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Molecular mechanisms for corrosion of silica and silicate glasses

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Abstract

Dissolution, selective leaching, and stress-corrosion cracking are all processes which can degrade the performance of silica and silicate glasses exposed to aqueous environments. Reactions which corrode glass in water include hydration, hydrolysis and condensation, and ion-exchange processes. Techniques such as solid-state nuclear magnetic resonance, Raman and Fourier transform infrared spectroscopies, pH stat titrations and elemental depth profiling have been used to establish the relative importance of the above reactions on glass degradation as a function of solution pH and composition, temperature and stress level. This paper reviews results obtained for silica, alkali silicate, and alkali boro- and aluminosilicate glasses. For most glasses, the rate at which water enters the glass structure controls the kinetics of the other glass–water reactions, explaining the corrosion characteristics of different glass compositions.

1. Introduction: reactivity versus structure

Three general classes of reactions can occur between glass and aqueous solutions: (1) hydration, in which molecular water enters the glass as an intact solvent; (2) hydrolysis, in which water reacts with metal–oxygen bonds in the glass to form hydroxyl groups; and (3) ion-exchange reactions, in which modifier cations such as sodium are replaced by protons (or other cations). For complex glasses, all three reactions occur simultaneously. Each reaction influences the kinetics and mechanisms of the other reactions. However, before the dissolution behavior of different glass compositions are discussed, the features governing each reaction type are discussed independently.

2. Hydration and hydrolysis

Water can penetrate a glass surface via two distinct mechanisms. The water molecule can either diffuse into the glass through void space between oxygens in the structure as an intact molecular species or it can undergo hydrolysis and condensation reactions with metal–oxygen bonds:

$$H_2O + M{-}O{-}M \rightarrow M{-}OH + HO{-}M \rightarrow M{-}O{-}M + H_2O. \qquad (1)$$

The latter mechanism is never completely reversible, resulting in the presence of both hydroxyl groups and molecular water in the glass as

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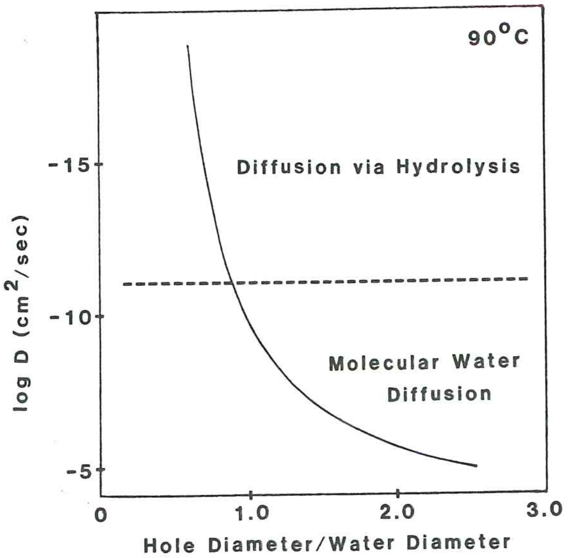
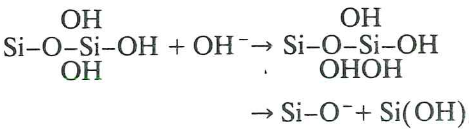


Fig. 1. Diffusion coefficient for water diffusion through silicates as a function of the ratio of the free ring opening to the diameter of the water molecule. The dashed line shows the approximate transition between when water diffuses into glass as an intact molecular species and via a reversible hydrolysis mechanism corresponding to a ring containing six silicate tetrahedra.

seen via nuclear magnetic resonance techniques [1].

The dominant mechanism for water penetration into the solid depends on the relative rates for the two pathways. The rate of the molecular diffusion pathway is primarily controlled by steric constraints imposed by the size of the voids present in the glass network. For silicates, the void size is determined by the distribution of rings in the structure consisting of interconnected silicate tetrahedra. For complex glasses, modifier cations such as Na^+ can fill or partially block such voids. The effect of ring size on diffusion has been determined for crystalline aluminosilicate zeolites [2] (Fig. 1). When the structure contains voids which are large (> 0.7 nm) relative to the kinetic diameter of the water molecule (0.28 nm), the molecule can diffuse through silicates as rapidly as it can through liquid water ($D = 3 \times 10^{-5}$ cm^2/s). For puckered rings containing six silicate tetrahedra where the ring opening (0.24 nm) is comparable in size with the water molecule, diffusion in zeolites is much slower ($D = 2 \times 10^{-13}$ cm^2/s). If smaller rings are present, molecular water cannot penetrate the voids. The only way for water to penetrate such structures is to break open the rings via hydrolysis.

Since most glass structures do not contain openings which are large enough to admit molecular water, reversible hydrolysis and condensation reactions (Eq. (1)) are critical to the dissolution behavior of most glasses. The kinetics of network hydrolysis depend on both the distribution of local structural units present in the glass and on the chemistry of the solution. The tetrahedral SiO_4 sites common to all silicate glasses are susceptible to nucleophilic attack [5] primarily by OH^- to form a reactive five-coordinated intermediate which can decompose to rupture the Si–O–Si bond:



$$\mathrm{Si{-}O{-}\underset{OH}{\overset{OH}{Si}}{-}OH + OH^- \rightarrow Si{-}O{-}\underset{OHOH}{\overset{OH}{Si}}{-}OH \rightarrow Si{-}O^- + Si(OH)_4}. \qquad (2)$$

In pure silica, the above hydrolysis reaction is inhibited by the high connectivity of the glass network, which makes network rearrangement to accommodate the five-coordinated intermediate difficult. However, glasses containing non-bridging oxygens (e.g., alkali silicate glasses) contain local sites which are attached to the network by fewer bridging bonds, allowing more facile rearrangement into the five-coordinated intermediate. In general, network hydrolysis is more rapid when non-bridging oxygens are present. Site reactivity follows the trend $Q_1 > Q_2 > Q_3 > Q_4$ where the Q notation refers to the number of bridging oxygens on a particular tetrahedral Si site (e.g., a Q_2 site is a Si tetrahedron bonded to two bridging and two non-bridging oxygens). Rearrangement of the network to open up reactive sites for creation of the five-coordinated intermediate can also be promoted by deforming local bonding configurations, either by creation of small rings (containing two, three or four interconnected tetrahedra) or by the application of external stress to the glass. Finally, substitution of other elements for Si in network sites can change both the kinetics and mechanism of network hydrolysis.

For example, borate units in either borate or borosilicate glasses [5] are susceptible to electrophilic as well as nucleophilic attack and can be hydrolyzed in both acids and bases.

The role of solution chemistry on hydrolysis can be predicted if the hydrolysis mechanism for a given structural unit is known. For example, for the network hydrolysis reaction shown in Eq. (2), it is apparent that the rate of hydrolysis leading to dissolution will increase if the pH (i.e., the OH^- concentration) increases. Factors leading to an increase in $Si(OH)_4$ will decrease the rate of the forward dissolution reaction. For limited solution volumes, glass dissolution reactions can change both the pH and $Si(OH)_4$ concentrations with time, leading to time-dependent dissolution kinetics. Environmental temperatures can also have a large impact on kinetics, not only because temperature can activate reactions such as the hydrolysis reaction shown in Eq. (2), but because the temperature influences parameters such as the solubility of dissolved species such as $Si(OH)_4$.

3. Ion-exchange

Selective leaching of modifier cations present in complex silicate glass compositions is often attributed to ion-exchange reactions such as

$$\text{Si–O–Na}^+ + \text{H}_3\text{O}^+ \rightarrow \text{Si–OH} + \text{Na}^+ + \text{H}_2\text{O} \quad (3)$$

$$\text{Si–O–Na}^+ + \text{H}_2\text{O} \rightarrow \text{Si–OH} + \text{Na}^+ + \text{OH}^-. \quad (4)$$

The rate and extent of ion-exchange depend on solution chemistry as well as glass structure.

The role of solution chemistry on leaching can be demonstrated by examining the behavior of ion-exchange sites which are clearly exposed to aqueous environments, either on silica surfaces [6] or in open structures such as zeolites. The extent of ion-exchange for reactions such as Eq. (3) can be described by ion-exchange equilibrium constants such as

$$K = \frac{[\text{Si–OH}][\text{Na}^+]}{[\text{Si–O–Na}^+][\text{H}^+]}. \quad (5)$$

Eq. (5) illustrates that the extent of ion-exchange should depend on the Na^+ concentration in solution (which should inhibit exchange), the pH (solutions containing more H^+ should enhance exchange) and the value of the equilibrium constant, which is a measure of how effectively protons compete with sodium ions for occupancy of a given anionic site. Eq. (4) shows that, as the glass dissolves, the exchange process can promote a dramatic increase in the pH (and Na^+), retarding further exchange and enhancing network dissolution. For this reason, mechanistic studies of glass dissolution are best performed under pH stat conditions [3] in which a pH electrode commands a burette to add acid to the solution to keep the pH constant. The leaching kinetics can be monitored continuously by measuring the moles of H^+ added to the solution as a function of time. Using pH stat titrations, it is possible to measure effective diffusion coefficients for the early stage of alkali leaching, effective reaction constants for steady-state leaching and the commonly observed transition time between the stage in leaching which proceeds as a function of the square root of time and the stage which exhibits a linear time dependence (see below).

The magnitude of the ion-exchange equilibrium constant describing the pH and concentration regime where protons exchange for Na^+ depends on the electronic charge distribution (acid–base properties) of the site in the glass. Fig. 2 shows the extent of site protonation predicted on the basis of known ion-exchange equilibrium constants for silanol groups, tetrahedral anionic sites such as AlO_4^- and BO_4^-, and non-bridging oxygen sites in phosphate glasses [7]. For silanol groups, little exchange is predicted in highly basic solutions ($pH > 12$), with complete exchange being expected below a $pH \sim 8$. The AlO_4^- group is predicted to be much more resistant to leaching, resisting exchange down to almost pH 5. Therefore, for complex glasses, the distribution of sites present in the glass structure must be known to make accurate predictions concerning the leachability of modifier cations.

Glass structure not only determines the distribution of exchangeable sites, but influences the kinetics of the exchange process. Initial leaching via ion-exchange appears to be a transport rather than a reaction-limited process. Classical theories

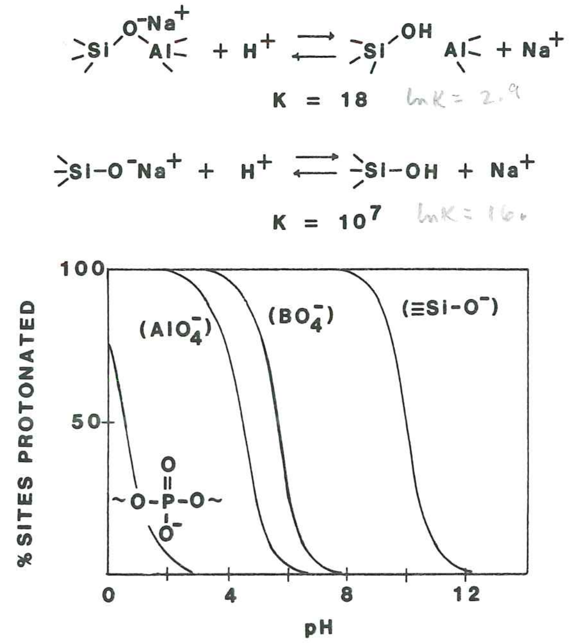


Fig. 2. Predicted ion-exchange of protons for sodium ions on different anionic structures in glass as a function of solution pH.

for leaching via ion-exchange [8] describe the process as interdiffusion of cations such as Na^+ and H_3O^+ through the structure of bulk glass, with the leach rate controlled by the diffusion coefficient of the slower cation. However, there is now considerable evidence that the rate-controlling step is penetration of the glass surface by water. Interdiffusion coefficients measured via pH stat titrations and solution analyses are usually 100–1000 times faster than predicted based on bulk ionic diffusion [3,9]. Solution analyses and elemental depth profiles of leached mixed-alkali glasses indicate that modifier cations having dramatically different diffusion coefficients in bulk glass exhibit exactly the same leach rates. Measured leach rates more closely match the kinetics of water penetration into the glass.

While it appears that water penetration into glass is the rate-controlling step in selective leaching, the factors controlling water penetration are not quantitatively understood. Ion-exchange, network hydrolysis, and hydration reactions in glass are strongly coupled. Hydrolysis reactions can open up rings to facilitate the penetration of the glass by both the water and H_3O^+ involved in the exchange process. In addition, ion-exchange reactions create voids which water can penetrate and create reactive species such as silanol groups which are active sites for network repolymerization (Eq. (1)). Polymerization of silanol groups removes ion-exchange sites from the leached glass surface, making the ion-exchange reaction kinetically irreversible. Finally, the combination of hydrolysis and repolymerization can open up the structure of the surface, enhancing the rates of diffusion of water and other species. All of the above features are seen in the leaching behavior of alkali silicate and alkali alumino- or borosilicate glasses as described below.

4. Silica–water reactions

Silica has the simplest structure to consider when considering glass–water reactions. Modifier cations capable of ion-exchange reactions are not present. All oxygens are bridging oxygens and all Si tetrahedral sites are Q_4 sites predicted to be resistant to hydrolysis. The Q_4 sites interconnect to form rings. Rings containing five or more Q_4 units can pucker to produce relatively strain-free configurations which are spectroscopically indistinguishable. However, rings containing four, three and two tetrahedra contain enough internal strain to change the frequencies associated with vibrational modes as detected via Raman [10] or infrared [11] spectroscopies. Significant concentrations of three- and four-fold rings are detected in fused silica. The distribution of larger rings is difficult to determine. However, comparisons involving He and Ne diffusion into silica glass [12] and into zeolites suggest that four-, five- and six-membered rings are most common and that there are few interconnected voids involving larger rings. In the absence of ring opening via hydrolysis, hydration of silica is predicted to be negligible.

Experimental results on both the dissolution and hydration of silica indicate that it is highly resistant to attack by water as expected on the basis of glass structure. Below pH 8 at room temperature, silica glass dissolves at a rate of around 10^{-16} mol/cm^2 s [13], or of the order of 10 nm/y. As the solution pH is increased from 8 to 14, the dissolution rate increases [13] to as high as 10^{-12} mol/cm^2 s as expected due to both the increases in the concentration of OH^- (see Eq. (2)) and the enhanced solubility of silica at high pH due to the formation of silicate anions. In aqueous solutions, hydrated layers are not produced on silica surfaces because the silica dissolves via network hydrolysis before it can be hydrated. When silica is exposed to steam atmospheres [14], hydrated layers can form, but only because the reaction products of network hydrolysis do not have a solution phase to dissolve into. Isotopic labeling experiments [16] (Fig. 3) clearly show that steam hydration of silica glass involves 'reversible' network hydrolysis leading to extensive exchange of oxygen between the water and the glass. The activation energies (ranging from 17 to 20 kcal/mol) [15] and absolute rates for steam hydration and network hydrolysis leading to dissolution are similar, which is also consistent with a hydrolysis mechanism for steam hydration.

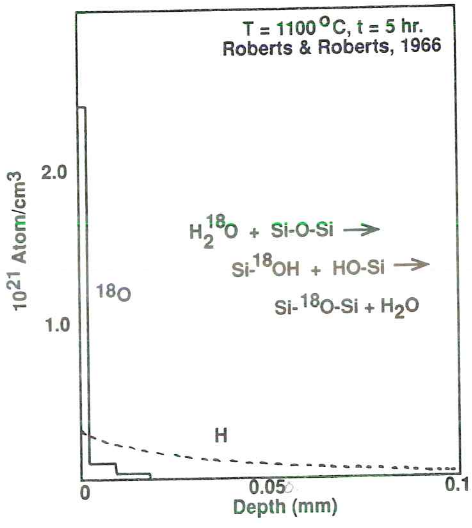


Fig. 3. Diffusion profiles [16] for ^{18}O and H in silica surfaces exposed to $H_2^{18}O$ steam at 1100°C for 5 h. If water entered the glass as a molecular species, the ^{18}O and H profiles would be coincident. Instead, oxygen from the water is clearly exchanging with oxygen in the silicate network indicative of the reversible network hydrolysis.

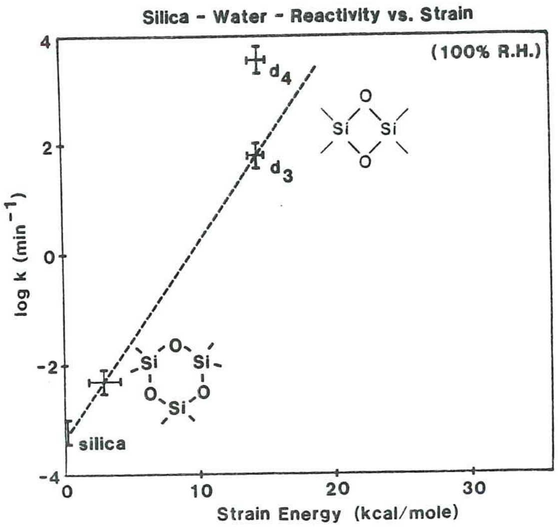


Fig. 4. Reactivity of silicate rings with water as a function of ring strain (estimated from molecular orbital calculations) [19]. The most highly strained rings (edge-shared tetrahedra or two-membered rings) are one million times more reactive than unstrained silica. Rings containing three tetrahedra are much less strained and much less reactive (ten times as reactive as silica). The strain energy in rings containing four or more tetrahedra is negligible in terms of promoting reactivity with water.

While silica is not susceptible to aqueous corrosion (except in strong base), silica glass is highly susceptible to environmentally assisted crack growth, or stress corrosion cracking [16]. In stress corrosion, water can greatly accelerate the rate at which cracks in silica grow from surface flaws under an applied load, leading to catastrophic failure. The mechanism for stress corrosion involves the rapid hydrolysis of local Si–O bonds which are deformed via applied stress. The kinetics of silica hydrolysis as a function of local strain energy have been modeled by studying the rate of hydrolysis of strained bonds in silicate rings containing three or two tetrahedral units [17] (Fig. 4). The latter edge-shared tetrahedra, found in the surfaces of dehydroxylated silica, react over one million times faster than normal unstrained rings [18], illustrating how local deformations can influence the reactivity of silica. Although the level of strain is lower in three- and four-fold rings, the presence of such rings and other strained bonding configurations accounts for the enhanced dissolution of fused silica relative to quartz.

5. Leaching of alkali silicate glasses

Hydration, hydrolysis, and ion-exchange reactions all occur on the surfaces of alkali silicate glasses exposed to water. By contrast with silica, network hydrolysis is not the only factor contributing to the rate of surface hydration. As alkali cations are removed from the surface via ion exchange, voids which were occupied by the alkali ions can be replaced by water, facilitating diffusion of water into the surface. Except in highly basic solutions, the silicate network dissolves at a rate slower than the rate of water penetration. As a result, thick hydrated, alkali-depleted surface layers can form on alkali silicates even at room temperature.

6. Composition dependence

Simple alkali silicate glasses contain charge-compensated ion pairs such as Si–O–Na^+, introducing Q_3 and Q_2 groups into the Q_4 network. Therefore, the alkali silicates are more susceptible to network hydrolysis than is silica. The total number of non-bridging oxygens increases with the modifier content of the glass (e.g., from 0.5 to 0.67 to 1.0 in the series Na_2O–$4SiO_2$ to Na_2O–$3SiO_2$ to Na_2O–$2SiO_2$). For a given modifier, the reactivity of the alkali silicate glasses increases with the non-bridging oxygen content. However, glasses containing the same modifier content but different modifier cations (e.g., Na^+ versus K^+) do not react with water at the same rate. In general, the lower the charge-to-ionic radius ratio of the modifier cation, the more reactive the glass will be. For example, $30Li_2O$–$70SiO_2$ reacts with water at 60°C twenty times slower than $30Na_2O$–$70SiO_2$, while K_2O–$3SiO_2$ is six times more reactive than Na_2O–$3SiO_2$ [19]. Addition of CaO to make a soda–lime glass greatly enhances the corrosion resistance relative to a simple sodium silicate glass. Two factors appear to contribute to the above trends. First, exchange of large cations such as K^+ leaves behind larger voids in the network than does leaching of smaller cations such as Na^+, providing larger openings into which water can diffuse. Second, the distribution of non-bridging oxygens among the different Q species is different depending on which modifier is used. Smaller, more highly charged modifiers such as Li^+ and Ca^{2+} can promote clustering of non-bridging oxygens via reactions such as $2Q_3 \rightarrow Q_2 + Q_4$ as clearly demonstrated via Raman spectroscopy [20]. For example, K_2O–$2SiO_2$ contains Q_4:Q_3:Q_2 of 1:8:1, while Li_2O–$2SiO_2$ exhibits Q_4:Q_3:Q_2 of 1:2:1. The above clustering can lead to phase separation, in which reactive Q_2 regions are surrounded by silica-like Q_4 regions that are more resistant to both hydrolysis and hydration. However, even in the absence of phase separation, increases in the mole fraction of Q_4 appears to improve leach resistance. The alkali silicate dissolution results point out yet another structural feature (the Q distribution) which must be known to accurately predict glass dissolution behavior.

7. Environmental dependence

The environmental dependences for both ion-exchange and network hydrolysis are those expected on the basis of the acid–base properties of the silanol group and the hydrolysis characteristics of Q units in silicate networks. Surface silanol groups have an effective pKa of nearly 10, which should correspond to the transition pH between extensive ion-exchange (leading to selective alkali leaching) and little exchange. Measurement of the extraction of alkali versus pH are consistent with the exchange behavior of silanol groups [22]. Below pH 9, alkali leaching is extensive, and exhibits little pH dependence. The rate of alkali extraction drops sharply between pH 9 and 11, and in highly basic solutions is almost as slow as the rate of network dissolution. Above pH 9, where silicate anions become stable and nucleophilic attack by OH^- is promoted, the dissolution rate of the silicate network increases for all alkali silicates. The pH dependence for network dissolution is similar to that seen for silica [21], and again agrees with predictions. The one environmental factor which does not influence leaching as predicted is the Na^+ concentration in solution. While leaching can be retarded by as much as a factor of five in NaCl brine solutions [22], leach rates in more dilute solutions are almost independent of Na^+. The above observation indicates that leaching is not a simple ion-exchange process, as discussed in the following section.

8. Restructuring of leached layers

Alkali leaching is not a reversible ion-exchange reaction. The reason the reaction is irreversible is that silanol groups created via ion-exchange react with each other to form Si–O–Si bonds [6] (see Eq. (1)). The ultimate result of silanol polymerization is the total restructuring of glass from the initial random network into a material which resembles an aggregation of colloidal silica particles [23] (Fig. 5). Raman and nuclear magnetic resonance studies of leached layers show that the molecular structure of particulates within the restructured surface resembles fused silica [6]. Regardless of the initial Q distribution in the glass, the leached layer contains a predominance of Q_4 units, with Q_3 units primarily occupying surface sites on the particles. Many ion-exchange sites present in the original structure are eliminated. The other major implication of surface restructuring is that the leached layer is transformed from a diffusion barrier into a material containing 'large' (> 3 nm) interconnected voids through which water and other species can rapidly diffuse. Transmission electron micrographs show that the rate at which the above transformation occurs controls the kinetics of the commonly observed change in leaching kinetics from a diffusion-controlled square-root-of-time dependence to a reaction-controlled linear time dependence. The transfor-

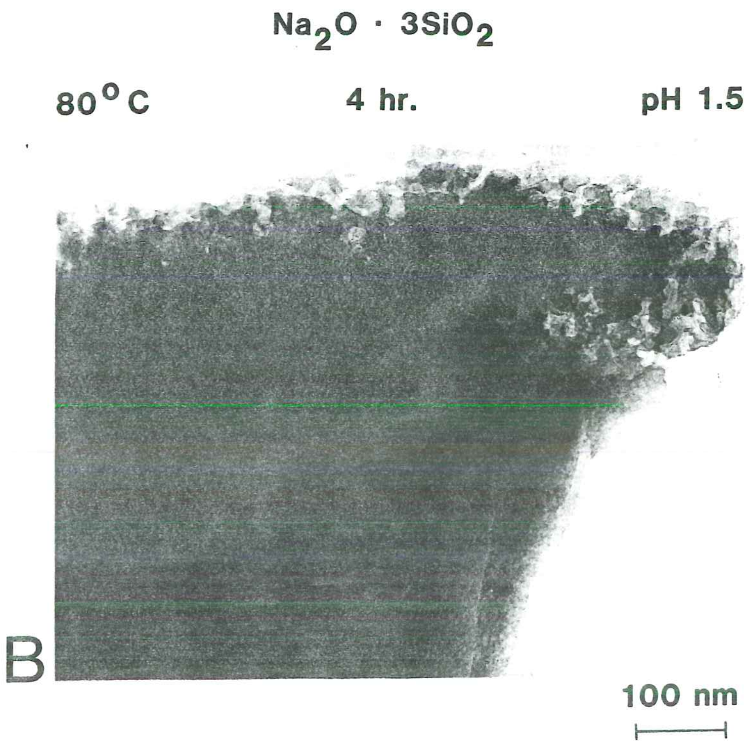


Fig. 5. Transmission electron micrograph (cross-section) of Na_2O–$3SiO_2$ glass after 4 h of leaching at 80°C. The top layer containing porous structure is leached glass, while the featureless material below is unleached glass.

mation rate increases as the initial Q_4 content of the glass decreases.

9. Corrosion of alkali boro- and aluminosilicate glasses

All the factors discussed above regarding the hydration, hydrolysis and ion-exchange of alkali silicate glasses also apply to alkali boro- and aluminosilicate glasses. However, to understand the relative rates at which the glass alteration reaction occurs, the structural differences between alkali silicates and glasses such as aluminosilicates need to be taken into account. In simple alkali silicate glasses, all modifier cations are charge-compensated by non-bridging oxygens. Creation of non-bridging oxygens lowers the effective crosslink density of the glass, creates Q_3 and Q_2 sites which are more prone to network hydrolysis and allows formation of silanol groups via ion-exchange, promoting structural alterations within the leached layer. In alkali boro- and aluminosilicate glasses, modifier cations can be charge compensated by BO_4^- and AlO_4^- sites in addition to non-bridging oxygens [24]. Such sites modify both the inherent reactivity and extended structure of the glass.

Anionic tetrahedral sites such as AlO_4^- are approximately five orders of magnitude more resistant to ion-exchange by protons than are non-bridging oxygens. Selective leaching from such sites does not occur above pH 5 (compared with pH 10 for non-bridging oxygen sites [8]. In neutral pH solutions, the fraction of Na^+ associated with non-bridging oxygens is selectively leached leaving the fraction associated with AlO_4^- or BO_4^- sites untouched.

Protonation of Al,B–O–Si bonds catalyzes their hydrolysis below pH 5. It is difficult to exchange modifier cations from Al,BO_4^- sites without also selectively leaching the Al [23] or B. Raman and ^{17}O NMR spectra of borosilicate glasses leached in acidified $H_2{}^{17}O$ confirm that boron leaching involves electrophilic attack by protons on Si–O–B bonds to form silanols [6]. The silanols, whether produced via Si–O–B bond hydrolysis or ion-exchange on non-bridging oxygens, repolymerize to produce 'colloidal silica' leached layers as seen for the alkali silicate glasses. In basic solutions, network hydrolysis is also enhanced. Bonds to borate groups are hydrolyzed slightly faster than the silicate network. Depending on the composition, either simultaneous selective leaching of both sodium and boron or uniform glass dissolution can be observed [8].

The role of network structure and chemistry in borosilicate leaching can be illustrated by considering glasses having a fixed silica content and systematically varying the Na_2O/B_2O_3 content. In sodium-rich glasses, most Na^+ is associated with non-bridging oxygens, and the dissolution of the glass mirrors that of simple sodium silicate glass. As Na_2O decreases and B_2O_3 increases, all boron initially enters the silicate network as tetrahedral borate groups [24], decreasing the mole fraction of sodium associated with non-bridging oxygens and decreasing dissolution rates. For example, the glass $30Na_2O–10B_2O_3–60SiO_2$ has two-thirds of its Na^+ associated with non-bridging oxygens and one-third associated with network borate groups. In neutral pH solutions, this borosilicate glass resembles $20Na_2O–80SiO_2$ in terms of its leaching behavior. At the composition $20Na_2O–20B_2O_3–60SiO_2$, essentially no non-bridging oxygens are present. All Na^+ is compensating network borate sites. Although the network is not quite as stable as fused silica, the glass exhibits uniform dissolution as long as the solution pH does not promote removal of borate groups via hydrolysis. Borate-rich compositions such as $5Na_2O–35B_2O_3–60SiO_2$ phase separate into a sodium borate phase (which readily dissolves) and a silica-rich phase (which is resistant to attack). For this composition, sodium removal occurs via hydrolysis of the borate phase rather than via ion exchange regardless of the solution pH.

10. Summary

Hydration, network hydrolysis, and ion-exchange reactions can all lead to degradation of silicate glasses exposed to water. The relative rates of the three reactions and the observed dissolution mode (selective leaching versus uniform dissolution) are critically dependent on the distribution and reactivity of specific sites and functional groups within the glass structure. Each site type exhibits different reactivity patterns as a function of environmental parameters such as solution pH. Different bond types in glass are hydrolyzed via different mechanisms and at different rates. Charge distributions at different sites, such as non-bridging oxygens and tetrahedral borate or aluminate sites, exhibit different local charge distributions and ion-exchange characteristics. Therefore, detailed information concerning the local structure of glass and the variation of structure with composition and preparation conditions is essential for predicting dissolution behavior.

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