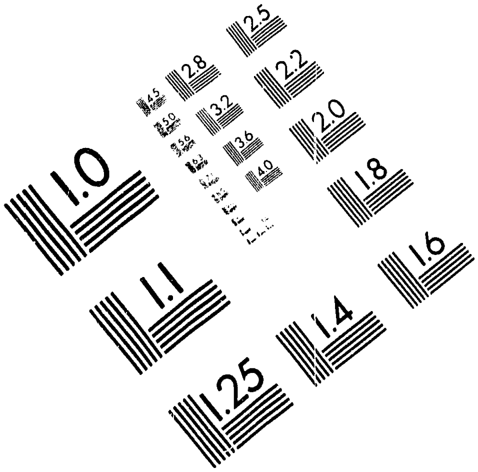

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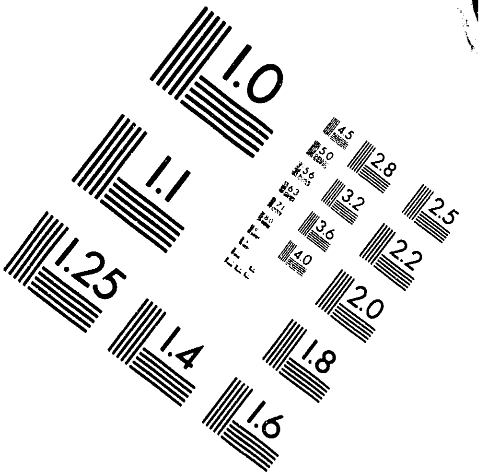

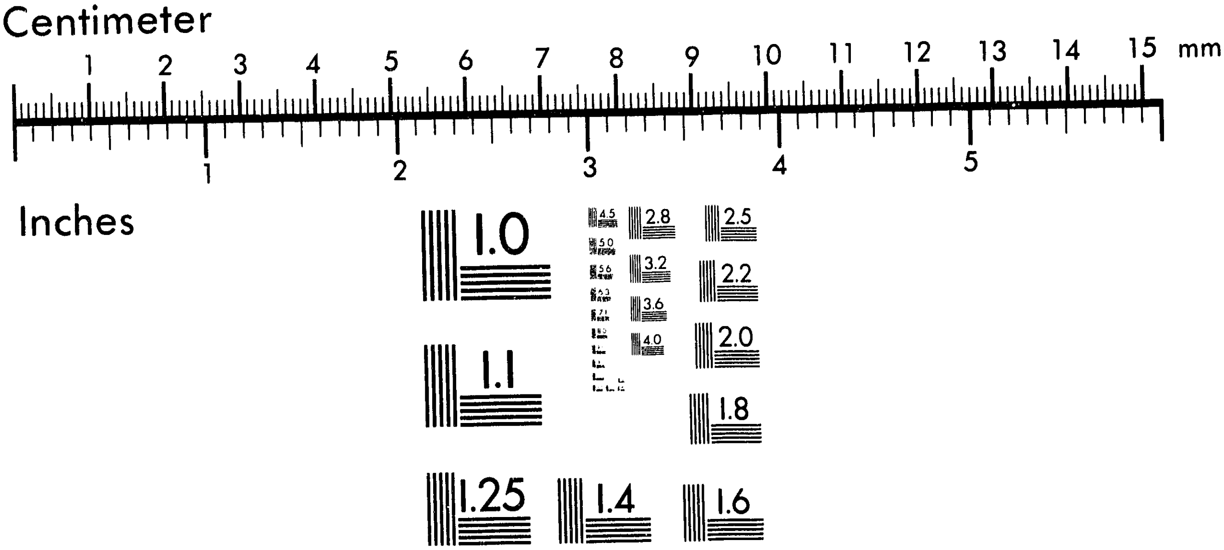

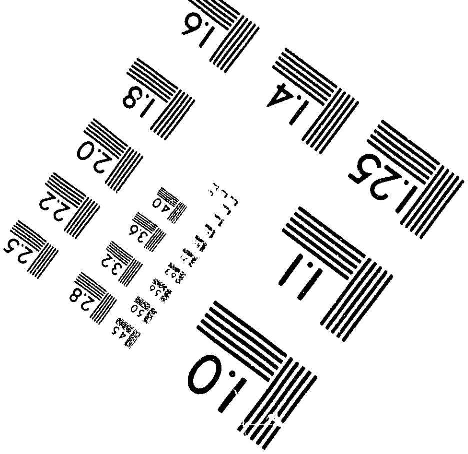

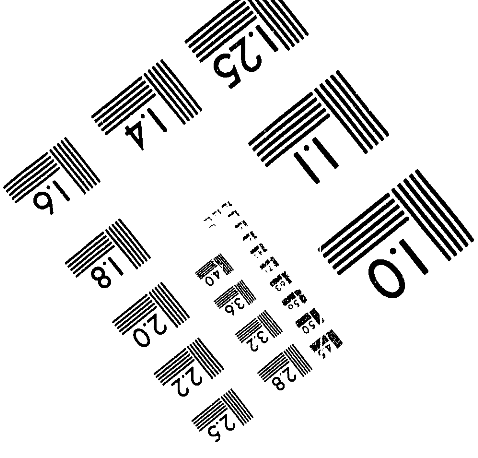

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This paper was prepared for submittal to the
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November 1992

Lawrence Livermore National Laboratory

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MODELING SURFACE AREA TO VOLUME EFFECTS ON BOROSILICATE GLASS DISSOLUTION

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ABSTRACT

We simulated the reaction of SRL-131 glass with equilibrated J-13 water in order to investigate the effects of surface area to volume ratio (SA/V) on glass dissolution. We show that glass-fluid ion exchange causes solution pH to rise to progressively higher values as SA/V increases. Because the ion exchange is rapid relative to the duration of the glass dissolution experiment, the pH effect does not scale with (SA/V)*time. Experiments compared at the same (SA/V)*time value therefore have different pHs, with higher pHs at higher SA/V ratios. Both experimental data and our simulation results show similar trends of increasing reaction rate as a function of SA/V ratio when scaled to (SA/V)*time. Glasses which react in systems of differing SA/V ratio therefore follow different reaction paths and high SA/V ratios cannot be used to generate data which accurately scales to long time periods unless the ion exchange effect is taken into account. We suggest some simple test designs which enable more reliable high SA/V accelerated tests.

INTRODUCTION

The use of high surface area to volume ratios (SA/V) has been proposed as a method to accelerate glass durability tests[1,2,3]. The basis for this is that because the glass dissolution rate is proportional to the amount of surface area, species build up in solution faster in high SA tests and reach conditions that would only be achieved at greater times in lower SA tests. It follows that if elemental concentrations measured in glass dissolution experiments are plotted versus (SA/V)*time rather than time, the data would all plot along a single curve if it is assumed that the glass reaction process is similar at all SA/V ratios. High SA/V tests may therefore speed up the glass dissolution process and advanced reaction stages can be investigated in relatively short time periods.

Some kinetic data for glass dissolution do scale along a single curve when plotted versus (SA/V)*time[4]. However, much of the experimental data do not [5,6,7,8]. The reason for a lack of systematic behavior is unclear. In some cases, data scale well with (SA/V)*time, particularly for tests at low SA/V ratios (less than $1000 m^{-1}$). Tests performed at high SA/V show a trend similar to that in Figure 1, with higher SA/V tests being accelerated relative to low SA/V tests at the same value of (SA/V)*time. Measured pH values are also higher in high SA/V tests than in low SA/V tests at the same value of (SA/V)*time.

(SA/V)*time scaling should also apply under conditions where the dissolution rate is affected by the concentrations of dissolved species. Machiels and Pescatore [9] show that for a rate equation of the form $\frac{dc}{dt} = \frac{SA}{V} k_f \left(1 - \frac{c}{c_o}\right)$, where c is the concentration of a dissolved species, c_o its value at saturation, SA is surface area, V is solution volume, and k_f is the rate constant, solution concentrations should scale according to (SA/V)*time. The key assumption here is that the dissolution rate slows down in a way proportional to the increase in concentrations of dissolved glass species, in particular, silica. Furthermore, even under conditions where secondary phases precipitate, (SA/V)*time scaling should still be applicable provided the same phases nucleate and grow from saturated solutions independent of the rate of approach to saturation (no nucleation and growth kinetics). Machiels and Pescatore [9] use a similar approach to show that diffusion limited glass dissolution will also scale according to (SA/V)*time.

The purpose of this modeling study is to determine those conditions where (SA/V)*time scaling is applicable to glass dissolution tests. We follow previous suggestions [7,8,10] and focus primarily at the effect of ion exchange on the glass dissolution reaction. Note that other non-equilibrium processes such as formation of colloidal species[12], nucleation and growth kinetics of secondary phases, and the formation of alteration layers that act as transport barriers may prevent (SA/V)*time scaling. Also, comparisons of glass dissolution experiments at different SA/V ratios are difficult because simple geometric approximations of surface area must be used for low SA/V tests whereas BET measurements of surface area are commonly used in high SA/V tests. The two methods measure different types of surface areas and cannot be compared directly.

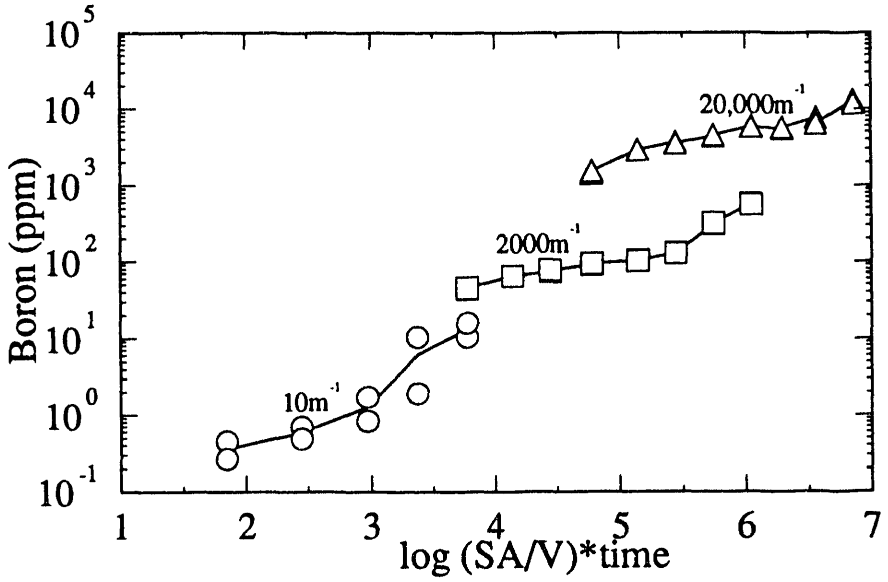

Figure 1. Boron concentrations [11] measured in closed system dissolution tests of SRL-131 glass at 90°C in equilibrated J-13 water for SA/V ratios shown in m^{-1}.

MODELING CALCULATIONS

Our modeling calculations* include provisions for the following processes: kinetically controlled glass dissolution, precipitation of secondary phases as they become saturated (no nucleation or precipitation kinetics), aqueous phase speciation, and ion exchange. The SA/V ratio was varied by changing the glass surface area while maintaining a constant leachate volume. Quartz, tridymite, and talc were suppressed from the modeling calculations because they are known not to form in glass dissolution experiments in the timeframe of our simulations (1000 days) but would be predicted to form in the simulations based on their thermodynamic properties. We used a rate constant of 4.5×10^{-11} g/cm^2/sec extrapolated up temperature from the results of flow-through tests of SRL-131 glass at 70°C at comparable pHs (unpub. data). For the simulations shown here, the rate constant did not change with pH.

Ion exchange was accounted for by including two reactants in the simulations, SRL-131 glass and a second reactant of Na, K, Li, and B oxide with the cations in the same proportions as in SRL-131 glass. Boron is included because it is known to be released at about the same rate as alkalis even though it is not involved in an ion exchange process. Boron hydrolysis affects the solution pH and therefore it must be included in the reactant.

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* Calculations were performed using the React code of the Geochemists Workbench software package[13].

The ion exchanger is set to react nearly to completion in the first two days of the reaction, simulating the early rapid ion exchange process that causes the initial pH rise in solution. The mass of the ion exchanger was fixed to maintain an alkali depleted surface layer of about 0.06 microns (see below). The combination of SRL-131 glass and ion exchanger reactants simulates the observed early non-stoichiometric glass dissolution during which the gel and diffusion alteration layers form, followed by steady-state dissolution where the alteration layers (not including secondary phases) maintain a nearly constant thickness as the glass dissolves. This model does not imply that ion exchange ceases but that the ion exchange zone maintains a constant thickness throughout the reaction period after the first two days.

MODELING RESULTS

We performed simulations for the experimental conditions of Figure 1: SRL-131 glass reacting for 1000 days with equilibrated J-13 water at 90°C [11]. SA/V ratios were the same as for the experiments (10, 2000, and 20,000m^{-1}) with an additional simulation at 1m^{-1}.

We first looked at the effect of ion exchange alone on the leachate pH, ignoring glass dissolution. The simulation consisted of ion exchanging some mass of glass in either distilled water or J-13 water. For a fixed glass surface area, the given mass corresponds to some finite depth of ion exchange in the glass. Figure 2 shows that for distilled water, ion exchange causes pH increases of 3.5 at the highest SA/V ratio of 20,000m^{-1} for an ion exchange depth in the glass surface of only 100 Angstroms. The effect is smaller but still appreciable for simulations in J-13 water because of the much higher pH buffer capacity of dissolved carbonate in the J-13 water versus distilled water. These calculations show that significant changes in leachate pH will occur even with water penetration depths and subsequent ion exchange of the glass to a depth of only a few hundred Angstroms. This process is expected to occur rapidly, within a few hours or days of glass reaction.

The next set of simulations consider glass dissolution at several SA/V ratios without accounting for ion exchange. The purpose of these simulations is to determine whether (SA/V)*time scaling should apply to the case where glass dissolution is kinetically controlled by a rate equation that includes an affinity term, such as the model of Grambow [14]. The model thus provides for dissolution kinetics of the glass and secondary phase precipitation where the phases begin to precipitate upon saturation and remain saturated during the reaction. Simulation results (not shown) show perfect (SA/V)*time scaling as expected. (SA/V)*time scaling may therefore be valid for some glass dissolution tests. In particular, those where ion exchange is not important due either to low alkali contents or low SA/V ratios.

A final set of simulations was performed which included provisions for an ion exchanged layer of approximately 60 nanometers thickness. The thickness chosen is an averaged value based on SIMS profiles through reacted glasses [15,16]. Figure 3 shows the predicted rate of boron release (an indicator of total amount of reacted glass) versus (SA/V)*time for an SRL-131 glass at 90°C in EJ-13 water (see Bates [16] for EJ-13 water composition). Experimental data from Bates [11] is shown for comparison. At low SA/V ratios of 1 and 10m^{-1}, the scaled calculated boron release rates are essentially identical. However, at higher SA/V ratios the scaled data deviate, with boron releases from high SA/V tests being higher than those from lower SA/V tests. Tests performed at different SA/V ratios therefore do not scale according to (SA/V)*time. Adding a simple ion exchange model to the simulations prevents (SA/V)*time scaling.

Figure 3 shows that for high (SA/V)*time values, the predicted glass dissolution rates eventually converge to a single curve. This occurs because for large amounts of glass dissolution, the amount of ion-exchanged glass becomes small relative to the total amount of glass dissolved. The simulations predict that given enough time the pH of the low SA/V test will catch up with the value for the high SA/V test and follow nearly the same reaction path. (Figure 4).

Our model predicts the same trends as the experimental data of Bates [11] but clearly underestimates the release rates at high SA/V ratios (Figure 3). Better agreement will result when we incorporate the pH dependence of the rate constant.

Good agreement between predicted and measured release rates in high SA/V tests depends on our ability to predict the "long-term" glass dissolution rate [14], where the glass approaches saturation and the dissolution rate is much smaller than the initial rate. In our simulations, the long term rate is calculated using the equation

$rate = Ak_f\left(1-\frac{Q}{K}\right)$ where A is surface area, k_f is the rate constant, Q is the activity product of the gel layer, and K the solubility product for the gel layer [17]. The affinity term (1-Q/K) is controlled by the concentrations of dissolved species in equilibrium with the surface gel layer. Solution concentrations are controlled in turn by the

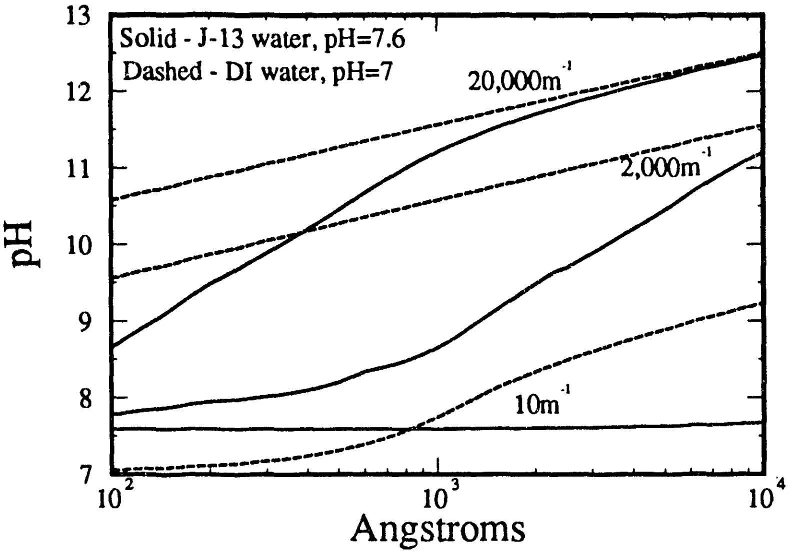

Figure 2. Calculated pH for distilled (DI) and J-13 [11] water which ion exchange with SRL-131 glass to depths given on the x axis. Numbers denote SA/V ratios of the simulations.

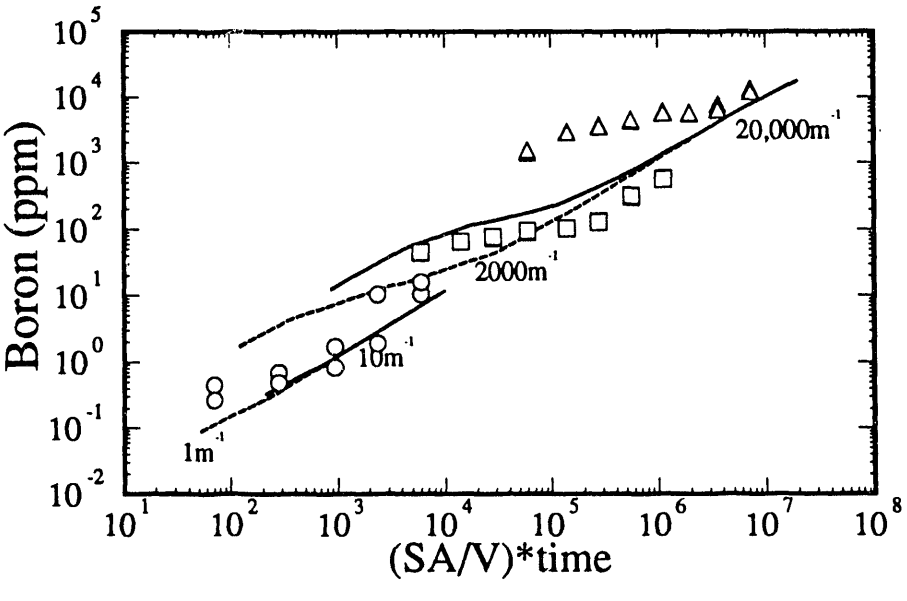

Figure 3. Calculated (lines) and measured (symbols) boron concentrations released from SRL-131 glass (same conditions as Figure 1) vs. log (SA/V)*time. Four lines (alternate dashed and solid) are for SA/V ratios of 1, 10, 2000 and 20,000m-1 bottom to top.

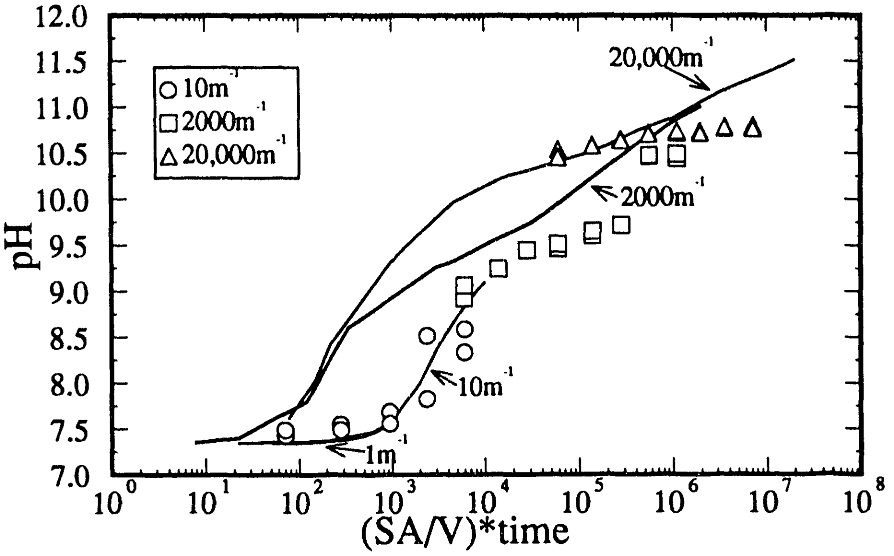

Figure 4. Calculated (lines) and measured (symbols) pH for solutions reacted with SRL-131 glass (same conditions as Figure 1) vs. log (SA/V)*time. Four lines are for SA/V ratios of 1, 10, 2000 and $20,000m^{-1}$ bottom to top. 1 and $10m^{-1}$ lines are almost identical.

secondary phases in equilibrium with the system. The long term glass dissolution rate therefore is determined by the secondary phases that precipitate and control dissolved element concentrations. Accurate predictions of long term rates by our model therefore are dependent on our ability to predict the amounts and types of secondary phases that precipitate. This is one of the reasons for the lack of agreement between model and experimental results in Figure 3.

DISCUSSION

Ion exchange is the primary reason glass dissolution data do not scale when plotted versus (SA/V)*time. When glass first begins to react with water, an ion exchange zone develops on the surface and alkalis and boron are released into solution. Alkali exchange reactions (e.g. $Na_{GLASS} + H^+ = Na^+ + H_{GLASS}$) raise the solution pH. The higher the SA/V of the system, the more the pH is raised. Because this effect takes place in the first few hours or days of reaction, depending on temperature, and is rapid relative to the duration of the test, the effect causes tests having different SA/V ratios to start at different pHs and follow different reaction paths. The different paths are characterized by different sets of secondary phases and therefore different long-term dissolution rates (see above). Such experiments are therefore not expected to scale according to (SA/V)*time. It is also known from flow-through glass tests that glass dissolution rates increase at higher pHs in alkaline solutions [18]. Experimentally observed faster dissolution rates observed at higher SA/V ratios (Figure 1) are probably mainly a consequence of this trend[19].

Figure 5 shows calculated values for the affinity term (1-Q/K) of the SRL-131 glass as a function of reaction progress. The affinity term is actually calculated for the reacted glass surface layer with its thermodynamic properties approximated as a solid solution of hydrous and amorphous endmembers [17]. Note on Figure 5 that the initial value of the affinity term is about 0.7, and not one. This is because the glass is being reacted in equilibrated J-13 water which has significant concentrations of dissolved glass species such as silica and aluminum already present. The glass is therefore partially saturated at the start of the experiment. At low SA/V ratios (1 and $10m^{-1}$), the affinity term gets smaller (the rate slows down) as the glass dissolves and species build up in solution, as expected. Note however that for high SA/V ratios (2000 and 20,000 m^{-1}), the affinity term actually increases at first, in spite of the fact that the solution is becoming more concentrated in dissolved glass species which should act to decrease the affinity term. The reason for this behavior is that ion exchange causes the pH to rise. The glass becomes more soluble with increasing pH, which tends therefore to increase the value of the affinity term. The effect of increasing pH is greater than the effect of increasing the concentrations of dissolved glass species during dissolution. The net effect is that the affinity term *increases* initially as the glass dissolves. The model therefore predicts that the glass dissolution rate should actually increase at first, and then slow down with time. Eventually the pH stops rising and the affinity term decreases as seen in Figure 24.

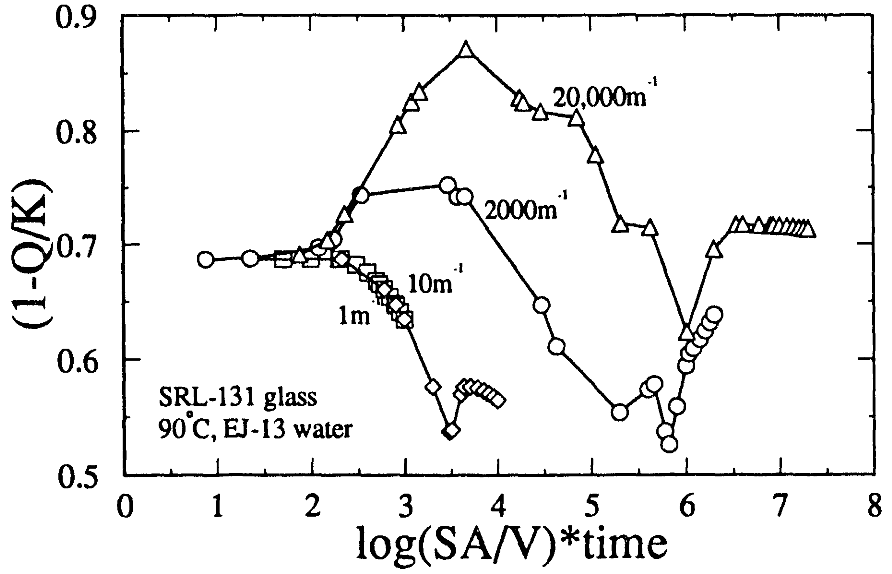

Figure 5. Calculated affinity term (1-Q/K) for SRL-131 as a function of reaction time for SA/V ratios shown.

The effects of glass dissolution on solution chemistry can be explained in terms of masses of reservoirs of two reactants, the ion exchanger (diffusion layer in the altered glass) and bulk glass. The dominant solution effect of the ion exchanger is to raise the pH through ion exchange. The effect of the unaltered glass is complex, but is a result the relative amounts of bulk glass dissolution, which raises pH, and the precipitation of secondary phases, which lowers pH. The net effect of bulk glass dissolution is commonly little change in pH, as evidenced by the nearly flat pH vs. time curves for most glass dissolution experiments at long times. Initially, the amount of ion exchanged glass is large relative to the total amount of glass dissolved. After the glass alteration layers develop and reach an approximately constant thickness (excluding secondary phases), the relative importance of the ion exchanged mass decreases as more glass dissolution takes place. After long time periods the solution chemistry is dominated by bulk glass dissolution and the precipitation of secondary phases. This is why the curves in Figure 22 converge at high values of (SA/V)*time.

Other factors contribute to whether (SA/V)*time scaling is achieved. The amount of exchangeable alkali is important. High alkali glasses that undergo relatively large amounts of exchange will tend to not scale, and the SA/V limit above which they deviate from (SA/V)*time scaling will be low. Durable alkali-poor glasses should scale to relatively higher SA/V ratios [7]. As mentioned above, time dependent processes such as nucleation and growth kinetics, and colloid formation may also invalidate (SA/V)*time scaling. We have also ignored changes in effective surface area that may arise due to precipitation of secondary phases.

CONCLUSIONS

We have used modeling to investigate the effect of variable SA/V ratios on glass dissolution behavior. The model provides for kinetic control of glass dissolution rate, precipitation of secondary phases, and ion exchange. Our results show that (SA/V)*time scaling may apply to experiments having low SA/V ratios. At higher SA/V ratios, rapid early ion exchange causes the solution pH to rise. The pH values do not scale according to (SA/V)*time. Higher SA/V tests reach higher pHs at the same value of (SA/V)*time and therefore follow different reaction paths. At the same value of (SA/V)*time, glasses in high SA/V tests react faster than those in low SA/V tests mainly because the glass dissolution rate is known to increase with pH under alkaline conditions [18]. The cutoff in SA/V ratio above which the test results are not expected to scale will vary with glass composition and durability. Glasses with a high alkali content will reach relatively higher pHs than glasses with low alkali contents, and thus will deviate from good scaling behavior at lower SA/V ratios. Most waste glasses may begin to scale poorly at SA/V ratios above 100 to 1000m^{-1}. High SA/V tests can therefore not be used to accelerate glass dissolution reactions unless the non-scaling pH effect is accounted for. Two possible ways to further investigate the SA/V effect include: (1) external control of solution pH during the test using a flow-through reactor or pH-stat; and (2) performing tests on pre-reacted glasses which have already formed steady state surface alteration layers

ACKNOWLEDGEMENTS

Work supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under contract W-31-109-ENG-38 through Argonne National Laboratory and under the auspices of the U.S.DOE by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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