicate glasses at a rate similar to the alkali metals, though the alkali metals occupy terminal sites while boron is modelled to occupy tetrahedral sites. Modifications have been proposed to better model observed behavior, such as the existence of compositionally-distinct phases within the glass [GOODMAN-1985]. Indeed, recent NMR studies have determined that boron segregates into regions in which boron is more readily leached [BATES-1993p153-164].

The basic description of the glass structure provides a point of origin for the discussion of the breakdown of the glass as it corrodes. Consider first the release of alkali metals from network terminal sites, which is modelled to occur through ion-exchange with protons from water to produce silanol groups and free alkali. The ion-exchange reaction can be written alternatively as



where $\equiv\text{SiO-H}$ represents a silanol group and M^+ is an alkali metal ion. While equation (1a) gives the basic reaction, an unhydrolyzed proton is not likely to be stable either in solution or in the glass. Different authors have expressed the ion exchange as equation (1b) and (1c), which are simply related through the ionization of water. Continued ion-exchange requires the proton-bearing species to diffuse into the glass to access other alkali metals. Diffusion of water into the glass is usually not accounted for specifically in reaction models, and alkali release is sometimes discussed in terms of the "interdiffusion" of hydronium and alkali metal ions [DOREMUS-1982]. Other evidence supports the diffusion of molecular water into glass [SMETS-1983]. Some have pointed to the observation that the measured proton to alkali exchange ratio is often near 3 to support the alkali for hydronium exchange in equation (1b) [SCHNATTER-1988], although exchange according to equation (1c) followed by sorption of a second water molecule would give the same result. Silanol is known to strongly sorb water.

Hydrolysis reactions are thought to be responsible for the degradation and dissolution of the silicate network. Hydrolysis of $\equiv\text{Si-O-Si}\equiv$ linkages is modelled to

occur through nucleophilic attack on a silicon atom by either molecular water or hydroxide. Hydrolysis of internal $\equiv\text{Si-O-Si}\equiv$ linkages may occur to break the network as



Hydrolysis of terminal $-\text{Si}(\text{OH})_3$ groups leads to dissolution of the glass as



The forward reaction in equations (2a and 2b) are referred to as network hydrolysis reactions and the forward reaction in equations (3a and 3b) are referred to as network dissolution reactions. The reverse reactions are referred to as condensation reactions. The $\equiv\text{SiO}^-$ groups generated in equations (2b) and (3b) may become protonated by interacting with another water molecule. Note also that silicic acid is a weaker acid than silanol. The fact that hydroxide is a stronger nucleophile than molecular water and the experimental observations of the pH effect on the rate of silicon release (discussed below) suggest that equations (2b) and (3b) better represent the hydrolysis reactions. Similar reactions can be written for the hydrolysis of other terminal metal-oxygen bonds, such as for boron



DESCRIPTION OF GLASS CORROSION

Initial contact of the glass by water results in the occurrence of both surface ion exchange reactions and surface hydrolysis reactions such that the surface of the glass is dissolved. These processes are interrelated through the solution chemistry and alteration of the glass structure, for example hydroxide produced by the ion exchange reactions assists in the hydrolysis of nearby metal-oxygen bonds. The replacement of alkali in the glass with protons and the hydrolysis of network bonds will enhance water diffusion into the glass, and larger amounts of water in the glass will enhance the ion exchange reactions. Because ion exchange reactions occur at higher rates than the hydrolysis reactions, an alkali depleted region develops at the glass surface. Water subsequently diffuses into the glass and ion exchanges with alkali metals that are encountered. The release of alkali metals via ion-exchange results in the generation of hydroxide which then catalyzes hydrolysis reactions.

The kinetics of the ion exchange and hydrolysis reactions are affected by the solution chemistry, particularly the increased pH, alkali metal ion, and silicic acid concentrations. Ion-exchange is slowed by the build-up of alkali and hydroxide in solution, while hydrolysis is slowed by high silicic acid concentrations but is accelerated by high pH. Therefore, the pH increase accompanying ion exchange slows the ion exchange reactions but

accelerates the hydrolysis reactions. The slowing of the ion exchange reactions may also slow the water diffusion through the glass. Because they are faster reactions, the early stages of corrosion will be dominated by ion exchange until the pH and alkali content of the solution become sufficiently high that the ion exchange reactions slow to the same rate as the hydrolysis reactions. Alkali metals are commonly observed to be released from the glass at an initial rate that is greater than that for the release of silicon, but at longer times the alkali metals and silicon are released at the same rate. The preferential release of the alkali metals during the early stages of corrosion results in an alkali-depleted layer at the surface of the glass [see also FENG-1993]. It is likely that, while the alkali metals and silicon are being released into solution at the same rate at later reaction times, they are released from different regions of the reacting glass: the alkali are released from beneath the depletion layer and silicon is probably released primarily from the outer surface of the depletion layer. Because the release of both the alkali metals and silicon are controlled by the solution chemistry, their release remains stoichiometric. Ion-exchange is usually considered to be a transient effect that is important only during the initial stages of glass corrosion. The kinetics of ion-exchange are not normally accounted for in reaction models.

As the hydrolysis reaction proceeds to release silicic acid into solution, the reaction rate decreases until a very low rate is reached, although the reaction does not stop completely. The corrosion may become controlled by a process other than hydrolysis at this stage, and the low rate that is achieved may represent the rate of the ion exchange reactions or perhaps the rate of water diffusion into the glass. The long-term behavior of glass corrosion is not presently well understood.

LABORATORY TESTING AND EXPERIMENTAL MEASURES OF GLASS CORROSION

Laboratory tests of chemical durability are performed by contacting the glass sample with a solution and measuring changes in either the glass or the solution. Standard testing procedures have been developed to directly compare results obtained at different laboratories for different glass compositions. These tests can be categorized as dynamic tests, in which the solution is continuously or periodically refreshed, or as static tests, in which the solution is not disturbed during the test. Static tests may be performed using either monolith samples or powdered samples of specific size fractions to provide various surface areas which may be contacted by different solution volumes. Static tests are characterized according to the ratio of the glass surface area, usually given in m^2 , and the solution volume, usually given in m^3 , so that the glass surface area/solution volume ratio (S/V) is in units of reciprocal meters (m^{-1}). Commonly performed static leach tests

include the MCC-1 leach test [DOE-1982], where monolithic samples are used and the S/V is specified to be 10 m^{-1} , and the Product Consistency Test (PCT) [JANTZEN-1990], which specifies 1 gram of powdered glass in the size fraction of -100+200 mesh per 10 mL leachant, which is equivalent to a S/V of about 2000 m^{-1} . Dynamic tests include Soxhlet tests where solution is continuously boiled, condensed onto the sample, and drained [DELAGÉ-1991], continuous flow tests, such as the MCC-4 test [DOE-1982], and periodic replacement tests, such as the ISO test [IAEA-1992].

The extent of glass corrosion is usually quantified by measuring the amount of one or more glass component in solution. Although silicon is the most abundant glass component and the silicon concentration is often used to monitor the glass corrosion, appreciable amounts of silicon usually remain on the reacted surface and silicon is contained in secondary phases so that the concentration of silicon in solution may not represent the amount of glass that has reacted. Other glass components are therefore commonly used to monitor the extent of glass corrosion. The alkali metals and boron are often used to monitor the glass corrosion because they are usually released from the glass at the highest rates, although boron is generally the best monitor of glass corrosion because the alkali metals may become incorporated into secondary phases [SCHEETZ-1985].

The amount of an element released into solution is usually used to calculate the equivalent amount of glass that has reacted. This is expressed as a normalized elemental mass loss value, wherein the measured solution concentration is normalized to the glass surface area and to the amount of that element in the glass, by weight. The normalized elemental release is given as the number of grams of glass reacted per square meter of surface area, based on the solution concentration of a particular element. Unless the corrosion is stoichiometric, the normalized mass loss value will depend on which element is used in the calculation. The values based on the alkali and boron releases are usually greater than those based on silicon.

The alteration of the glass surface due to the release of different glass components at different rates can also be used to monitor the extent of corrosion, and is often the only measure available, such as in field tests where the solution cannot be collected. In these cases, either the sample mass loss or the thickness of the alteration layer can be used as a measure of the extent of corrosion. The latter is related to the normalized mass loss by the glass density.

EFFECTS OF SILICIC ACID CONCENTRATION AND pH ON GLASS CORROSION

The rate of the glass corrosion has been modelled to be controlled by the amount of silicic acid in solution [GRAMBOW-1985]. The validity of representing the corrosion of a

multicomponent glass based on the solution concentration of a single element rests primarily on the general success of the model. Many tests have shown the corrosion rate to be affected by the silicic acid concentration over a range of pH values [PEDERSON-1983; GRAMBOW-1987]. The aluminum content also affects the rate under acidic conditions, while boron, calcium, and magnesium do not affect the corrosion rate [BATES-1992; BOURCIER-1992]. It is likely that any error due to omission of other glass components is corrected by utilizing test data to define various model parameters (see below). The rate of the hydrolysis reaction to release silicic acid given in equation (3a or b) has been modelled based on irreversible thermodynamics, where the rate is expressed as the product of a forward rate term and a term representing the chemical affinity for the reaction to release silicic acid from the glass, the latter being a measure of the difference between the actual silicic acid concentration and a "saturation" concentration of silicic acid, where the reaction affinity decreases as the solution concentration of silicic acid approaches the "saturation" concentration [GRAMBOW-1985]. The solid phase which establishes the "saturation" concentration is not identified, although the empirically determined "saturation" concentration is usually found to be intermediate between the solubilities of quartz and amorphous silica. Although glass is metastable and cannot equilibrate with the solution, this model and the concept of "saturation" has been found to describe glass corrosion well. In its simplest form, the rate of silicic acid release can be expressed as

$$\left(\frac{dn(\text{H}_4\text{SiO}_4)}{dt} \right) / S = k_+ \left(1 - \frac{[\text{H}_4\text{SiO}_4]}{[\text{H}_4\text{SiO}_4]_{\text{sat}}} \right) \quad (5)$$

where $n(\text{H}_4\text{SiO}_4)$ is the number of moles of silicic acid released from the glass into solution, k_+ is the rate coefficient for hydrolysis, S is the surface area of the glass, $[\text{H}_4\text{SiO}_4]$ is the molar silicic acid concentration in solution, and $[\text{H}_4\text{SiO}_4]_{\text{sat}}$ is the molar "saturation" concentration of silicic acid. Another term is sometimes included to account for the diffusion of material through the alteration layer which forms on the glass surface during corrosion [GRAMBOW-1985; GRAMBOW-1987]. This term may be important for glass compositions with relatively large values of k_+ , but will not be further considered here. The term $(1 - [\text{H}_4\text{SiO}_4]/[\text{H}_4\text{SiO}_4]_{\text{sat}})$ is the reaction affinity. Two limiting cases to equation (5) exist: when the affinity term is near one (when $[\text{H}_4\text{SiO}_4] \ll [\text{H}_4\text{SiO}_4]_{\text{sat}}$), and when the affinity term is near zero (when $[\text{H}_4\text{SiO}_4] \approx [\text{H}_4\text{SiO}_4]_{\text{sat}}$). When the affinity term is one, the rate is given simply by k_+ . It has been found that the reaction rate under these conditions depends on the solution pH, and so models have been modified to use either a pH-dependent rate coefficient [BOURCIER-1992] or include a pH term explicitly [EBERT-1992]. The pH-dependence of the rate coefficient may be expressed as $k_+ = k_f [\text{H}^+]^h$, where k_f is the pH-independent rate coefficient and h is an experimentally determined

value. The value of h has been measured to be about -0.4 for both a simulated DWPF glass at 70°C [KNAUSS-1990] the French glass R7T7 at 90°C [ADVOCAT-1991].

While the glass corrosion is assumed to be controlled by hydrolysis reactions and corrosion models do not generally include ion exchange reactions, some models have recognized the need to account for the effects of early ion exchange reactions on the solution composition and, more importantly, on the solution pH [BOURCIER-1993b].

According to equation (5), the hydrolysis rate is predicted to become nil as the affinity approaches zero. Some experiments show the glass corrosion rate to approach a very low, yet nonzero value at long reaction times [FREUDE-1985; GRAMBOW-1985]. An ad hoc, constant "residual rate" term is sometimes added to the rate expression to account for the continued reaction under "saturated" conditions. Values of this term can be approximated from long-term tests at high glass surface area-to-leachant volume ratios (see also below). Although the origin of this term is uncertain, continued corrosion has recently been attributed to diffusion-limited ion exchange [VAN ISEGHEM-1992] or water diffusion into the glass [GRAMBOW-1992]. However, diffusion through surface layers has been previously discounted since thinner layers are generally formed in tests at high S/V while the measured long-term rate decreases at higher S/V [VERNAZ-1990].

EFFECTS OF TEMPERATURE

The reaction temperature will affect the rates of all activated processes involved in glass corrosion, including water diffusion, ion exchange, and hydrolysis reactions. The temperature dependence of these reaction steps can be described using the Arrhenius equation, which relates the thermal distribution of the reactants to a threshold or activation energy for the step. The extent of reaction will be related to the activation energies of all steps involved in the corrosion mechanism. Because glass corrosion is comprised of several processes which may occur simultaneously or in series, and because changes in the temperature will affect each reaction step differently, the observed effect of increasing the temperature on glass corrosion may be the result of several affected processes and may not be identifiable with a particular reaction step. The particular test conditions used to measure the corrosion rate may affect the observed temperature dependence.

The temperature dependence of the forward reaction rate of R7T7 glass was measured in a high temperature Soxhlet device [DELAGE-1991]. The activation energy (based on the boron release) was measured to be 59 kJ/mol over the temperature range of 90 to 230°C, as shown in Figure 1. Previous measurements from static leach tests ($S/V=0.5\text{m}^{-1}$) gave an activation energy (based on the boron release after 1 day) of about

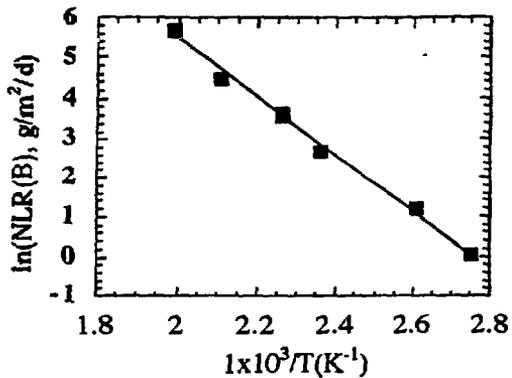


Figure 1. Logarithm of Normalized Boron Leach Rate vs. Reciprocal Temperature for Corrosion of R7T7 Glass in a Soxhlet Device (data from [DELAGÉ-1991]).

20 kJ/mol over this temperature range [VERNAZ-1988]. The static leach tests probably measured the temperature dependence of the reaction at lower reaction affinities and at higher pH values than were achieved in the Soxhlet tests. The normalized releases measured in static tests at 300°C were also much higher than predicted by the activation energy determined at lower temperatures. Similar anomalies have been observed in static leach tests with SRL 131 glass at high temperatures [WESTSIK-1981]. The non-Arrhenius behaviour indicates a change in the reaction mechanism. Higher activation energies were also measured in dynamic replacement tests having high effective flow rates than in tests at lower flow rates [BARKATT-1986]. These differences suggest that the build-up of reaction products in solution decreases both the corrosion rate and the measured activation energy.

Parameters used to model glass corrosion based on the release of silicic acid will likewise vary with the temperature. With regard to the rate expression given in equation (5), the temperature dependence of k_+ can be determined based on Soxhlet [DELAGÉ-1991] or flow through tests [KNAUSS-1990], while the values of $[\text{H}_4\text{SiO}_4]_{\text{sat}}$ and the "residual rate" under "saturated" conditions must be regressed from static leach tests conducted at the temperature of interest. The values of both are usually found to increase with the temperature. The determination of the forward rate and the rate under "saturated" conditions is further discussed later.

EFFECTS OF GLASS COMPOSITION

Probably the most important parameter concerning the glass reactivity is the glass composition itself, since a main goal of formulating waste glass compositions is to produce glasses having acceptable durability. The effects of individual glass components on the reactivity of the glass in general has been studied in many testing programs and some generalizations can be made. Based on the simple model of glass structure presented above, elements which behave as network formers usually enhance the glass durability, while elements which terminate the network usually decrease the glass durability. Thus

inclusion of silicon, aluminum, ferric iron, zirconium, and alkaline earths generally increases the glass durability, while alkali metals generally decrease the glass durability, although a certain amount of alkali metals are required for charge compensation of network formers.

The effects of individual glass components on the glass durability have been quantified in several models where a stability index is assigned to a glass composition based on a linear combination of contributions due to each component. The overall stability index is then correlated with test results to predict the durabilities of other compositions under the same test conditions. The coefficient for each component may be regressed from test data or may be assigned based on other data. A thermodynamic model is being utilized to formulate glass compositions for high-level defense wastes at the Defense Waste Processing Facility wherein the coefficients are the free energies of hydration [GOLDSTON-1992]. Representative free energies of hydration are computed for various glass compositions from the known hydration free energies of oxides and silicates which are modelled to comprise the glass. The free energy values computed for actual glasses are then correlated with their measured response in leach tests, and the correlation used to predict the stabilities of other glass compositions. Data for waste glasses, natural glasses, and historic glasses have been utilized to correlate the glass composition of a glass with its anticipated performance in a leach test [JANTZEN-1992].

Coefficients for high-level waste glass compositions to be produced at other vitrification facilities have been determined by empirical regression methods [HRMA-1992]. Because the compositions of durable HLW glasses fall within a relatively narrow range, subtle effects of small changes in the amounts of individual components are difficult to discern experimentally. Indeed, parameters used to model glass corrosion, such as k_+ and $[H_4SiO_4]_{sat}$, are generally similar for different glass compositions.

The effects of some glass components on the corrosion rate may change as the reaction conditions and the dominant corrosion step change. The presence of aluminum may enhance glass stability under basic conditions by inhibiting water penetration, but becomes an important component of secondary zeolite phases, such as analcime ($NaAlSi_2O_6$), which may accelerate the glass corrosion rate upon their formation [VAN ISEGHEM-1988]. While varying the amount of aluminum in a glass over a small range may have little effect on corrosion in short-term tests [VAN ISEGHEM-1992], the aluminum content may have a very large effect at latter stages of the corrosion process when secondary phase formation becomes important. Hence, the durability of a glass under one set of testing conditions may be very different under other conditions which may be more or less relevant to potential repository environments.

Most laboratory tests are performed using glasses without radionuclides or glasses doped with lower levels of radionuclides than are anticipated to be present in actual HLW glass because of the difficulties in working with highly radioactive materials. It is important to verify that the corrosion behavior observed in non-active glass represents the behavior of the glass matrix of active glasses. The major effects of radioactive waste are expected to be the generation of α tracks within the glass and radiolysis of the fluid and gas environment surrounding the sample. In general, the glass matrix is usually found to behave similarly in leach tests conducted with simulated and actinide-doped samples [FILLET-1985; BIBLER-1986]. However, recent tests have shown some difference in the long-term reaction behavior of radioactive and nonradioactive glasses in small solution volumes due to the lower pH values attained in tests with radioactive glass [BATES-1992]. Further discussion of radiolysis effects are presented elsewhere [WRONKIEWICZ-1993].

EFFECTS OF GLASS SURFACE AREA-TO-SOLUTION VOLUME RATIO IN STATIC LEACH TESTS

The glass surface area/solution volume ratio (S/V) used in static leach tests affects the extent to which reaction products are diluted. The solution concentrations then affect the rates of various reactions critical to glass dissolution, including ion exchange and hydrolysis reactions. From the discussion above, higher pH values slow the ion exchange reactions but accelerate the hydrolysis reactions. Higher silicic acid concentrations will decrease the rate of silicon release and other hydrolysis reactions. If all silicic acid released from the glass remains in solution, then $n(\text{H}_4\text{SiO}_4)$ in equation (5) can be replaced with the molar concentration of silicic acid as $n(\text{H}_4\text{SiO}_4) = [\text{H}_4\text{SiO}_4] V$, where V is the volume of the reaction cell, and equation (5) can be written as

$$d [\text{H}_4\text{SiO}_4]/dt = (S/V) k_+ (1 - [\text{H}_4\text{SiO}_4]/[\text{H}_4\text{SiO}_4]_{\text{sat}}) \quad (6)$$

Integration leads to the form [GRAMBOW-1985]

$$[\text{H}_4\text{SiO}_4] = [\text{H}_4\text{SiO}_4]_{\text{sat}} (1 - \exp\{ -(S/V) t k_+ / [\text{H}_4\text{SiO}_4]_{\text{sat}} \}) \quad (7)$$

which shows the silicic acid concentration to approach the limiting value $[\text{H}_4\text{SiO}_4]_{\text{sat}}$ at a rate that is a function of the the product $(S/V) t k_+$. If k_+ is constant and is not sensitive to changes in the pH, then tests performed for the same $(S/V) t$ are expected to attain similar solution concentrations. This has been observed in tests with PNL 76-68 glass run at relatively low S/V [PEDERSON-1983], as shown in Figure 2. Both the boron and silicon concentrations increase linearly with the value of $(S/V) t$, and data from tests run at different S/V can be represented by a single line. If k_+ is sensitive to the pH, then tests performed for common values of $(S/V) t$ will generate different solution concentrations. This is seen to occur in tests at higher S/V with SRL 202 glass, where tests at higher S/V generate greater solution concentrations than tests at lower S/V at common $(S/V) t$

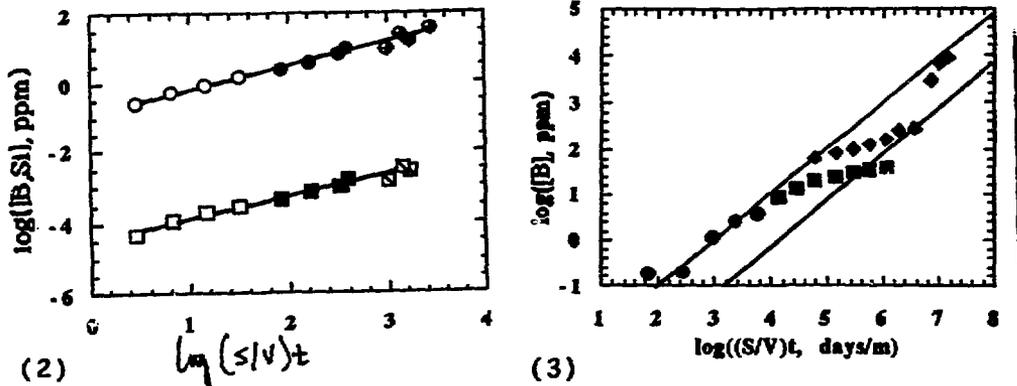


Figure 2. Concentration vs. (S/V)xTime for Release of Boron and Silicon from PNL 76-68 Glass at 90°C. (□) Si and (○) B at 1 m⁻¹; (■) Si and (●) B at 10 m⁻¹; (◻) Si and (⊙) B at 100 m⁻¹ (data from [PEDERSON-1983]).

Figure 3. Concentration vs. (S/V)xTime for Release of Boron from SRL 202 Glass at 90°C at (●) 10, (■) 2000, and (◆) 20,000 m⁻¹ (data from [EBERT-1993]).

[EBERT-1993], as shown by the boron data in Figure 3. The differences in the solution concentrations attained in tests run at different S/V can be attributed to the effect of the pH on the corrosion rate. Tests at 2000 m⁻¹ generated leachates with pH values near 10, while tests at 20,000 m⁻¹ generated leachates with pH values greater than 11. These results show that static leach tests cannot be scaled using the factor (S/V) t without accounting for the effects of the pH.

DETERMINATION OF MODEL PARAMETERS FROM LEACH TESTS

Modeling glass corrosion using Equation (5) requires the definition of the rate coefficient, the reaction order with respect to the pH, the silicic acid saturation value, and the "final rate". Values for these parameters are usually obtained experimentally. Grambow utilized a plot of the measured normalized reaction rate (NR) based on the release of several glass components versus the ion activity product of silica to determine the forward rate constant, k_+ , at $IAP(\text{SiO}_2) = 0$ and the "final rate" at $NR(\text{average}) = 0$ [GRAMBOW-1987]. In an alternate approach, Equation (7) can be rearranged to obtain

$$\log\{[B]\} = \log\{k_+ (1 - [H_4\text{SiO}_4]/[H_4\text{SiO}_4]_{\text{sat}})\} + \log\{(S/V) t\} \quad (8)$$

where the extent of corrosion is measured using the boron concentration rather than the silicic acid concentration (see [BUNNELL-1986; EBERT-1993]). According to Equation (8), a line of slope one drawn through the any data point in a plot of log{[B]} vs.

$\log\{(S/V) t\}$ will have a y-intercept equal to $\log\{k_+ (1-[H_4SiO_4]/[H_4SiO_4]_{sat})\}$. Under dilute conditions at small values of $(S/V)t$, $[H_4SiO_4]$ will be much smaller than $[H_4SiO_4]_{sat}$ and the y-intercept will approach a maximum value which is $\log(k_+)$. Tests in flowing leachant such as those of Knauss et al. discussed above maintain highly dilute conditions and provide a good measure of k_+ at different pH values. Under saturated conditions at large values of $(S/V)t$, $[H_4SiO_4]$ will be similar to $[H_4SiO_4]_{sat}$, and the y-intercept of the line drawn through long-term test data will approach a minimum value sometimes referred to as the "residual rate".

Lines of slope one are drawn through data for tests with SRL 202 glass at $20,000\text{ m}^{-1}$ in Figure 4 to obtain the forward rate and the rate under "saturated" conditions, which are 0.04 and $0.0025\text{ g/m}^2/\text{day}$, respectively. The minimum rate for tests at $20,000\text{ m}^{-1}$ in Figure 4 occurs after about 180 days. At longer reaction times, the rate is seen to have increased to near the rate under dilute conditions. The increase occurs coincidentally with the formation of secondary phases, although the mechanism of the acceleration is not well understood [EBERT-1993; VAN ISEGHEM-1993]. Different long-term rates have been observed for tests run at different S/V [VERNAZ-1989]. This is also seen in Figure 3, where some data points for tests run at 2000 m^{-1} lie to the right of the line giving the "saturation" rate for tests at $20,000\text{ m}^{-1}$, which indicates that tests at 2000 m^{-1} proceed at an even lower rate than tests at $20,000\text{ m}^{-1}$ under "saturated" conditions, perhaps indicating that the "residual" rate term depends on the solution chemistry.

EFFECTS OF THE FLOW RATE IN DYNAMIC LEACH TESTS

Because of the negligible flow rates anticipated in repositories, laboratory tests in flowing solutions are used to characterize modeling parameters [KNAUSS-1990; DELAGE-1991]. The leachant flow rate used in dynamic tests also affects the effective silicic acid concentration at the glass surface and the pH. Solutions contacting the glass in tests at high flow rates maintain the initial leachant conditions, while tests at low flow rates allow reaction products to accumulate in the solution. The glass corrosion rate in terms of the flux of silicic acid from the glass surface can be related to the leachant flow rate by a mass balance equation for the reaction of glass in a well-mixed reactor of volume V and flow rate f as

$$d[H_4SiO_4]/dt = (S/V)k_+ (1-[H_4SiO_4]/[H_4SiO_4]_{sat}) - f [H_4SiO_4]/V \quad (6)$$

where the first term on the right hand side represents the release of silicic acid from the glass (see equation (5)), and the second term represents the removal of silicic acid from the reaction cell via flow. This simple treatment ignores the possible effects of mass

transport either through the solution or through alteration layers that may form on the glass surfaces. Under constant flow conditions, a steady-state silicic acid concentration is attained that depends on the flow rate and sets the glass corrosion rate. Under sufficiently high flow rate conditions, the glass corrosion rate becomes

$$dn(\text{H}_4\text{SiO}_4)/dt = (S/V)k_+ \quad (7)$$

and is independent of the flow rate, while under low flow rate conditions it becomes

$$dn(\text{H}_4\text{SiO}_4)/dt = [\text{H}_4\text{SiO}_4]_{\text{sat}} f \quad (8)$$

and is proportional to the flow rate. At very low flow rates, a steady-state concentration is not achieved and Equation (6) becomes equivalent to Equation (5). The effect of flow rate on glass corrosion is well illustrated by tests performed using SRL-131 glass [ADIGA-1985]. Figure 4 shows the measured mass loss as a function of reaction time for tests utilizing various flow rates. Tests run using flow rates less than 1.0 mL/h show continually decreasing rates similar to static tests, while tests at higher flow rates show linear reaction rates that increase with the flow rate through a rate of about 50 mL/h. Tests at 100 mL/h react at the same rate as tests 50 mL/h, which is the maximum rate under these temperature and pH conditions. From this data, the forward rate is about 2.5 g/m²/day.

Difficulties associated with attaining the very low flow rates relevant to repository scenarios in laboratory tests have led to the use of leachant replacement tests (sometimes called pulsed-flow tests) where some or all of the leachate is periodically replaced with fresh leachant. The frequency and extent of replacement is then related to an effective flow rate. The results of pulsed-flow laboratory tests are well described by equations (7) and

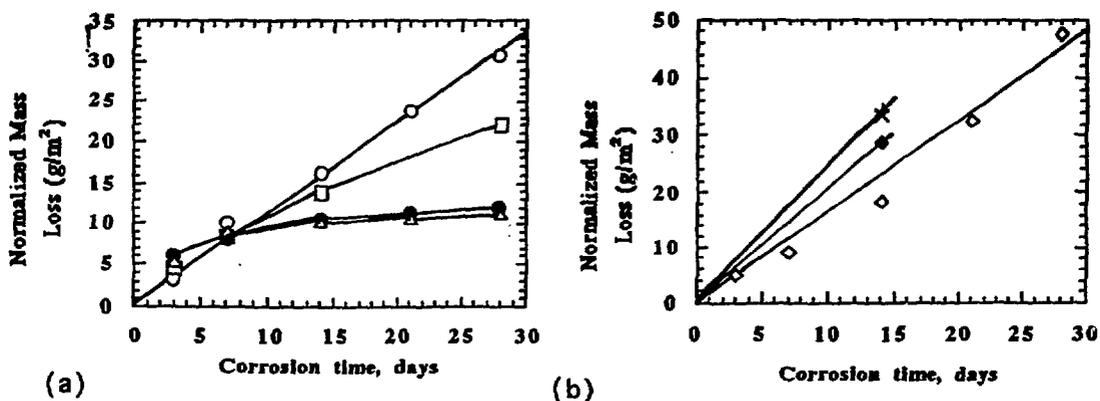


Figure 4. Mass Loss vs. Corrosion Time for SRL 131 Glass at 90°C at Various Flow Rates. (a) (Δ) Static, (●) 0.1 mL/h, (◻) 0.5 mL/h, (○) 1.0 mL/h, and (b) (◇) 10 mL/h, (◆) 25 mL/h, (+) 50 mL/h, (×) 100 mL/h (data from [ADIGA-1985]).

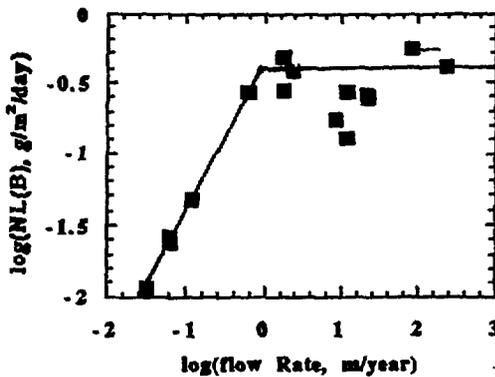


Figure 5. Boron Release from SRL TDS-131 Glass as a Function of Flow Rate (data from [BARKATT-1984]).

(8), as shown by the reaction of SRL-131 glass in Figure 5 [BARKATT-1984]. These tests also show a maximum rate of about $2.5 \text{ g/m}^2/\text{day}$ to occur at sufficiently high flow rates.

SUMMARY

A relatively concise description of the corrosion of borosilicate high-level waste glasses at temperatures near 90°C has emerged based on laboratory testing and modeling carried out over the past several years, although some important phenomena remain unclear. Glass corrosion can be described as occurring through three processes: water diffusion, ion exchange, and hydrolysis. Ion exchange is important in the early stages of corrosion and affects the solution pH. Hydrolysis is important during the intermediate and long-term corrosion stages. The glass corrosion rate is well-described using an affinity-based model where the reaction slows as the silicic acid concentration in the solution contacting the glass approaches a "saturation" value. Reaction under "saturated" condition proceeds at a low rate, which may represent the rate of water diffusion into the glass. The corrosion rate may increase significantly at later times under some conditions, perhaps due to secondary phase formation.

The results of laboratory tests performed to characterize the reactivity of waste glasses are affected by the test parameters used, including the reaction temperature, the ratio of the available glass surface area to the solution volume, the glass and leachant compositions, and the reaction time. The temperature affects each reaction process differently according to the activation energy of each process. The temperature dependence observed in a test will likely be affected by all processes, so that the "activation energy" of the overall reaction does not represent any one process. Changes in test temperatures may result in a change in the dominant reaction step observed in the test, which is expected to give rise to a discontinuity in the Arrhenius plot.

The glass surface area/solution volume ratio (S/V) used in static leach tests affects the dilution of the reaction products, including the silicic acid concentration and the pH, both of which affect the glass corrosion rate. Simple correlation variables such as $(S/V)t$ cannot be used to relate tests run at different S/V unless the effects of the pH are accounted for. Likewise, the use of tests at high S/V to measure the rate after long reaction times must account for the different pH values that are attained.

The flow rate used in dynamic tests also affects the concentration of silicic acid at the glass surface. The corrosion rate will be proportional to the flow rate at intermediate flow rates, but a maximum corrosion rate is attained at high flow rates. At low flow rates, the corrosion rate is limited by the low reaction affinity. Tests using pH buffered leachants performed at high flow rates can be used to measure the forward reaction rate as a function of pH.

The chemical composition of the glass affects its corrosion rate, although the effects of individual components may vary as the dominant process of the corrosion mechanism changes as the reaction conditions change. The silicon contents of the leachant has been found to affect the corrosion rate in basic and acidic solutions, and the aluminum content has been found to affect the corrosion rate in acidic solutions. Other glass components have no measurable affect on the corrosion rate.

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