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**Effects of Glass Surface Area-to-Solution Volume
Ratio (S/V) on Glass Dissolution
Part One: Relationship Between S/V and Leachate pH**

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ABSTRACT

The observed relationship between S/V and leachate pH is discussed in terms of a simple model of the glass dissolution process. Data from leach tests on several nuclear waste glass compositions at different S/V ratios show that the leachate pH increases with time and then stabilizes at a nearly constant value beyond about 28 days. This stabilized pH increases systematically with the S/V ratio of the test. The model developed here reproduces the essential features of the data and suggests that a single parameter describing the intrinsic rate of alkali diffusion and ion exchange from the glass is sufficient to represent the major glass composition dependence. Interestingly, the results are essentially independent of the rate constant for matrix dissolution. This study suggests that the diffusion-ion exchange process is central in determining the solution pH and its dependence on S/V and the glass reaction, at least under static or low-flow-rate test conditions, is "driven" by alkali release.

INTRODUCTION

The ratio of glass surface area to solution volume (S/V) has long been recognized as an important parameter in glass corrosion tests [1-2]. Much of the recent literature has resulted from

studies on nuclear waste glasses for a number of reasons. First, the unsaturated hydrology of the host tuff rock at the possible location of the U. S. high-level nuclear waste repository at Yucca Mountain, Nevada [3], suggests that only water vapor and perhaps small volumes of migrating water will contact cracked waste glasses in breached canisters, which will result in a very high S/V system. Alternatively, after breaching, a canister may fill with liquid water giving rise to a low-S/V scenario. Consequently, the durability of the waste glass over the entire range of S/V environments, from a glass-dominated, high-S/V system to a water-dominated, low-S/V system, must be understood in order to predict waste glass performance under repository conditions. Nuclear waste glasses have been tested under very different S/V conditions in a variety of standard tests such as the MCC1, MCC3 [4], and PCT [5] tests. A better understanding of the effect of S/V would be an important step towards a unified interpretation of the large body of data from such tests.

Second, the amount of leachant available per unit glass surface area determines the rate at which the solution reaches saturation in dissolved glass components leading to the precipitation of secondary phases. Tests at high S/V are therefore often used to accelerate the attainment of solution saturation. In fact, the product of S/V and time t has been proposed as a scaling factor for comparing experimental results obtained at different S/V ratios [6,7]. There is an obvious appeal to the existence of such a simple scaling factor since then short-term test results could be easily extrapolated to longer periods of time to predict the performance of nuclear waste glass during the approximately 10,000-year-service-life of the repository. The validity of $(S/V)t$ scaling appears limited, however [8].

Recent efforts towards modelling the glass dissolution process, which is one element in assessing the performance of nuclear waste glass under the repository conditions, have focussed on coupling simple kinetic equations with well-developed geochemical computer codes for solution speciation and equilibrium secondary phase formation [9, 10, 11]. In these approaches the S/V effect on glass dissolution is incorporated into the models in an equation of the form

$$Rate = k \frac{S}{V} \left(1 - \frac{Q}{K} \right). \quad (1)$$

The approaches of Grambow [9] and Bourcier et al. [10, 11] differ in the interpretation of the terms Q and K: Q is either the activity of silicic acid [9] or activity products of the gel layer [10] and K is either the activity of silicic acid at saturation [9] or the solubility product of gel layer [10]. In both cases, S is the glass surface area, V is the solution volume, and k is a rate constant [9, 10, 11]. The approach of Bourcier et al. is rather more general and also addresses the problem of applying transition state theory to a situation in which the reverse reaction does not occur (glass cannot form from solution) by considering instead solution saturation with respect to an altered or pre-reacted glass surface layer (gel layer). Grambow's approach also incorporates parameters for the diffusion of silicic acid from the reaction zone, and for a nonzero long term rate. Neither approach incorporates well-known ion exchange and alkali diffusion effects since these are assumed to be essentially short-term transient effects that are not important in the long term. While it has been recognized that, as written, k depends on pH [10,11], it is usually held constant during computer simulations and the efforts to incorporate ion exchange effect in computer simulation of waste glass performance has also begin [12]. In this paper we argue that ion exchange and alkali diffusion effects are essential in determining not only the effects of S/V on solution pH, but also the long-term values of solution pH and elemental concentrations attained in static leach tests.

The S/V effect incorporated in Eq. (1) is a simple concentration effect. A higher S/V implies that more glass surface area is in contact with a given volume of leachant which, other things equal, would result in an increased amount of all species entering the solution per unit time, that is, an increased rate. The intrinsic glass reaction rate, or amount of material leaving a unit area in a unit time (flux), is controlled by the affinity term $(1-Q/K)$ and the rate constant k in Eq. (1).

As mentioned earlier, S/V effects on glass dissolution have been studied extensively experimentally [6-9,12-17]. (S/V)t-scaling appears to have some merit in the short term but the general validity seems to be highly glass composition dependent [8]. Previous studies have also shown that S/V changes resulted in systematic changes in leachate pH [17,18,19]; in changes in the thicknesses of reacted layers [6,20]; in the identities of the secondary phases that are formed [19,21]; and in changes in the dominant leaching mechanisms [22,23]. The detailed effects of S/V on glass dissolution thus appear to be quite complex. In this paper we focus on one

particular characteristic, the relationship between solution pH and S/V. Given the central role of solution pH on the dissolution process, this would appear to provide a logical first step in any attempt to correlate and explain the various observations listed above.

EXPERIMENTAL

Glass Compositions

The compositions used in this study are all simulated high-level nuclear waste glasses. Two preliminary reference glass formulations for defense-related nuclear waste, SRL131 and SRL165, both made at Westinghouse Savannah River Co., were used. In addition, the study used four preliminary reference glass formulations for commercial nuclear waste stored at West Valley, SF6, SF10, WVCM59 and WVCM62, of which SF6 and SF10 were made at West Valley Nuclear Service Inc. and WVCM59 and WVCM62 were made at The Catholic University of America. The detailed compositions as weight percent oxides are given in Table 1.

Leach Tests

The leach tests were conducted at The Catholic University of America's Vitreous State Laboratory. A slightly modified version of the SRL PCT [5] procedure, using 304L stainless steel vessels with fittings to permit sampling at multiple times, was used. The leach test uses crushed and sieved glass powders of 74 micron to 149 micron (100 to 200 mesh) particle size. The leachant volumes used were 40-100 mL, depending on the S/V ratio of the test. Different values of S/V were achieved by varying the ratio of the weight of the glass powder to the volume of the leachant. The leachant was deionized water in all cases. The requisite mass of glass powder was immersed in the corresponding volume of leachant in the precleaned vessel. The vessel was then placed in a convection oven preheated to 90°C. At each sampling interval, 4 mL of the leachate were withdrawn from the vessel by a syringe inserted through a rubber septum fitted on the vessel; the leachate sample was then filtered through a 0.45µm filter. An equal amount of fresh leachant was then injected into the vessel to maintain a constant S/V ratio. The vessel was

then returned to the oven to continue the test. Each test was run in triplicate with samplings after 1, 3, 7, 28, 56, 120, 180, 270, 365, 547, and 730 days. The pH was measured immediately after the sample had been quenched to room temperature by placing the leachate solution in a thin-walled plastic vial in water at 25°C. The elemental concentrations were determined by DC plasma and AA spectroscopy. A blank test (i.e. one without glass) was run for each glass composition. The analyzed blank concentrations were not subtracted from sample concentrations due to the very low elemental concentrations found in the blanks compared to the sample concentrations. The relative standard deviation is estimated to be less than 10% for all of the major elements analyzed, as estimated from the reproducibility of the triplicates. Some of the reacted glass powders were analyzed at Argonne National Laboratory with SEM/EDS and TEM after they were rinsed with deionized water and air dried at room temperature. Results of these studies will be reported elsewhere.

The advantage of this testing method is that it yields data at multiple times from a single test while maintaining an essentially constant S/V ratio. However, it should be noted that the exchange of 4 mL of leachate for fresh leachant, usually out of a total of 100 mL solution, will influence the reaction progress to some extent. On the other hand, such disturbances might be expected in some repository scenarios.

Data were collected on the six glasses in deionized water at S/V values of 10, 20, 200, 2000, 10000, 20000, and 40000 m⁻¹ for up to 600 days.

RESULTS

The leachate pH is plotted against time for each glass composition and each value of S/V in Fig. 1. At each S/V, the pH increases rapidly with time initially and then stabilizes at a nearly constant value for the duration of the test. In the most striking example, the pH of the leachate for SF10 glass at S/V = 40000 m⁻¹ increased significantly with time during the first month of testing and then stabilized at pH=11.30 from 28 to 547 days. The average of the 18 measurements in tests at S/V = 40000 m⁻¹ between 28 days and 547 days (triplicate samples at 28, 56, 180, 270, 365, and 547 days) exhibited a standard deviation of 0.06 pH unit, which is within the analytical error of our laboratory measurements. We will refer to this stabilized pH value as the

"steady-state pH" since concentrations of components such as B, Si, Li, Na, etc. are continuing to increase during this period. As Fig. 1 shows, the steady-state pH value increases systematically as the S/V increases from 10 to 40000 m⁻¹. The standard deviation of the 18 pH values for SF10 obtained from the triplicate measurements at each of the 28, 56, 180, 270, 365, and 547 day samplings is between 0.04 and 0.07 pH units for all S/V values studied. Similar calculations were performed for the data from the other five glasses in Fig. 1 with the result that all of the standard deviations are less than 0.2 pH unit. While the general behavior is the same for all of the glasses the two glasses showing the highest leachate concentrations, SRL131 and SF6, are somewhat distinctive: SF6 shows a peak pH at short times at high S/V and SRL131 shows a slightly declining pH at longer times. This latter behavior may be due to a combination of the effect of leachate replenishment and secondary phase formation in view of the high solution concentrations involved.

For SF10, the pH changed by 1.75 units when the S/V changed from 10 to 40000 m⁻¹. The pH variation for SRL131 glass is even larger with a 2.38 unit change when the S/V changed from 10 to 20000 m⁻¹. Thus, the steady-state pH is a strong function of both S/V and glass composition.

DISCUSSION

When glass initially contacts water one would expect the non-bridging oxygen sites on the glass surface to react rapidly with water according to Eq. (2).

This reaction will clearly tend to increase the solution pH. This reaction might also be written as

where instead of the generation of a hydroxyl ion in solution, a hydrogen ion is removed from

solution. In either case the net result is an increase in the solution pH. The hydronium ion has been proposed [24] to exist with a symmetric bond involving a proton and two water molecules. The large mobility of the proton in aqueous solution can then be accounted for in terms of slight shifts of the positions of two H nuclei within this ion, resulting in the displacement of the positive charge through the solution. Both reactions (2) and (3) involve a proton transfer from the solution to the glass surface and result in an increase in both solution pH and the concentration of R^+ . However, the identity of the attacking agent has been proposed to be either molecular water, hydronium ion, or hydrogen ion [25-28].

From a very simplistic point of view, Eq. (2) and (3) alone would suggest that the solution pH would tend to increase with S/V since at high S/V there are more accessible reaction sites per unit volume of solution than at low S/V . However, as the OH^- concentration in solution increases, the reverse of reaction (2) is increasingly favored which would tend to slow the rate of pH rise at high pH; a similar argument can be made for Eq. (3). Other factors also tend to offset the pH rise resulting from these reactions. The matrix dissolution reaction in Eq. (4) does not, in and of itself, affect the solution pH since the OH^- is regenerated at the end of the reaction.

However, the resultant introduction of silicic acid and other species into solution can affect the pH through dissociation of those species (silicic, boric, phosphoric acids, etc.). Other such processes include the binding of hydroxide ions by heavy and transition metals in the hydrated glass surface [29] and secondary phase formation reactions that may involve the incorporation of H^+ or OH^- ions [30]. A further reaction in which OH^- is consumed is shown in Eq. (5)

This reaction is important when both the solution pH and the alkali concentration R^+ are high (R^+ may also include cations other than alkalis). This reaction was utilized by Budd and Frackiewicz in their interpretation of the equilibrium pH of glasses [31,32].

Summarizing the above components of the overall reaction, we see that at the beginning of the reaction, the OH^- concentration is low, the ion exchange reaction (2) is favored, and reaction (5) and other hydroxide-consuming reactions should be relatively insignificant, resulting in a rapid initial increase in solution pH. As time elapses, the OH^- concentration in the solution increases, the driving force for OH^- -producing reactions such as Eq. (2) decreases, and the driving force for OH^- -consuming reactions such as Eq. (5) increases. It does not seem unreasonable therefore, that a steady-state situation may ensue in which the rate of OH^- production equals that of OH^- consumption and the solution pH attains a nearly constant, steady-state value, despite the fact that the reaction front is still progressing into the glass matrix. The time required to reach such a steady-state pH would then depend on the S/V ratio, the glass and leachant compositions, and the temperature.

As mentioned above, secondary phase formation reactions may also involve the incorporation of OH^- or H^+ from solution. However, the fact that the solution pH stabilized at such an early stage of the reaction in the data shown in Fig. 1 suggests that secondary phase formation is not the major factor affecting pH. Consequently, these effects have been largely neglected in the discussion of the simple model we present below.

First, however, we comment briefly on the glass composition dependence exhibited by the data in Fig. 1. As an example, at $S/V = 2000 \text{ m}^{-1}$ the steady-state pH values for the six glasses cover a range of about 1.8 pH units. From the above discussion one might expect that the solution pH should correlate with the number of non-bridging oxygen bonds in the glass. However, a function based only on the direct counting of non-bridging oxygen bonds was found to have a very poor correlation with solution pH, even for a simple $\text{Na}_2\text{O-CaO-SiO}_2$ system [32]. This is due in part to the fact that the rate and the completeness of the ion exchange reaction (2) depends not only on the number of non-bridging bonds, but also on the type of cations attached to those bonds and the matrix site involved (e.g. $\sim\text{Si-O}\sim$, $\sim\text{B-O}\sim$, $\sim\text{Al-O}\sim$, etc.) [33]. Glass composition effects may therefore be quite complicated in multicomponent glasses of the type studied here.

Finally, it is important to examine the extent to which simple dilution effects can explain the observed dependence of steady-state pH on S/V for each glass composition. If we consider increasing the leachant volume at fixed glass surface area (i.e. decreasing S/V) the direct effect

on the H^+ concentration is a proportional reduction. In other words, the simple effect of dilution is that the pH should be proportional to $\log(S/V)$. Figure 2 shows the steady-state pH values for each glass plotted against $\log(S/V)$ where the line of unit slope represents the simple dilution behavior. None of the glasses follow this behavior very well, with the possible exception of SRL131 at S/V ratios above 200 m^{-1} . What is striking about Fig. 2 is the general similarity between the behavior of the six glasses. As discussed earlier, the high solution concentrations attained for SF6 and SRL131 make precipitation of secondary phases more likely, especially at high S/V ratios; this may be responsible for the observed drops in pH at high S/V for those glasses. Table 2 shows the limiting slopes at high S/V regressed from the data in Fig. 2. While SRL131 gives a slope close to that expected on the basis of simple dilution arguments, the values for the other glasses are all significantly less than unity. In the next Section we discuss these features of the data in relation to the results from a simplified model of the glass-water reaction that we have investigated.

MODEL

Consider a two-component silicate glass composed of SiO_2 and R_2O , where R is an alkali metal, and define the composition variable $r = M_R/M_{\text{Si}}$, where M_i is the number of moles of that element in the glass. Assume that a surface area S of this glass is placed in contact with a fixed volume V of pure water at time $t = 0$. For simplicity, we will assume that all solution activities may be replaced by the corresponding concentration in what follows. Furthermore, we neglect the effect of the small volume of leachate that is replaced after sampling that occurs in our experiments but this could be easily incorporated into the model. We introduce the two basic leaching sub-mechanisms discussed above - (a) interdiffusion and ion exchange, and (b) matrix dissolution - into the model in the following way. First, we adopt the standard square-root-of-time diffusion form for the rate of alkali release:

$$\frac{d[R^+]}{dt} = \frac{1}{2} k_d \frac{S}{V} t^{-\frac{1}{2}} \quad (6)$$

where k_d represents an effective rate constant (or diffusion coefficient) for that process. The basic assumption here is that the ion exchange process itself is rapid compared to diffusion of the reactants and products to the reaction site in question. Accordingly, Eq. 6 yields instantaneous ion exchange of surface alkali ions for protons followed by a rate that decreases with time as the reaction front penetrates into the glass. No assumption about the identity of the diffusion controlling species (R^+ , H_3O^+ , H_2O , etc.) is necessary at this stage since such information is subsumed into the phenomenological parameter k_d .

Second, to introduce the matrix dissolution process we use a simplified form of the reaction affinity rate equation, discussed above, of the type used by Grambow [9]. We denote the total concentration of all silicon-bearing species in solution as $[Si]$ and write its rate of increase with time as:

$$\frac{d[Si]}{dt} = k_f \frac{S}{V} \left(1 - \frac{[Si]}{[Si]_{sat}} \right) \quad (7)$$

where the subscript "sat" denotes a value at saturation, and k_f is a rate constant. Silicon saturation is reached when the concentration of undissociated silicic acid H_4SiO_4 has reached its solubility limit, $[H_4SiO_4]_{sat}$. Thus, while $[Si]_{sat}$ is highly pH dependent, $[H_4SiO_4]_{sat}$ is not. In fact, if, for simplicity, we include only the first dissociation constant of silicic acid, denoted by $K = [H^+][H_3SiO_4^-]/[H_4SiO_4]$ then

$$[Si] = [H_3SiO_4^-] + [H_4SiO_4]$$

and

$$[Si] = [H_4SiO_4] \{ 1 + K/[H^+] \} \quad (8)$$

Thus, at any pH, the concentrations and the corresponding saturation values are related by

and therefore Eq. 7 becomes

$$\frac{[Si]}{[Si]_{ss}} = \frac{[H_4SiO_4]}{[H_4SiO_4]_{ss}}$$

$$\frac{d[Si]}{dt} = k_f \frac{S}{V} \left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{ss}} \right) \quad (9)$$

Next, we impose charge balance on the solution to find the pH:

$$[OH^-] + [H_3SiO_4^-] = [R^+] + [H^+]$$

which, with $K_w = [H^+][OH^-]$, yields

$$[H^+]^2 + [R^+][H^+] - \{K_w + K[H_4SiO_4]\} = 0$$

and therefore

$$[H^+] = (-[R^+] + \{[R^+]^2 + 4\{K_w + K[H_4SiO_4]\}\})/2 \quad (10)$$

Equations 6, 8, 9 and 10 form the basis of the model; these can be integrated given the initial conditions $[R^+] = 0$ and $[Si] = 0$ at $t = 0$, and values for the constants K , K_w , $[H_4SiO_4]_{ss}$, k_d , k_f , and S/V . At each integration step new values for $[R^+]$ and $[Si]$ are obtained, permitting Eqs. 8 and 10 to be solved self-consistently for $[H^+]$, and therefore $[H_4SiO_4]$, which in turn permits calculation of the new rates for the next step.

One additional condition is imposed on this model. If the intrinsic rate of alkali release due to diffusion and ion exchange (Eq. 6) should fall below that of the matrix dissolution rate (Eq. 9) one would expect that, effectively, the former is replaced by the latter. Presented another way, the ion exchange reaction front propagates into the glass at a velocity proportional to Eq. 6 while the matrix dissolution reaction front (the glass surface in contact with the solution) propagates into the glass with a velocity proportional to Eq. 9. Detailed solution of this moving boundary problem [34-36] reveals that the separation between these reaction fronts increases

towards a steady-state value at which point the two velocities become equal. This general behavior is incorporated simplistically into the present model by imposing the condition:

$$\frac{d[R^+]}{dt} = r \frac{d[Si]}{dt} \quad \text{for} \quad \left(\frac{d[R^+]}{dt} \right)' < r \frac{d[Si]}{dt} \quad (11)$$

where the prime denotes the value calculated from Eq. 6. We note, however, that this condition was not necessary over the range of parameters discussed below.

We next introduce two generalizations of this basic model. Firstly, since the net effect of the diffusion - ion exchange process represented by Eq. 6 is the exchange of a proton in solution for R^+ , one might expect the rate to show some dependence on $[H^+]$, the hydrogen ion concentration in solution. Accordingly, we replace Eq. 6 by:

$$\frac{d[R^+]}{dt} = \frac{1}{2} k_d \frac{S}{V} \left(\frac{[H^+]}{[H^+]_0} \right)^{\alpha} t^{-\frac{1}{2}} \quad (6a)$$

where α is a constant and $[H^+]_0$ is simply a scale factor to retain comparable values for k_d for different values of α .

A somewhat analogous critique may be offered for Eq. 9 since the matrix dissolution mechanism involves nucleophilic attack of an hydroxyl ion on siloxane bonds in the glass network to effect hydrolysis of the silicate groups. Thus, one might expect the reaction to depend on the hydroxyl ion concentration in solution $[OH^-]$. This is indeed the case; in fact, experimentally determined rates obtained under rapid flow conditions (essentially constant affinity) are highly pH dependent [37], implying that k_t in Eq. 9 is itself a function of pH. Under these conditions Knauss et al. [37] found that the logarithm of the rate was a linear function of the pH in pH-buffered experiments between pH 6-12. This behavior can be incorporated into the present model by replacing Eq. 9 by

The measurements of Knauss et al. on a five-component borosilicate glass suggest a value for

$$\frac{d[Si]}{dt} = k_f \frac{S}{V} \left(\frac{[H^+]_0}{[H^+]} \right)^\beta \left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}} \right) \quad (9a)$$

β close to $\frac{1}{2}$. Ebert [38] also derived a similar rate law with pH dependence for matrix dissolution.

Model Results

Several forms of the model, with combinations of values of α and β between 0 and 1, were investigated. In all cases the value of $[H^+]_0$ was set to 10^{-10} mol l⁻¹ which essentially makes the values of k_a and k_f comparable at different values of α and β at pH 10, which is near the center of the range of interest here. Other constants used in the calculation were $K = 10^{-9.7}$, $K_w = 10^{-14}$ and $[H_4SiO_4]_{sat} = 80$ mg/l = 7.40×10^{-4} mol/l. The general behavior of the calculated results does not depend strongly on the values of α and β that are assumed and we will therefore focus our discussion on the results from the model with $\alpha = \frac{1}{2}$ and $\beta = \frac{1}{2}$. The reasons for selecting these values are as follows. First, as discussed above, there is experimental evidence to suggest that the value of β is close to $\frac{1}{2}$ [37]. Second, it can be shown that, according to this model, γ , the limiting slope at high S/V of a plot of steady-state pH against log(S/V), is given by [39]

$$\gamma = 1/(1 + \alpha);$$

note that the slope is independent of β . In view of the experimental values of γ in Table 2 we set $\alpha = \frac{1}{2}$ for the following discussion, yielding $\gamma = \frac{2}{3}$, in reasonable agreement with the experimental data.

The set of equations was solved numerically using a fifth-order Runge-Kutta algorithm with adaptive stepsize control. Particular care must be taken to ensure that the initial transient from Eq. 6a is captured. Figure 3 shows the calculated effect of k_a when k_f and r are held constant; the steady-state pH values were taken to be those attained after 100 days for comparison with the experimental data. Similarly, Fig. 4 shows the effect of r which seems to

be important only at low S/V ratios. Interestingly, varying k_f between 0.3 and 30 $\text{gm}^{-2}\text{d}^{-1}$ had an effect that would be imperceptible in these figures since although the solution concentrations are affected, the steady-state pH is not. Thus, while k_f determines the initial rate of increase of the concentration of silicon species in solution, the saturation term in Eq. 9a rapidly dominates, essentially regardless of k_f . The residual degree of undersaturation is then pH driven, through the dissociation of silicic acid, as a consequence of the declining but continuous release of alkali according to Eq. 6a. Thus, the model results show that, after a short time (a few days), comparable to that required for the pH to stabilize, $d[\text{Si}]/dt$ approaches $d[\text{R}^+]/dt$ and the two remain essentially equal thereafter; this, of course, implies as a consequence a constant pH.

The independence of the results in Figs. 3 and 4 of k_f indicates that the product $k_d S/V$ provides a simple scaling variable such that plots of steady-state pH against this variable should give a one-parameter family of curves depending only on r . This is indeed the case. Figures 5 through 9 show such scaled plots of the model results together with the experimental data for five glasses using the best-fit values of k_d . The values of k_d determined in this way are shown in Table 3. The values of r for the actual glasses range from about 0.35 to 0.55 but this simple composition parameter is clearly inappropriate for these multicomponent glasses. It is perhaps more useful to think of r as simply a measure of the overall "alkalinity" of the glass. An improved composition parameter derived from consideration of the bond strength with oxygen and the structurole of each cation in glass is discussed elsewhere [40]

A detailed discussion of the time dependence of the solution concentrations and rates that result from this model will be presented elsewhere [39]. Here we show only the calculated behavior of pH with time for the SF10 glass since those experimental data are the most extensive. Figure 10 shows a comparison of the model with those data. The general agreement is quite good but it is important to highlight the discrepancies: the experimental data show a slower rise of pH at low S/V and short times than is calculated and the initial slope of pH against time is more S/V dependent. This effect may be due to the buffering effect of boric acid ($\text{pK} \sim 9.3$) that is important for these glasses but is ignored in this model. A simple method of incorporating this effect might be to use an effective pK that depends on the Si/B ratio in the glass, assuming that both Si and B leach by matrix dissolution. Alternatively, it would be straightforward to extend the model to include additional components and pKs (e.g. pK_2 for silicic acid). However,

geochemical codes handle this type of multicomponent speciation problem admirably and in addition offer the benefit of permitting equilibration with secondary phases.

CONCLUSIONS

The simple model presented here yields results that are in general accord with the salient features of the experimental data. An important conclusion is that the diffusion-ion exchange process is central in determining the solution pH and its dependence on S/V ; this process has been largely neglected in computer simulations based on the models of Grambow [9] and Bourcier et al. [10]. Modifications of the basic reaction affinity equation, Eq. 9, by either adjusting k_r or adding a pH dependence have relatively minor effects compared to similar changes in Eq. 6. The suggestion is that, at least in static or low-flow-rate tests the reaction is "driven" by alkali release. The affinity rapidly approaches zero and, in this simple model, the residual affinity is a result of the declining but continuous release of alkali which causes the pH to rise. Therefore, the ion exchange and alkali diffusion may influence the long-term leach behavior of the glass. This suggestion is consistent with our recent work on the leach behavior of nuclear waste glass WV205 in various salt solutions under low-flow conditions [41]. In this study we observed the ion exchange effects for the entire test period up to 280 days [41]. The most recent work by Grambow et al. [42] on R7T7 nuclear waste glass in brines, Van Iseghem et al. [43] on five Al-rich waste glasses in deionized water, and Lemmens and Van Iseghem [7] on SM527 waste glass in deionized water and in clay water suggest that the long-term glass corrosion rate is diffusion controlled. Van Iseghem et al. [43] further suggest that the long-term rate-controlling process is the ion exchange reactions between H_3O^+ in solution and the Na^+/Li^+ ions in the glass. Under high-flow-rate conditions with pH buffering, reaction affinity effects can be probed, as was shown by Borcier et al. [11].

The fact that glass dissolution is non-stoichiometric when alkali release is compared to release of matrix components is well recognized but rarely incorporated into computer simulations until the most recent efforts by Bourcier et al. [12]. For example, if we use the experimental concentrations for sodium and boron for the SF10 glass, the data suggest an alkali depletion zone thickness of about 500 nm at $S/V = 10 \text{ m}^{-1}$ falling to about 2 nm at $S/V = 40000$

m^{-1} . Thus, at high S/V a very thin depletion zone is sufficient to account for the observed increase in pH.

A further interesting implication of our results is that the parameter that seems primarily responsible for determining the long-term pH and its dependence on S/V, that is k_d , can in principle be measured in very short-term experiments. We emphasize here that the effects of precipitation of secondary phases, which we have neglected in our model, will ultimately dominate solution pH and the reaction progress [44]. However, the nature of the phases formed is often highly pH dependent and it is therefore important to include in any simulation an adequate representation of the pH behavior in the period before secondary phase formation becomes important.

One might expect the value of k_d for each glass to be the result of a combination of factors including the strength of alkali binding in the glass and, therefore, to be dependent on the types of alkali and host matrix sites present, as well the effective diffusion coefficients for H_2O or H_3O^+ and alkali ions. SRL131 exhibits by far the highest value of k_d of the six glasses studied. This glass also shows the most significant deviations from the model in terms of the value of γ . While this deviation can, of course, be corrected by setting $\alpha = 0$ (and therefore $\gamma = 1$) for this glass, it is not clear why α should exhibit such a step-like composition dependence; indeed, the suggestion is that SRL131 reacts by a mechanism that differs from that of the other five glasses in some essential way. This behavior is reminiscent of the highly non-linear effects of glass composition on leachate concentrations that has been reported previously [45].

A final point worth noting here is that this model may provide a possible explanation for leachate concentrations that show a power law dependence on time, e.g. $[\text{Li}^+] \sim t^\theta$, with values of θ below the value of $\frac{1}{2}$ that is characteristic of diffusion [46,47], since θ has a simple dependence on α [39].

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Table 1
Glass Compositions (wt%)

	SRL165	SRL131	SF6	SF10	WVCM59	WVMCM62
Al ₂ O ₃	6.69	3.70	3.30	6.36	6.47	6.45
B ₂ O ₃	6.63	9.90	9.96	9.70	10.29	12.89
BaO			0.60	0.34	0.16	0.16
CaO	1.97	0.80	0.61	0.48	0.68	0.68
CeO ₂	0.10	1.00	0.15	0.00	0.70	0.16
CoO			0.00	0.09	0.02	0.02
Cr ₂ O ₃	0.02		0.22	0.12	0.02	0.02
Cs ₂ O	0.30	0.70	0.10	0.06	0.08	0.08
Fe ₂ O ₃	10.40	13.60	11.80	11.45	12.04	12.02
K ₂ O	0.44		3.50	3.16	3.62	3.18
La ₂ O ₃		0.30	0.00	0.04	0.04	0.04
Li ₂ O	4.94	3.70	3.10	2.75	3.16	2.71
MgO	0.88	1.40	1.30	1.13	0.89	0.89
MnO ₂	1.77	4.50	1.36	0.92	1.01	1.01
Na ₂ O	9.04	12.10	11.00	10.31	11.17	9.82
Nd ₂ O ₃	0.10		0.00	0.13	0.14	0.14
NiO	1.90	2.30	0.70	0.24	0.25	0.25
P ₂ O ₅	0.20		2.50	2.71	2.38	2.37
SO ₃		0.10	0.13	0.00	0.23	0.23
SiO ₂	50.32	43.90	45.22	46.76	40.93	41.16
SrO	0.48	0.90	0.00	0.26	0.02	0.02
ThO ₂			0.00	0.00	3.60	3.56
TiO ₂	0.10	0.70	1.00	0.92	0.77	0.80
UO ₂	3.01		0.00	0.00	0.58	0.59
ZrO ₂	0.82	0.30	3.10	2.11	0.32	0.32
TOTAL	100.11	99.90	100.00	100.00	99.69	99.69

Table 2 Limiting slopes of pH vs. log (S/V) at high S/V from experimental data (standard deviations in parentheses).

Glass	Slope
SRL165	0.70 (0.03)
SF10	0.79 (0.05)
WVCM62	0.73 (0.05)
SRL131	1.02 (0.11)
WVCM59	0.79 (0.04)

Table 3 Values of k_d obtained from the model with $\alpha = 1/2$, $\beta = 1/2$; k_f was fixed at $3 \text{ gm}^{-2}\text{d}^{-1}$ but the results are insensitive to this.

Glass	$k_d, \text{ gm}^{-2}\text{d}^{-1}$
SRL165	0.014
SF10	0.004
WVCM62	0.002
SRL131	0.15
WVCM59	0.028

Figure Captions

- Figure 1 Leachate pH data vs. time showing the effects of S/V.
- Figure 2 "Steady-state" pH values from data in Figure 1 vs. $\log(S/V)$. The bold line has unit slope representing simple dilution behavior.
- Figure 3 Steady-state pH values vs. $\log(S/V)$ as calculated from the model with $\alpha = 1/2$, $\beta = 1/2$, $r = 0.5$, and $k_t = 3 \text{ gm}^{-2}\text{d}^{-1}$. Values of k_d are in units of $\text{gm}^{-2}\text{d}^{-1/2}$.
- Figure 4 As Figure 3 but showing the effect of r at $k_d = 0.016 \text{ gm}^{-2}\text{d}^{-1/2}$.
- Figure 5 Steady-state pH vs. $k_d S/V$ for WVCM62 compared to model results for $r = 0.3, 0.5$, and 0.7 (bottom to top).
- Figure 6 Steady-state pH vs. $k_d S/V$ for WVCM69 compared to model results for $r = 0.3, 0.5$, and 0.7 (bottom to top).
- Figure 7 Steady-state pH vs. $k_d S/V$ for SF10 compared to model results for $r = 0.3, 0.5$, and 0.7 (bottom to top).
- Figure 8 Steady-state pH vs. $k_d S/V$ for SRL165 compared to model results for $r = 0.3, 0.5$, and 0.7 (bottom to top).
- Figure 9 Steady-state pH vs. $k_d S/V$ for SRL131 compared to model results for $r = 0.3, 0.5$, and 0.7 (bottom to top).
- Figure 10 Comparison of measured pH values for SF10 glass with calculated results using $\alpha = \beta = 1/2$, $k_d = 0.004 \text{ gm}^{-2}\text{d}^{-1/2}$, $r = 0.45$, and $k_t = 3 \text{ gm}^{-2}\text{d}^{-1}$.

Fig. 2

Fig. 3

Fig. 4

Fig. 5

* WVCM59, $k_d=0.028 \text{ gm}^{-2} \text{d}^{-1}$

Fig. 6

$\log(k_d S/N, \text{g m}^{-3} \text{d}^{-1})$
 * SF10, $k_d = 0.004 \text{ g m}^{-2} \text{d}^{-1}$

Fig. 7

Fig. 8

$\log(k_d S/V, \text{g m}^{-3} \text{d}^{-1})$
 * SRL131, $k_d = 0.15 \text{ g m}^{-2} \text{d}^{-1}$

Fig. 9