Towards a consistent rate law: glass corrosion kinetics near saturation

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Abstract: Although glass corrosion resistance has been tested with laboratory methods for decades, investigators are now just beginning to understand the reaction phenomena at or close to saturation with respect to the rate-limiting phase(s). Near saturation, the phenomena that govern element release rates include alkali–hydrogen (species) exchange, differential reactivity of phase-separated glass, and accelerated corrosion rates due to precipitation of key secondary phases. These phenomena were not anticipated by early models of glass dissolution and are incompletely quantified in current rate representations. This review discusses the two over-arching models for glass reactivity, diffusion and surface reaction control, and demonstrates the importance of glass reactivity in terms of glass composition and micro-heterogeneity of the glass. Our conclusion is that surface reaction control best describes the release of elements to solution, but that models based on current interpretations of transition state theory (TST) must be modified to account for reported anomalies in behaviour near saturation.

Glass has been studied for millennia, and our forbearers used the existing technology and science to create vitreous objects with desirable colour, durability, patterning, and quality. At the dawn of recorded human history the 'technology' of the times typically included religious rituals so that the glass objects could be fashioned with the approval of the gods. For example, we have this glass-making 'recipe' from a clay tablet found in the Assyrian Temple of Nabu from the seventh century BCE:

'When thou settest out the ground-plan of a furnace for 'minerals' thou shalt seek out a favorable day in a fortunate month, and thou shalt set out the ground-plan of the furnace ... The wood which thou shalt burn underneath the furnace shall be styrax, thick, decorticated billets which have not lain exposed in bundles but have been kept in leather coverings, cut in the month of Ab ... Thou shalt mix them [components of the frit] together and put them down in the furnace ... then thou shalt keep a good smokeless fire burning until it liquefies: then thou shalt pour it on burnt brick.' (Horton 1929)

Modern techniques to fashion glass do not call upon fortune or the favour of gods, but upon the insights of glass structure garnered from modern science. Production of homogeneous unflawed glass resulted in the invention of the microscope and telescope, which presaged revolutionary discoveries on vastly different scales, from the immense (astronomy) to the minute (biology).

In more modern times, use of manufactured glass has expanded to a variety of demanding environments and the chemical durability of glass has become another highly prized quality. Commonplace glass objects, such as windows, laboratory equipment, vessels for preserving materials are subject to corrosion, reaction, or decay, optical and electrical components, and insulation may be subject to chemically harsh settings. Therefore, the corrosion resistance of a glass item is an important consideration in its manufacture. More relevant to this review, recognition of glass as a candidate waste form for disposal of hazardous and radioactive waste has sparked a vigorous research effort to understand the chemical durability of glass, yet there are still many divisions among investigators over the interpretation of experiments aimed at quantifying corrosion resistance. These controversies have fostered a large number of reviews of glass dissolution kinetics, and, almost by ritual, every two to three years a new review is offered. Among the many excellent reviews are those of Bourcier (1991, 1994), Casey & Bunker (1990), Vernaz & Dussossoy (1992), Barkatt *et al.* (1986), Hench *et al.* (1986), Bunker *et al.* (1988), Werme *et al.* (1990), and Vernaz *et al.*

(2001). This burgeoning set of reviews serves as a starting point for our discussion of glass corrosion resistance, although our review differs from those noted above by emphasizing dissolution behaviour near saturation with respect to potential rate-limiting phases.

The reasons for this shift are multifarious and include the observation that rates acquired from field studies (typically on natural vitreous materials, such as obsidian) (Yokoyama & Banfield 2002) do not accord with those obtained from laboratory experiments. In general this observation parallels results on tests of periodic solids (i.e., minerals); rates derived from the field on common rock forming minerals are up to a factor of $1000\times$ slower compared to laboratory rates (Velbel 1993). There has been much discussion of this topic in the literature (e.g., Sverdrup & Warfvinge 1995) and the difference is ascribed to differences in surface area, temperature, saturation state, and manner of aqueous solution contact (partial versus full) and the presence of corrosion resistant coatings of other minerals (such as aluminum or iron oxyhydroxides) on the solid of interest (Hochella & Banfield 1995; White 1995). Although no single factor can be presented as the reason for such a large discrepancy, the influence of solution saturation state is a clear target for consideration. The second reason for studying reaction rates near saturation is that it goes to the heart of the debate surrounding reaction mechanisms. For example, it can easily be shown that dissolution kinetics of glass and minerals near saturation do not conform to expectations founded upon current interpretations of transition state theory (TST), as elucidated more fully below. The third reason for studying reaction rates near solution saturation is that the relative importance of reaction mechanisms changes near saturation. Because the pore fluids in many of the waste disposal settings under consideration are at a near-saturated state (Murphy & Palaban 1994; Bacon *et al.* 2000), understanding the corrosion durability of glass under these conditions takes on a high importance for predicting long-term release of radionuclides or other elements to the environment.

In this review we will outline the major themes in glass dissolution kinetics and point out the papers that best describe these models. In pursuit of these themes, the reader will note that we accept or reject certain fundamental ideas embedded in the two principal models presented below. This should hardly come as a surprise, given the wide division in the two chief models and the disparate outcomes predicted from each. However, in pointing out our underlying bias, it is our aim to educate the reader and allow him or her to arrive at his/her own conclusions based on the facts presented. If this admitted bias disturbs some, it should be pointed out that this quote from Jacques Barzun is most appropriate: 'It does not follow that bias cannot be guarded against, that all biases distort equally, or that controlled bias remains as bad as propaganda' (Barzun 2000). Barzun concludes that the essence of objectivity lies not in the eradication of opinion, but in the open display of conflicting ideas: 'One has then the duty to report the informed judgment of others' (Barzun 2000). It is this body of 'informed judgement' that is presented below.

Specifically, the major topics covered by this review are: (1) a brief discussion of models of element release rates based on diffusion and on TST, and (2) glass–water reactions that dominate near equilibrium. We will discuss these themes with the assumption of some general understanding of chemical kinetics, but the concepts should be comprehensible to readers from outside this field as well.

The two over-arching models for glass/water reactivity

Diffusion through a reaction layer

Early glass/water experiments demonstrated the relatively quick release of alkali ions to solution at the beginning of the test. Another observation noted in these early days was the presence of a macroscopically visible alteration layer forming on the surface of the reacting glass. More modern instruments, such as Rutherford back-scattering spectroscopy (RBS) (Bunker *et al.* 1983; Baer *et al.* 1984; Pederson *et al.* 1986), nuclear reaction analysis (NRA) (Lanford *et al.* 1979; Dran *et al.* 1988; Pederson *et al.* 1990), X-ray photoelectron spectroscopy (XPS) (McGrail *et al.* 2001*a*), and nuclear magnetic resonance (NMR) (Bunker *et al.* 1988; Tsomaia *et al.* 2003), by themselves or in combination, have been used to characterize and quantify the chemical composition of such reaction layers. However, these sophisticated techniques, instead of clarifying the role of reaction layers, have revealed a complex chemistry, both temporally and spatially (laterally and in terms of depth). Because of these complications, attempts to quantify the role of reaction layers in the reactivity of glass are hampered.

Models for the development of reaction layers have centered on ion exchange between hydrogen species (OH^-, H_3O^+, H^+) or water (H_2O)

and cations in the glass (e.g., Li^+, Na^+, K^+). Doremus (1977a, b, 1981, 1983, 2000) pioneered the model that diffusion of H_2O into glass is the *primary* rate-limiting mechanism, at least during the initial stages of dissolution. More complex models were later developed in which diffusion-control through a 'transport' or 'passivating' layer was identified as the chief mechanism for release of dissolved species to solution (Leturcq *et al.* 1999; Jégou *et al.* 2000; Gin & Mestre 2001; Advocat *et al.* 2001; Gin *et al.* 2001a, b; Linard *et al.* 2001; Vernaz *et al.* 2001). This emphasis gained considerable currency in some circles, especially when the observation that TST-based models (see below) may not be adequate for solutions near saturation with respect to the rate-limiting solid.

Note, however, that even proponents of this idea disagree on the long-term effects of diffusion control on element release rates through a passivating surface layer. While a more traditional model holds that element release decreases as the square root of time, new long-term experiments (up to five years) have exhibited evidence for a constant rate of release (Gin & Frugier 2003). All of this underscores the dilemma faced by stewards of waste repositories; one diffusion model indicates a low, but constant release of elements with time, the other a low and decreasing rate. Comparing the two models reveals that the gap between predicted element releases becomes significantly large over time (Gin & Frugier 2003).

Another important consequence of the constant rate of release diffusion model is that it mimics many of the features that have commonly been attributed to surface reaction (matrix dissolution) control. If one were to account for changes in surface area over time, the predicted long-term dissolution rate due to surface reaction control would also yield constant element release. In surface reaction controlled models, the invariant release rate with respect to time is considered to be the natural consequence of the system achieving steady-state conditions. Other features of experiments commonly cited as evidence for surface reaction control, such as relatively high experimental activation energies (60–70 kJ/mol), could be explained as easily by the diffusion-control model. These findings show how similar the observations are between proponents of the two models: it is only the *interpretation* of the mechanism that differs.
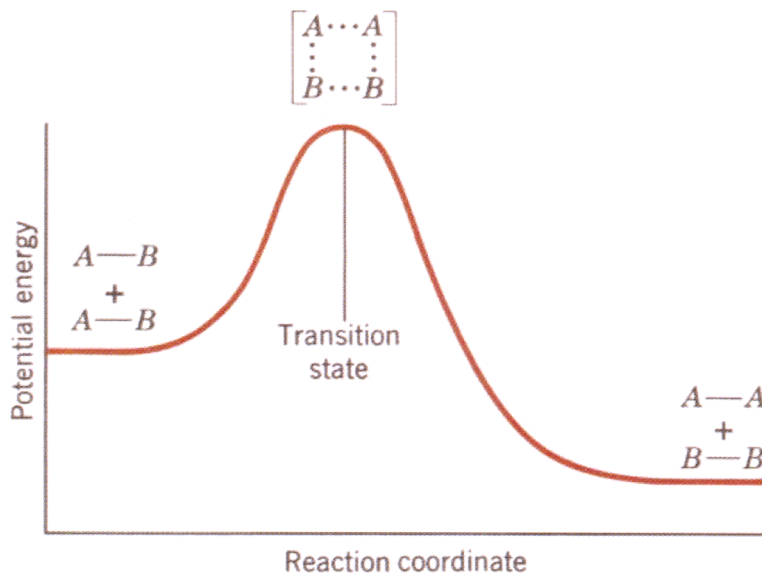
Transition state theory

Eyring (1935a, b) developed 'Transition State Theory', or 'Absolute Rate Theory', in the 1930s.

He was motivated by the theoretical constructs of collision theory (CT), in which 'correction factors' of up to 10^{-8} had to be applied to force theory to comply with experiment (Eyring 1935b). The reason why CT failed to accurately predict reaction rates is that one would have to estimate the number of collisions between reacting molecules based on observed momentum transfers. The estimated cross-section area of the reacting molecules is likely to be incorrect since momentum transfer can occur without products forming due to a lack of proper orientation or relative velocities of the reactant molecules. However, TST-based models have been able to avoid this problem by considering only the momentum of the so-called 'activated complex' on the potential energy surface in the region near the transition to products. By activated complex, we mean an aggregate of atoms at a higher potential energy than reactants or products that have a statistically defined probability of decaying back to reactants or proceeding to products. Figure 1 illustrates the relationship between reactants, products, and the activated complex along the reaction coordinate. Therefore, statistical mechanical constructs can be devised to calculate the activities of activated complexes and their velocity over the activation energy barrier.

Investigations in succeeding years demonstrated that TST was able to correctly square theory with experiment for gas phase reactions by allowing investigators to map out the potential energy surface of simple molecular reactions (Golden 1979; Karplus *et al.* 1965). In contrast, application to solid/aqueous solution systems has not been universally accepted. Aagaard & Helgeson (1982) developed the most comprehensive and detailed treatment of TST for such systems. The current application of TST to reactions describing the dissolution of a solid into aqueous solution can be written:

$$r_+ = \vec{k}_o a_{H^+}^{-\eta_{H^+}} \exp\left(\frac{-E_a}{RT}\right) \times \left(1 - \frac{Q}{K}\right)^\sigma \prod_{i=j}^{j} a_j \tag{1}$$

where r_+ is the dissolution rate, $\vec{k}_o$ is the reaction constant, E_a is the activation energy, RT is the product of the gas constant and absolute temperature, Q is the ion activity product, K is the equilibrium constant of the rate-determining solid, and σ is the ratio of the order of the elementary reaction to that of the overall reaction and is generally considered to be unity for theoretical reasons. The last term, $\prod_{i=j}^{i} a_j$, is the

Fig. 1. Illustration of the relationship between reactants (designated as $2 \cdot A - B$), products ($A - A$ and $B - B$), and the activated complex. According to transition state theory, reaction kinetics is limited by the irreversible decay of the activated complex minus the rate at which the activated complex reversibly breaks down to reactants.

activity product of all rate catalyzing or inhibiting species, aside from H^+.

For the purposes of this review, the key concept embedded in equation (1) is the chemical affinity term, which is expressed as $1 - Q/K$. The chemical affinity of a system is related to the free energy of the reaction and is a measure of the degree of departure from equilibrium (i.e., $f(\Delta G) = 1 - Q/K$). The form of the chemical affinity term indicates that as the concentrations of dissolved elements build up in solution, the system approaches saturation in a rate-limiting solid and the overall dissolution reaction slows down, and, at equilibrium, the rate would be zero. In the case of glass dissolution, there are many circumstances, which are reviewed below, where the rate behaviour does not comply with these expectations.

Some of these difficulties can be traced to unproven, and perhaps incorrect, assumptions implicit within the Aagaard & Helgeson (1982) model. For example, reaction rates at the glass/water interface are modelled as sequential. As we discuss below, there is good reason to consider reactions as taking place concurrently. In a system that is close to equilibrium, the identity of the dominant dissolution mechanism among a set of concurrent elementary reactions may change as conditions shift. Another potential pitfall is the assumption that the 'principle of

detailed balancing' applies to glass/water reactions. In the principle of detailed balancing, the equilibrium constant, K, is equal to the ratio of the forward to reverse rate (i.e., k_+/k_-). While this may be true for systems that come to equilibrium, it is clearly untrue for glass/water reactions because equilibrium between glass and water is never realized (e.g., Bourcier 1994). Further, it is also untrue for a large set of minerals that formed under high temperature and pressure conditions: these phases cannot be in equilibrium with solution at near surface conditions. In summary, these assumptions, although unverified at the time, represented a good starting point to evaluate dissolution kinetics, but may require amendment based on the data presented in the next section.

Reactions near equilibrium

There are a number of mechanisms that pose potential problems to predicting dissolution rate kinetics as the system approaches saturation. Part of this conundrum originates from current models of glass corrosion kinetics that cannot yet incorporate these unanticipated phenomena into a mathematical equation that is consistent with the constraints of thermodynamics or kinetics. These phenomena include: (1) alkali–hydrogen exchange; (2) dissimilar reactivity of

phase-separated glass; and (3) acceleration or deceleration of rates as secondary corrosion products precipitate.

Alkali–hydrogen exchange kinetics

Models of glass corrosion that include alkali–hydrogen exchange are some of the earliest and most long-lived in the literature, beginning with papers by Rana & Douglas (1961a, b) and Douglas & El-Shamy (1967). These papers noted that at the start of the experiment, release of alkalis to solution occurred to a greater extent than could be explained by stoichiometric dissolution alone. Further measurements demonstrated that, for experiments in which excess alkalis are released to solution, the contacting solution pH increased, resulting in a more rapid dissolution of glass. The explanation given for these observations is ion exchange (IEX) between Na^+ in glass and hydrogen species in solution. Accordingly, for every mole of Na^+ released to solution by IEX reactions, one mole of H^+ or H_3O^+ must be incorporated into glass. Therefore, IEX reactions are driven by chemical potential differences between glass and solution:

$$\mu^i_{glass} > \mu^i_{solution} \qquad (2)$$

where μ^i_{glass} and $\mu^i_{solution}$ are the chemical potentials of an element, i, in glass and aqueous solution, respectively. One expectation from this chemical potential inequality is that as the concentration of alkali elements increases in solution, the chemical potential difference will diminish, resulting in slower alkali release rates.

A number of experiments, however, demonstrated that alkali release rates do not decrease, even in solutions with high ionic strength. For example, Pederson et al. (1993) reported that IEX rates in experiments with aluminosilicate glasses were not dependent upon the concentration of Na up to 6.11 molal. Even simple alkali silicate glasses demonstrated no decrease in IEX rates, provided that the solution was kept at the isoelectric point of the glass (pH 2.3). Apparently, the chemical potential difference of Na^+ in glass and solution is insensitive to ionic strength, even in the case of highly concentrated brines. However, this was not the only surprising observation that was revealed in more recent sets of experiments.

Sodium-rich glass compositions tested in single-pass flow-through (SPFT) apparatus at Pacific Northwest National Laboratory support the low-activity waste (LAW) glass disposal programme. The LAW glass compositions are non-radioactive analogues of waste that is currently being held in large underground single- and double-shell tanks. The glass chemistries are characterized by a high molar ratio of Na to the sum of trivalent cations (such as Al, B, and Fe), but release of Na and B are at the same rate in dilute solutions. However, as the concentration of dissolved silica in solution increases, either by addition of Si to the input solution or by slowing the flow rate, release of Na^+ is anomalously fast with respect to B (McGrail et al. 2001a, b). Figure 2 illustrates this behaviour; congruent dissolution is indicated in dilute solutions, but as the activity of silicic acid [H_4SiO_4(aq)] increases, a difference in rate between B and Na release begins to surface. Both the B and Na rates decrease, but the decrease in Na release rate is not strong and becomes constant towards amorphous silica saturation. Boron release rates are more strongly affected, with a sharp decrease in rate appearing even as small quantities of silicic acid are added to solution. Surprisingly, as in the case of Na, boron release rates also become independent of silicic acid activity. At conditions of amorphous silica saturation, Na release rates are up to a factor of $50\times$ faster than that of B (McGrail et al. 2001b), depending on glass composition, temperature, and pH conditions.

Clearly, the rate of release of Na^+ is not due solely to stoichiometric dissolution of the glass; rather, Na^+ release is a consequence of two reactions occurring in parallel: (1) matrix dissolution (i.e., the breakup of the polymerized glass structure, as evidenced by B release), and (2) alkali–hydrogen exchange reactions. In dilute solutions matrix dissolution is the dominant reaction such that the slower IEX reaction cannot be detected. However, as matrix dissolution slows as a consequence of higher concentrations of dissolved silica, the IEX reaction becomes dominant and the apparent rate of Na^+ release increases over that of B. The rate of the IEX reaction can be computed by subtracting out the matrix rate from the apparent Na rate (e.g., McGrail et al. 2001b, 2002). These results underscore the importance of conducting tests over a range of solution saturation states.

Although the operation of parallel reactions explains why B and Na rates are different, there is no immediate explanation for why B rates become independent of solution saturation state as Si builds up in solution. Models of glass dissolution fashioned from TST arguments do not anticipate these results. According to TST-based models, the glass dissolution rate should depend solely on the solution saturation state
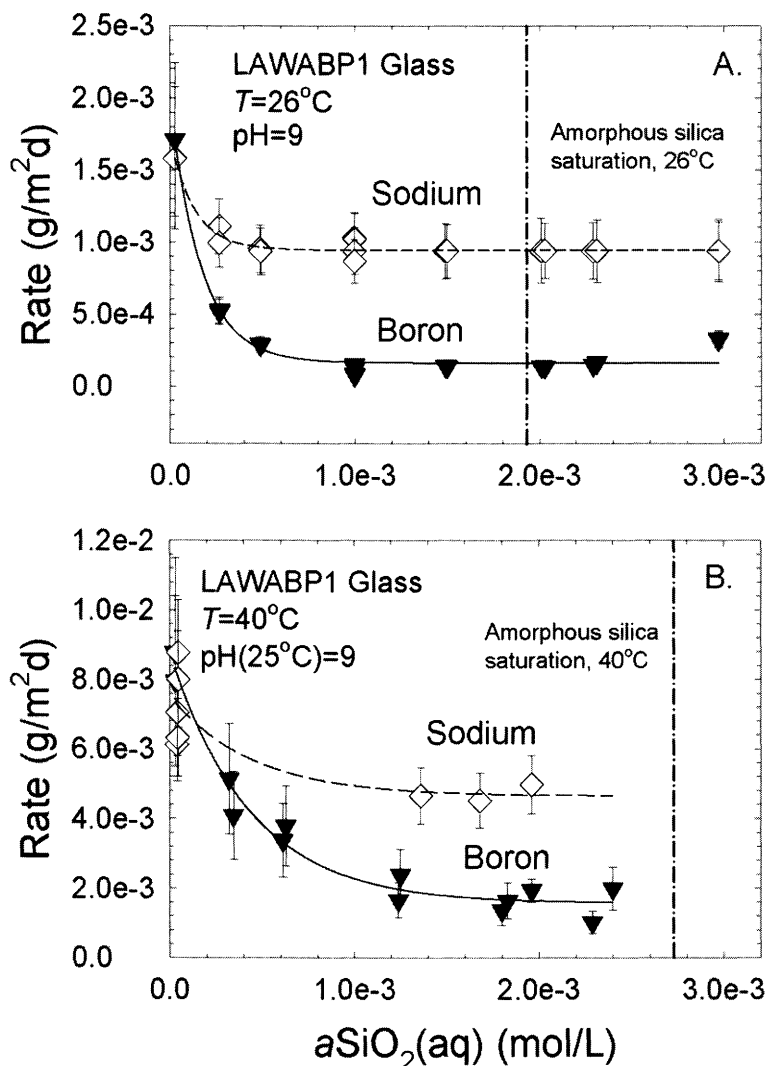
Fig. 2. Plot of normalized rate vs. the activity of silicic acid for the LAWABP1 (see Table 1) glass composition at two temperatures (26 and 40 °C). Rates are all computed at steady-state conditions. Boron and Na release rates are identical at low silica activities, then decrease, and become constant at or near saturation with respect to amorphous silica (vertical dot-dashed line). Note that the B rate decreases more than the Na rate. This behaviour can be rationalized as competition between two concurrent reactions: alkali–hydrogen exchange and matrix dissolution (see text). Error bars represent 2-σ experimental uncertainties.

(Aagaard & Helgeson 1982), provided that solution pH and temperature remain constant. However, the solution saturation state is difficult to define because glass cannot be in equilibrium with aqueous solution. Accordingly, the identity of the rate-limiting solid for glass is controversial, but for the moment, we will consider the simplest of the potential candidates.

Grambow, who perhaps wrote the most commonly referenced paper in the glass corrosion literature (Grambow 1985), proposed that a state of 'micro-equilibrium' exists (between Si–O–Si polymers and solution) and can be written as follows:

$$2\,H_2O + SiO_2(am) \Leftrightarrow H_4SiO_4(aq) \qquad (3)$$
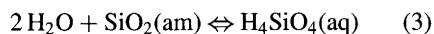
Grambow (1985) based this proposal on the tenet of TST that says that with any set of reactions releasing element i to solution, the slowest

reaction rate will be rate limiting. He noted that the Si–O bond is the least likely to break out of all the bonds present in glass, and that a layer relatively enriched in Si forms on the surface of the glass. The redistribution of Si on the surface, including condensation (re-polymerization) reactions, is an expression of the importance of Si–O bonding during glass reactions and has been the subject of numerous papers (e.g., Baer *et al.* 1984; Pederson *et al.* 1986, 1990). Direct measurement of silica-like surface species was carried out on sodium borosilicate glass by Bunker *et al.* (1988).

The constant rate of reaction at high activities of silicic acid can be explained by IEX reactions. Exchange reactions between a monovalent alkali cation M^+ (e.g., Na^+) and H^+ species can be written in the following manner:
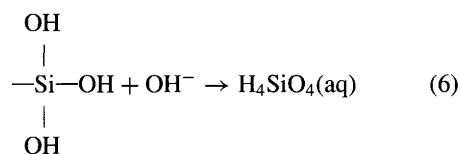
$$\equiv Si-O-M + H^+ \rightarrow \equiv Si-OH + M^+ \quad (4)$$

or

$$\equiv Si-OM + H_3O^+$$
$$\rightarrow \equiv Si-OH + M^+ + H_2O \quad (5)$$
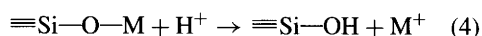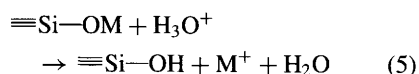
where $\equiv Si$ symbolizes a Si atom bound to the glass structure by three bonds. Note that either

equation (4) or (5) produces a silanol group and increases the *local* pH, thus catalysing the irreversible hydrolysis reaction:

$$\begin{array}{c} OH \\ | \\ -Si-OH + OH^- \rightarrow H_4SiO_4(aq) \quad (6) \\ | \\ OH \end{array}$$

The reaction in equation (6) is irreversible since glass cannot precipitate from solution. Equations (4) or (5) affect the overall rate at which equation (6) proceeds because they impact the rate at which Si–OH groups are produced. However, three silanol groups must be formed before the last anchoring bond is broken, releasing a silicic acid (H_4SiO_4) molecule into solution.

The above reactions occur only when Na^+ is vulnerable to release via IEX reactions. Therefore, the *structure* of the glass (molecular arrangement of glass species) clearly impacts the overall hydrolysis rate. In order to visualize the impact of glass structure on IEX rates, consider Fig. 3. This figure is a plot of the normalized Na IEX rate, in which the contribution of Na from matrix dissolution, Na_{matrix}, is subtracted out (i.e., $Na_{matrix} - Na_{IEX}$), versus the amount of 'excess'
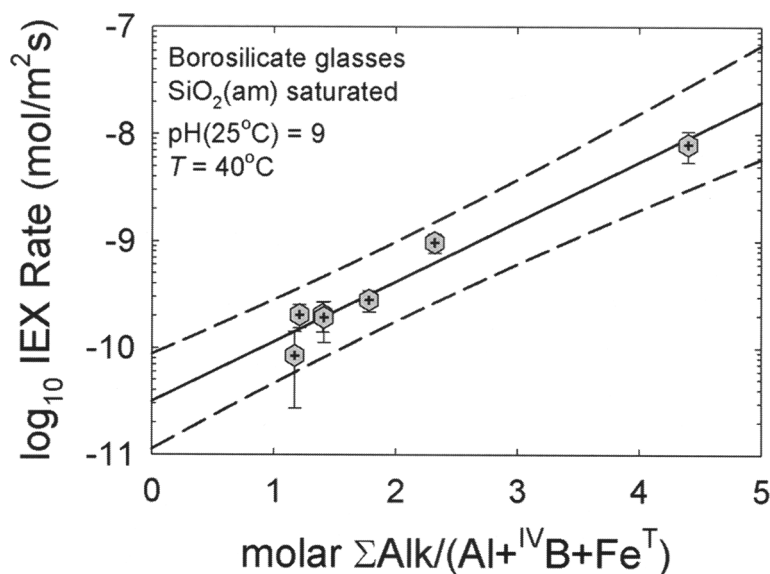
Fig. 3. Plot of $\log_{10}$ normalized ion-exchange rate at amorphous silica saturation vs. the amount of 'excess' alkalis (Na, K), denoted by the molar ratio $\Sigma Alk/(Al + {}^{IV}B + Fe^T)$. All boron is treated as four-fold coordinated (${}^{IV}B$) and total iron (Fe^T) is regarded as ferric. The ion-exchange rate subtracts out the contribution of alkalis to solution from matrix dissolution. As the amount of 'excess' alkali increases, the ion-exchange rate increases. This increase in rate reflects the increasing amount of alkalis in non-bridging oxygen (NBO) configurations. Error bars represent 2-σ experimental uncertainties and the dashed lines signify the prediction interval.

Na in glass, as indexed by the molar ratio $Na^+/(Al + B + Fe)$. This ratio assumes that: (1) all B is in four-fold coordination, and (2) that all Fe is trivalent. The first assumption is undoubtedly false, yet the correlation between ratio and the IEX rate in Fig. 3 is very good. What the molar ratio really expresses is that Na ions, in excess of what can be charge-compensated for by the sum of trivalent Al, B, and Fe, must be relegated to non-bridging oxygen (NBO) positions (sometimes referred to as 'sites'). In other words, not all Na^+ is incorporated into the matrix structure, but is in a different bonding environment: one that is energetically more susceptible to IEX reactions (Pederson *et al.* 1986, 1990; McGrail *et al.* 2001*a*). This observation is especially important for Na-rich glass compositions, such as those contemplated for disposal of Hanford, USA, tank waste (Table 1), and high-level waste from Japan. The highly sodic glass compositions typical of the bulk of US wastes may be one reason why US and European scientists differ in their interpretations of glass corrosion mechanisms.

Finally, our observations regarding the long-term impact of alkali ion exchange on glass dissolution now provide a mechanistic basis for the empirical 'residual' rate of reaction appended to the TST rate law articulated by Grambow (1985). The 'residual' rate was appended to prevent calculated glass dissolution rates from dropping to zero under silica-saturated conditions, which is not in accord with experimental observations.

As we have demonstrated, IEX reactions occur independent of the saturation state of the aqueous solution, raise the local solution pH, and so cause additional glass dissolution via reaction (6). The 'residual' rate for alkali-rich glass compositions, therefore, is simply the net rate of glass dissolution controlled by the rate at which the ion-exchange reaction proceeds.

Dissolution of phase-separated glass

By virtue of its ability to act as a fluxing agent, even in small concentrations, boron is included in most waste glass compositions worldwide. However, this positive property is somewhat lessened by the propensity of B to exist in two different forms in melt and glass. Four-fold coordinated B (^{IV}B), manifested as BO_4 units, is the desired moiety since these molecules co-polymerize with the Si–O–Al framework. Investigations using different techniques indicate that three-fold coordinated B (BO_3 or ^{III}B) can also exist in borosilicate glasses (Bray 1978; Mozzi & Warren 1970; Konijnendijk & Stevels 1975, 1976). The BO_3 units can readily be identified by spectroscopic techniques as predominantly three-membered boroxyl rings (B_3O_6), and it is easy to understand how such a configuration would have difficulty fitting into the relatively rigid SiO_4^{4-}- or AlO_4^{5-}-based framework. As a result of this maladaptation, phase separation, resulting in BO_3- and BO_4-rich domains, occurs in many borate and

Table 1. *Target chemical compositions of typical glasses tested at Pacific Northwest National Laboratory*

	LAWA33 (wt%)	LAWABP1 (wt%)	LAWA44 (wt%)	LD6-5412 (wt%)	HLP-9 (wt%)	MAGNOX (wt%)	HLP-31 (wt%)	Na–B–Si (wt%)
Al_2O_3	11.97	10.00	6.20	12.00	6.84	7.72	4.00	n.a.[†]
B_2O_3	8.85	9.25	8.90	5.00	12.00	27.87	12.00	20.23
CaO	n.a.	n.a.	1.99	4.00	0.01	0.01	n.a.	n.a.
Cl	0.58	0.58	0.65	n.a.	0.27	n.a.	0.32	n.a.
Cr_2O_3	0.02	0.02	0.02	n.a.	0.07	0.92	0.09	n.a.
F	0.04	0.04	0.01	n.a.	0.01	n.a.	0.01	n.a.
Fe_2O_3	5.77	2.50	6.98	n.a.	5.38	3.36	3.36	n.a.
K_2O	3.10	2.20	0.50	1.46	0.40	0.02	0.47	n.a.
La_2O_3	n.a.	2.00	n.a.	n.a.	n.a.	0.67	n.a.	n.a.
MgO	1.99	1.00	1.99	n.a.	1.47	2.99	0.92	n.a.
Na_2O	20.00	20.00	20.00	20.00	19.56	7.36	23.00	14.21
P_2O_5	0.08	0.08	0.03	0.19	0.05	0.36	0.06	n.a.
SO_3	0.10	0.10	0.10	n.a.	0.07	0.12	0.08	n.a.
SiO_2	38.25	41.89	44.55	55.91	47.98	35.95	52.00	65.56
TiO_2	2.49	2.49	1.99	n.a.	2.93	0.01	1.83	n.a.
ZnO	4.27	2.60	2.96	n.a.	1.47	0.65	0.92	n.a.
ZrO_2	2.49	5.25	2.99	n.a.	1.47	0.68	0.92	n.a.
Others*	n.a.	n.a.	n.a.	n.a.	n.a.	11.31	n.a.	n.a.
Total	100.00	100.00	99.86	98.56	99.98	100.00	99.98	100.00

*'Others' refers to BaO, CeO_2, Cs_2O, HfO_2, Li_2O, MoO_3, Nd_2O_3, NiO, RbO_2, RuO_2, Pr_2O_3, Sm_2O_3, SrO, TeO_2, and Y_2O_3.
[†]n.a. = not analysed.

borosilicate glass compositions (Charles & Wagstaff 1968; Haller *et al.* 1970). In the case of borosilicate glass compositions, there is a tendency for glass to separate into two chemically distinct regions: one rich in alkali-metaborate – the other in silicon (Bray 1978). Accordingly, the thermodynamic properties of glasses prone to phase separation display large values of configurational entropy as the various cations (Si, Al, B) compete for oxygen atoms and their moieties jostle each other for space (Hervig & Navrotsky 1985).

What is particularly problematic about this phase separation process from a chemical corrosion point of view is that the B-rich phase (which can be modeled as a sodium-metaborate component; $Na_2O \cdot 2B_2O_3$ or $Na_2B_4O_7$) is highly water-soluble. As dissolution of sodium-metaborate is independent of dissolved silica activity:

$$Na_2B_4O_7 + 7H_2O = 4H_3BO_3(aq)$$

$$+ 2Na^+ + 2OH^- \quad (7)$$
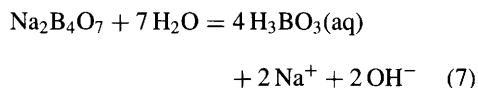
we should expect to find unequal dissolution behaviour in phase-separated glass with only the Si-rich regions (modelled as a reedmergnerite ($NaBSi_3O_8$) component) responding to differences in chemical affinity of the system based on dissolved silica activity. Areas of fast dissolution corresponding to alkali-metaborate regions should form etch pits as the chemical affinity of the system approaches saturation with respect to amorphous silica.

Such 'pits' have recently been observed in a reacted phase-separated glass using vertical scanning interferometry (VSI) techniques, and an image of the pitted surface is shown in Fig. 4. The glass composition is the simple Na–B–Si glass included in Table 1; note that the glass is relatively B-rich (molar B > Na). The glass specimen was a 10 mm × 10 mm × 2 mm coupon that was run in an SPFT apparatus for 24 h at 90 °C at pH 9. The coupon was examined *ex situ* by VSI techniques and height differences were recorded with a resolution down to 1 nm. For a further discussion of the VSI techniques, the reader is referred to Lüttge *et al.* (1999).
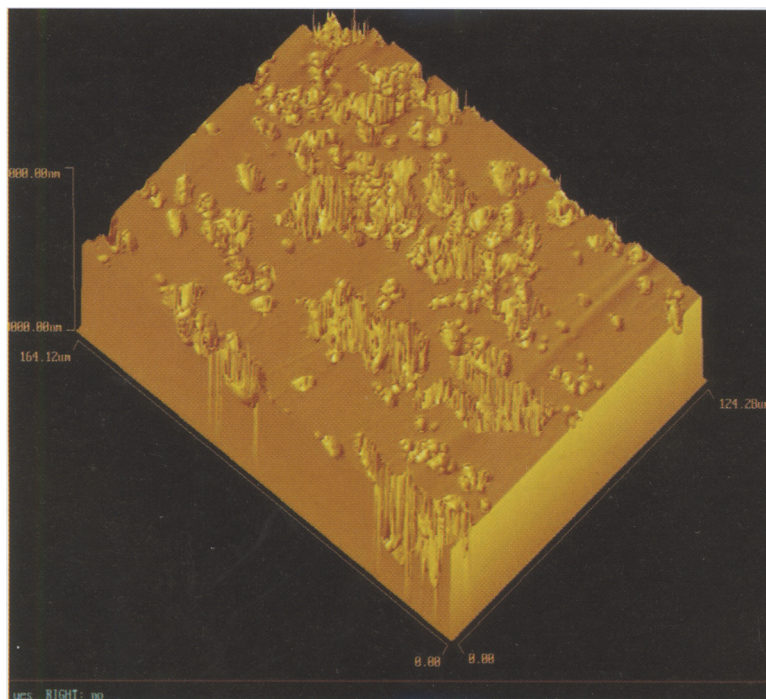

Fig. 4. An image (124 × 164 μm) illustrating height differences on a $Na_2O–B_2O_3–SiO_2$ glass that is phase-separated (composition 'Na–B–Si' in Table 1). Height differences were measured using the vertical scanning interferometer (VSI) technique. The 'etch pits' correspond to domains rich in water-soluble sodium-metaborate. Thus, the figure indicates differential rates of dissolution of phase-separated domains consisting of sodium-metaborate and Si-richer (and, therefore, more corrosion resistant) matrix.

Figure 5 illustrates the effect that glass–glass phase separation can have on dissolution rates of alkali borosilicate glass compositions. On this diagram, we have plotted the normalized $\log_{10}$ rates as a function of silicic acid activity for both homogeneous and phase-separated glass. One notable feature of this diagram is that the phase-separated glass dissolution rates (plots of MAGNOX and HLP-31 data) are a factor of $\sim 10 \times$ faster than those of the homogeneous glasses. Note also that the release rates of Na and B from the phase-separated glasses are, unlike in the case of the homogeneous glasses (LAWA33 and HLP-9 data), independent of the activity of silicic acid activity. The reason that the phase-separated glass compositions do not display evidence for silica-saturation control can be seen in equation (7). If the sodium-metaborate region dissolves rapidly with respect to the Si-richer matrix, then the release of Na and B to solution should show no dependence upon silicic acid activity. As pre-dicted, the release rates of Na and B are faster than for their homogeneous counterparts. In addi-tion, the phase-separated glasses display an equal *mass* release rate of Na and B, which is predicted through the stoichiometry of the glass (McGrail *et al.* 2002). This behaviour is in keeping with a chemical affinity control over glass dissolu-tion. Another relevant point is that the rate of release of Na and B from phase-separated glass depends on the relative proportions of reedmerg-nerite- and sodium-metaborate- rich regions that make up the phase-separated glass. A phase-separated glass made up predominately of a reed-mergnerite-like phase will dissolve relatively slowly. In contrast, a phase-separated glass con-taining a high proportion of sodium-metaborate glass, especially if such domains are intercon-nected, will dissolve more rapidly. Again, the theme of parallel reactions, one of which will be dominant, is reiterated.

The tendency of B to promote phase sepa-ration in glass specimens predicts that a wide
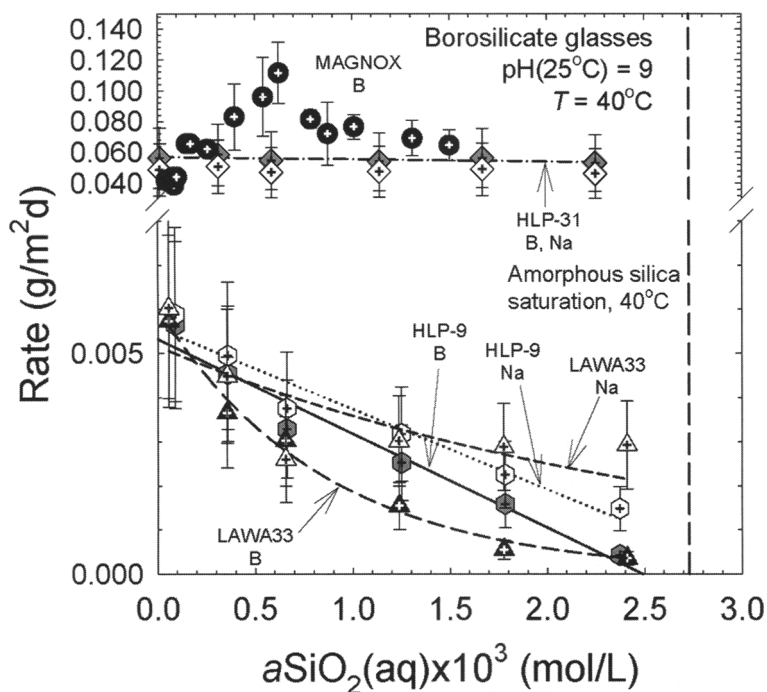
Fig. 5. Plot of $\log_{10}$ B and Na normalized release rates vs. the activity of silicic acid for both phase-separated and physically homogeneous glass specimens. All rates were plotted at steady-state conditions. MAGNOX and HLP-31 represent phase-separated whereas LAWA33 and HLP-9 represent homogeneous glass specimens. The behaviour of homogeneous glass includes an inverse relationship between rates and silicic acid activity and a difference between B and Na rates as silicic acid activity increase. The magnitude of the difference between B and Na rates is related the amount of 'excess' Na (see Fig. 3). Relatively faster element release rates ($\sim 10 \times$), identical release rates of Na and B, and independence from activity of silicic acid appears to characterize phase-separated glass.

variety of borosilicate glasses should be phase-separated. We have tested numerous glass compositions that show consistently high dissolution rates and do not respond to increasing concentrations of silica activity (McGrail *et al.* 2001*b*). These findings are in accord with the expectation that many borosilicate glass compositions, especially those that have low Al_2O_3 concentrations, are phase-separated. However, both compositionally simple and complex glass specimens can show evidence for phase separation. For example, ample evidence exists that both the >15 oxide component MAGNOX and the simple three-component ($Na_2O-B_2O_3-SiO_2$) glass are phase-separated (McGrail *et al.* 2002). This evidence includes NMR data, secondary electron microscope observations of acid-reacted glass, and direct documentation of etch pit formation caused by dissolution of the soluble sodium-metaborate glass (see Fig. 4 and Icenhower *et al.* 2003).

However, this begs the question of why other investigators have not detected phase separation over a wide range of borosilicate compositions. The answer seems to be that the very fine scale of phase separation typically complicates detection efforts. Typical micro-heterogeneity of the glass is on the order of 10 to 500 Å (Konijnendijk & Stevels 1976; Porai-Koshits *et al.* 1982), which means that many modern techniques used to detect phase separation (>100 Å) are not necessarily sensitive enough.

Influence of secondary mineral precipitation

Over the last 20 years investigators have reported that precipitation of secondary phases can accelerate the corrosion rate of glass. This is because precipitation can cause a sudden drop in the activity of a key aqueous species. In other words, we hypothesize that the rate is affected through the chemical affinity of the system.

Bates & Steindler (1983) first reported the linkage between dissolution rates and secondary mineral precipitation, and a number of more recent papers (Van Iseghem & Grambow 1988; Strachan & Croak 2000) have reported similar findings. In these studies, precipitation of the zeolite phase, analcime, $Na(AlSi_2O_6) \cdot H_2O$, consumed silicic acid, causing the corrosion of the glass to accelerate back up to the maximum or forward rate of reaction. Again, these findings argue against control of element release via a thickening reaction layer. The mineral herschelite, $(Na, K)AlSi_2O_6 \cdot 3H_2O$ (Fig. 6), covers the surface of many of the glass specimens that we have worked with (along with analcime and kaolinite), and, like analcime, controls the activities of silicic acid and Al in solution. Because zeolite minerals can completely coat the glass surface,
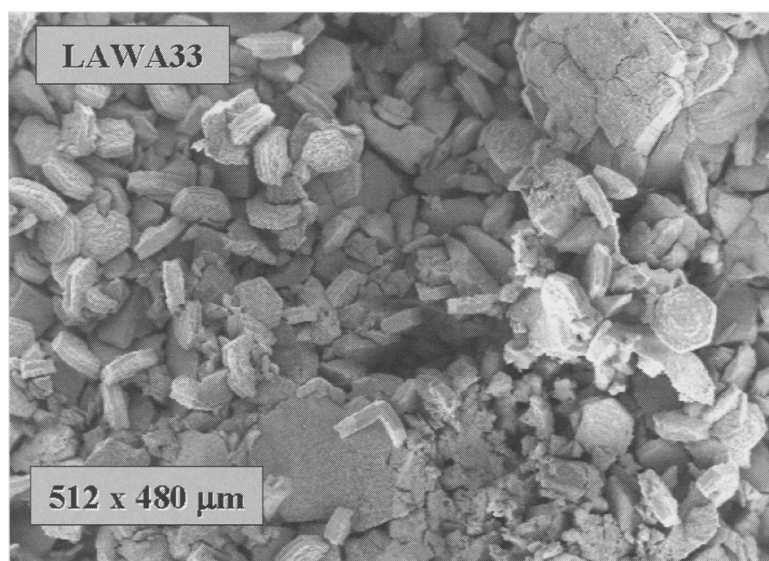
Fig. 6. Scanning electron micrograph picture of borosilicate glass (LAWA33, see Table 1) reacted with solution at an elevated temperature. The hexagonal phase is herschelite, $(Na, K)AlSi_2O_6 \cdot 3H_2O$.

why should the rates of reaction increase? Why should zeolite minerals not also behave as a diffusion barrier? The simplest way to interpret these results is to invoke changes in the chemical affinity of the system triggered by the precipitation of silica-consuming phases.

If secondary minerals affect the dissolution rate of glass, then the composition of glass itself becomes important because the chemistry of the glass ultimately determines which phase or phases will precipitate. Strachan & Croak (2000) made a set of empirical plots of the effects that glass composition exerts on the corrosion resistance of glass. These plots were based on their original research and that of Van Iseghem & Grambow (1988), which showed that a critical concentration of Na and, especially, Al, is needed to stabilize analcime. Therefore, Al – and not just Si – were shown to adversely affect dissolution. Furthermore, their investigation found that a critical volume of analcime must form before the rates can accelerate to the forward rate. This last finding explains why precipitation of analcime by itself is not sufficient for controlling rates; a threshold volume of analcime must form in order to control the dissolved Si-activity of contacting water.

Although these investigations are immensely helpful for deciphering dissolution behaviour of borosilicate glass, they are, in the end, only empirical relationships. One of the more difficult aspects of investigating glass corrosion behaviour is that phases that should form, using thermodynamic criteria, often do not (at least on the time-scale of laboratory experiments). This has to do with the inherent precipitation kinetics of secondary phases; typically, thermodynamically metastable phases form before their fully crystalline, and thermodynamically stable, counterparts. Note that this is especially true in experiments performed at high temperatures; typically, more crystalline phases are favoured by higher temperatures and can obfuscate interpretations of glass corrosion performance under (lower) repository temperatures where the metastable phases may persist over the entire time of interest with respect to repository performance.

Another difficulty presented by precipitation of secondary phases is that other aqueous species, such as those of Al, can be affected, as stated above. Under certain conditions the activity of $Al(OH)_4^-$ in mildly alkaline solutions can drop to near zero due to precipitation of zeolite phases. The question is how to represent this change in aluminate activity using a rate equation based on chemical affinity concepts. For example, in equation (1), the activity of the

aluminate ion can be accommodated a number of different ways, but they all ultimately cause problems for long-term prediction of glass corrosion rates.

If the aluminate ion is a component in the chemical affinity term, then the activity of dissolved silica, by itself, cannot describe the change in rate with changes in chemistry of the contacting fluid. A number of attempts have been made to explicitly include Al activity in the chemical affinity term. Gin (1996) suggested that glass dissolution could be modelled using a 'mixed' Si/Al term for the ion activity product (Q):

$$f(\Delta G) = \left(1 - \frac{Q}{K}\right)$$

$$= \left(1 - \left[\frac{a_{Al(OH)_4^-}^x \times a_{H_4SiO_4}^y}{K_g}\right]\right) \quad (8)$$

where the terms $a_{Al(OH)_4^-}^x$ and $a_{H_4SiO_4}^y$ are the activities of the aluminate ion and silicic acid, respectively. The exponents of the activities (x and y) represent the stoichiometry of the rate-limiting reaction. The term in the denominator, K_g, represents the fictive glass equilibrium constant. As noted above in the 'alkali–hydrogen kinetics' discussion, concepts such as K_g as applied to glass are not valid, but aid in developing the concepts of solution composition control on glass dissolution. Bourcier *et al.* (1994) proposed that the solution is in equilibrium with an amorphous gel and the saturation state could be defined using the components Si, Fe, Al, Ca, and Mg. This view is similar to that of Daux *et al.* (1997), in which the aqueous activities of Si, Fe, and Al should be used to define Q for basaltic glass. Oelkers advocated a rate law for basalt and aluminosilicate materials in general that is based upon the activity of Al^{3+} (Oelkers 2001; Oelkers & Gislason 2001). This model is echoed in models for aluminosilicate glass compositions containing variable amounts of Al (Hamilton *et al.* 2001). Advocat *et al.* (1998) went further than the others, suggesting that the affinity term include *all* glass components.

Although all of these ideas have merit, they suffer from the same problem: saturation with respect to certain solid phases causes one or more activities to decrease to near zero, causing the entire $1 - Q/K$ term to go to unity. In other words, the model implies that rates should accelerate to the maximum or forward rate, despite how much silicic acid is present in solution, contrary to experimental results. As long as the glass is physically homogeneous

(i.e., no phase separation), some decrease in the rate must occur, even with relatively sodic glass compositions (see above section on 'ion exchange kinetics'). Therefore, models based upon multicomponent ion activity products do not allow for an accurate picture of the rate dependence.

Equally problematic is representing Al as a rate inhibitor – thereby removing the activity of Al from the ion activity quotient term to the $\prod_i a_i^{n_i}$ term (see equation 1). Yet, precipitation of an Al-bearing phase, such as zeolite, can dramatically lower the activity of Al in solution. Because inhibitor species will have a negative exponent, the term gets very large at low activities of Al, which again causes the rate to increase, despite high activity of silicic acid in solution. McGrail et al. (2001b) reported a number of cases of this phenomenon. These findings make plain that a more mathematically stable form of the rate equation must be fashioned.

Conclusions

We are only beginning to understand the dissolution kinetics of alkali borosilicate glass under the context of conditions most likely to persist in subsurface environments. Because of typically slow pore water recharge rates, especially in relatively dry repository settings (e.g., Hanford, Washington; Yucca Mountain, Nevada; and Los Alamos, New Mexico, USA), aqueous solutions in contact with glass will be extremely concentrated in dissolved glass components and subject to the chemical affinity of the system. However, this chapter vividly illustrates that the conventional means of linking element release rates to solution saturation state fail for a number of circumstances. Failure is likely related to assumptions of consecutive, rather than concurrent, reactions and the idea that chemical affinity solely explains glass dissolution behaviour. The data presented in this review indicate that element release rates are governed by competing reactions that: (1) limit release through the dominant reaction, and (2) the identity of the dominant reaction changes as the system approaches saturation. The dominance of 'secondary' reactions, unanticipated by earlier investigators, govern rates in concentrated solution and include: (1) the magnitude of excess alkalis in glass, (2) dissolution of micro-heterogeneous borosilicate glass, and (3) the identity and volume of precipitating phases on the surface of glass. The fact that failure to conform to conventional rate laws will occur for common, as opposed to exotic, conditions germane to waste glass disposal is reason for

further serious contemplation. Fortunately, there is an expanding list of detailed dissolution kinetics studies that have proven their value by withstanding scrutiny from an informed and perceptive group of peers. These works provide a sound basis for evaluating a spectrum of glass corrosion behaviour.

The failure of models based on application of TST rate laws to glass/water systems does not mean, however, that diffusion through a 'leach layer' is by default the answer to this dilemma. Clearly, the set of recently reported data on glass corrosion resistance shows that it is not an 'either-or' situation between affinity- and diffusion-based rate laws. Finding a mathematically stable form of the rate equation appears to be more worthy of pursuit.

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