

Compositional effects in the dissolution of multicomponent silicate glasses in aqueous HF solutions

G. A. C. M. SPIERINGS

Philips Research Laboratories, P.O. Box 80000, 5600JA Eindhoven, The Netherlands

The dissolution rate of multicomponent silicate glasses in a 2.9 M aqueous HF solution is investigated as a function of its composition. The glasses studied are composed of SiO_2 , B_2O_3 , Al_2O_3 , CaO , MgO , ZnO , Na_2O and K_2O , covering the compositions of most of the technologically important glasses. Unlike many physical properties, no linear relations are observed between the composition of the glass and its dissolution rate. The dissolution rate of a multicomponent silicate glass is found to be largely determined by two factors: The degree of linkage or connectivity of the silicate network and the concentration of SiO_2 in the glass. It is proposed that the dissolution of the glasses is preceded by the leaching of alkali and alkaline earth components present in the glass, followed by the subsequent dissolution of the leached layer. Probably fluorine species will diffuse into the leached layer to enhance the dissolution rate. Analysis of the activation energy data indicates that in some corrosive glasses the leaching itself becomes rate determining.

1. Introduction

The use of photolithography for microfabrication or micromachining purposes is a technological field which is currently being explored [1]. In this technology, structuring by deposition and etching of a wide variety of materials on different substrates such as mono-crystalline materials (Si, GaAs, LiNbO_3 , quartz), metals, glasses, etc., and their combinations, is used for the fabrication of miniature mechanical parts or complete devices.

Multicomponent silicate glasses are a class of materials which are of interest in this field because, using their flexibility in chemical composition, it is possible to combine, in one material, a number of physical property requirements. At present only wet chemical etching in HF-based etchants is available for etching these multicomponent silicate-based glasses. Plasma-etch methods, such as reactive ion etching in fluoro-containing plasmas, are only suitable to etch some glasses which form volatile reaction products such as vitreous SiO_2 .

Dissolution (or etching) of silicate glasses and particularly vitreous SiO_2 in aqueous HF solutions has been studied in a number of publications [2–10]. Mostly these investigations deal with the effect of the etchant composition on the dissolution rate of the silicate glass, and the problem of determining which fluorine-containing ion or molecule is the reactive species.

Little attention has been given to the influence of the chemical composition of the glass on its dissolution rate. Some glass composition–dissolution rate relations were already published in 1932 by Honig-

mann [11] for silicate glasses. She showed that the introduction of network modifiers (such as Na_2O , CaO , MgO , ZnO) in a sodium silicate glass increases the dissolution rate significantly. More recently Tso and Pask studied the effect of composition in calcium aluminosilicate glasses [4], so generally speaking little systematic data are available. Nevertheless it is well known that multicomponent glasses such as soda-lime-silicate glasses have a dissolution rate which is several orders of magnitude larger than that of vitreous SiO_2 [9].

In this paper a systematic investigation is presented on the effect variations in glass composition have on the rate and activation energy of the glass dissolution reaction in an aqueous HF solution. The glass compositions studied do have a large similarity with most of the technologically important glasses such as soda-lime-silicate, borosilicate and most optical glasses.

2. Experimental procedure

The glasses were melted in Pt–Rh crucibles from reagent grade starting materials at temperatures ranging from 1200 to 1500 °C in an electrically heated furnace. The molten glass is formed by fusing the starting materials and is homogenized by bubbling oxygen through it. The bubble-free glass melt is poured into graphite moulds and annealed for 30 min and cooled to room temperature inside a furnace. Polished discs, 2 mm thick with a diameter of 2.5 cm, were prepared from these glass blocks. The samples were polished with a suspension of 30 nm SiO_2 particles in a diluted NaOH solution (pH = 9) and were

kept sealed to minimize additional corrosion by water and CO₂. As SiO₂ glass, fused silica (Herasil, Hereaus Glaswerke, Hanau, FRG) discs were used.

Before the etch experiments the glass discs were cleaned by dipping in a H₂SO₄-K₂Cr₂O₇ solution for 10 min, rinsing in water and isopropanol and drying. The two corrosive glasses were not dipped into this solution. On the clean glass discs a 200 nm chromium film is sputtered and patterned into 100 μm chromium-free stripes using standard photolithographic processes and etching in a cerium(IV) ammonium nitrate solution [9].

The glass samples, with the patterned chromium as a mask, were etched at temperatures from 1 to 50 °C in a 500 ml stirred 2.9 M HF solution with etch times varying between 120 and 900 s. The depth of the etched region relative to the original surface was measured by using a surface profiler (Tencor Alpha-step 200, Tencor Instruments, Mountain View, Ca., USA).

3. Glass compositions

The glasses investigated are composed of oxides common in technologically important glasses. A number of variations in compositions were systematically investigated. The composition of the glasses and structural aspects of the variations in the various compositions, are discussed in this section.

1. $x\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$ with $x = 0, 0.20$ and 0.30 . Vitreous SiO₂ is built up from SiO₄ tetrahedra in which all the four corner oxygens are bridges between connected tetrahedra, thus forming a three dimensional silicate network. These oxygen atoms are called bridging oxygens (BOs). The introduction of one Na₂O unit causes the rupture of one Si-O-Si bond and two non-bridging oxygens (NBOs) are formed, and the network is partly broken up.

2. $(0.30-y)\text{Na}_2\text{O} \cdot y\text{CaO} \cdot 0.70\text{SiO}_2$ with $y = 0, 0.05, 0.10$ and 0.15 .

By this substitution one Ca²⁺ ion takes over the position of two Na⁺ ions. Because the Na⁺ ions are already found in pairs near two NBOs [12], all the glasses in this system are isomorphous, as far as the silicate network is concerned, and the concentration of BOs and NBOs does not vary with y .

3. $(0.30-y)\text{Na}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot 0.70\text{SiO}_2$ with $y = 0, 0.05$ and 0.10 .

In these glasses Al₂O₃ is incorporated as two AlO₄⁻ units which are incorporated in the silicate network at the same position as a SiO₄ unit [12, 13]. One Na⁺ ion is associated with such an aluminate unit. This effect decreases the number of NBOs and the three dimensional silicate network structure as found in vitreous SiO₂ is gradually restored. The complete three dimensional network structure is restored at the high melting composition $y = 0.15$.

4. $(0.30-y)\text{Na}_2\text{O} \cdot y\text{B}_2\text{O}_3 \cdot 0.70\text{SiO}_2$ with $y = 0, 0.05, 0.10$ and 0.15 .

At small contents, B₂O₃ is incorporated as a BO₄⁻ unit, similar to Al₂O₃. At larger contents ($y > 0.08$), metaborate (B₃O₆³⁻) and tetraborate (B₄O₇²⁻) are also formed [14]. In the metaborate units all the boron

atoms are 3-coordinated and three NBOs are present, while in the tetraborate unit only BOs are found, with two 3-coordinated and two 4-coordinated borons. The BO₄⁻ units are taken up by the silicate network as reedmergnerite units (BSi₄O₁₀⁻). According to Bray [14], the quantity of B₂O₃ taken up by the silicate network is limited by the fact that only reedmergnerite units (BSi₄O₁₀⁻) can be incorporated by the silicate network. The remaining borate units will form a separate borate network and the distribution of the units over both networks depends strongly on the overall glass composition. Both networks are intertwined in rapidly cooled glasses. By a heat treatment the two networks progressively separate at a more macroscopic level, often giving rise to phase separation.

5. $0.5x\text{Na}_2\text{O} \cdot 0.5xB_2\text{O}_3 \cdot (1-x)\text{SiO}_2$ with $x = 0, 0.22, 0.30$ and 0.44 .

As in the previous system these glasses contain both 3- and 4-coordinated boron in reedmergnerite (BSi₄O₁₀⁻), metaborate and tetraborate units [14].

6. $0.1\text{Na}_2\text{O} \cdot 0.1\text{B}_2\text{O}_3 \cdot (0.1-z)\text{CaO} \cdot z\text{Al}_2\text{O}_3 \cdot 0.70\text{SiO}_2$ with $z = 0, 0.025, 0.05$ and 0.10 .

7. $0.1\text{Na}_2\text{O} \cdot 0.1\text{B}_2\text{O}_3 \cdot (0.1-z)\text{ZnO} \cdot z\text{Al}_2\text{O}_3 \cdot 0.70\text{SiO}_2$ with $z = 0, 0.025, 0.05$ and 0.10 .

Structurally the glasses in systems 6-7 are complex due to the presence of both boron and aluminium. From an investigation by Araujo and Hares [15] it can be concluded that, as Na₂O is added, the formation of AlO₄⁻ precedes the formation of BO₄⁻ units. Furthermore, it is proposed that no B-O-B and Al-O-Al bonds are found in the silicate network. Considering the chemical composition, it can be expected that at $z = 0$, NBOs are present while at $z = 0.05$ most of the oxygens are BOs, but some metaborate and tetraborate units are also present [14]. At $z > 0.05$ the quantity of network-forming oxides capable of binding the network modifiers exceeds the quantity of network modifiers. This probably leads to the formation of BO₃ units which are taken up by the borate network.

8. Some special interesting glasses related to those mentioned in 1-7: (a) $0.125\text{Na}_2\text{O} \cdot 0.125\text{ZnO} \cdot 0.125\text{Al}_2\text{O}_3 \cdot 0.625\text{SiO}_2$; (b) $0.20\text{K}_2\text{O} \cdot 0.10\text{CaO} \cdot 0.70\text{SiO}_2$; (c) $0.20\text{Na}_2\text{O} \cdot 0.10\text{MgO} \cdot 0.70\text{SiO}_2$; (d) $0.20\text{Na}_2\text{O} \cdot 0.10\text{ZnO} \cdot 0.70\text{SiO}_2$. The $0.125\text{Na}_2\text{O} \cdot 0.125\text{ZnO} \cdot 0.125\text{Al}_2\text{O}_3 \cdot 0.625\text{SiO}_2$ glass is of interest because it contains no NBOs although the SiO₂ content is only 62.5%. It has a three dimensional network structure like SiO₂ [16, 17]. The three other glasses are related to the $0.20\text{Na}_2\text{O} \cdot 0.10\text{CaO} \cdot 0.70\text{SiO}_2$ glass, with K₂O substituted for Na₂O and ZnO and MgO substituted for CaO, respectively.

4. Results

The dissolution rate, v_e , of a glass is determined by measuring the depth of the etched groove as a function of time. Fig. 1 shows the groove depth versus time curves for some typical glasses. The curve is linear, indicating a time independent dissolution rate in these experiments. For two glasses: $0.30\text{Na}_2\text{O} \cdot 0.70\text{SiO}_2$ and $0.22\text{Na}_2\text{O} \cdot 0.22\text{B}_2\text{O}_3 \cdot 0.56\text{SiO}_2$, the line intersects with the dissolution depth axis. These two glasses

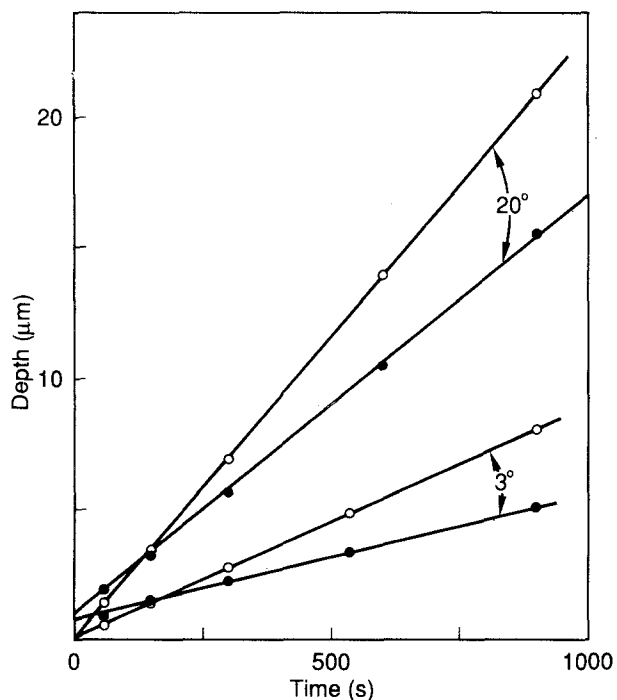


Figure 1 The depth of the etched region versus etching time for the glasses (●) $0.30\text{Na}_2\text{O}\cdot 0.70\text{SiO}_2$ and (○) $0.15\text{Na}_2\text{O}\cdot 0.15\text{CaO}\cdot 0.70\text{SiO}_2$ at 3 and 20°C.

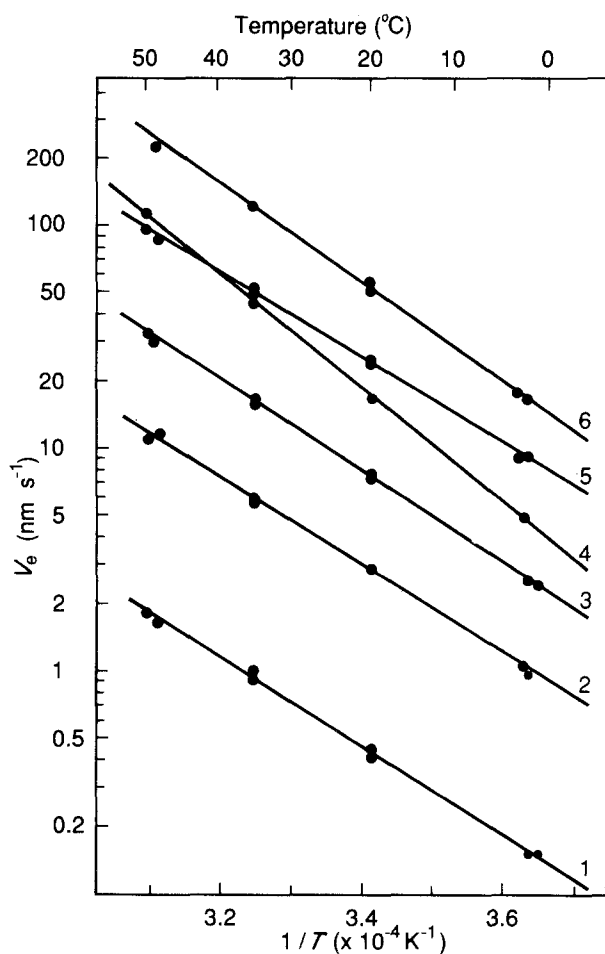


Figure 2 A selection of $\ln(v_e)$ versus $1/T$ curves of some typical glasses: 1. SiO_2 ; 2. $0.11\text{Na}_2\text{O}\cdot 0.11\text{B}_2\text{O}_3\cdot 0.78\text{SiO}_2$; 3. $0.15\text{Na}_2\text{O}\cdot 0.15\text{B}_2\text{O}_3\cdot 0.70\text{SiO}_2$; 4. $0.30\text{Na}_2\text{O}\cdot 0.70\text{SiO}_2$; 5. $0.15\text{Na}_2\text{O}\cdot 0.15\text{CaO}\cdot 0.70\text{SiO}_2$; 6. $0.125\text{Na}_2\text{O}\cdot 0.125\text{ZnO}\cdot 0.125\text{Al}_2\text{O}_3\cdot 0.625\text{SiO}_2$.

were also found to be very sensitive towards atmospheric corrosion and although care was taken to avoid any contact with the ambient atmosphere and to adapt the cleaning procedure, a corroded surface layer appears to be present, as is manifested in the fast dissolution rate in the first few seconds of contact with the etchant. For all other glasses this effect did not occur, as is illustrated with the data for the $0.15\text{Na}_2\text{O}\cdot 0.15\text{CaO}\cdot 0.70\text{SiO}_2$ glass. The dissolution rate was determined from the gradient of the dissolution depth versus time curve, thus eliminating effects of surface modifications caused by cleaning, chromium etching and corrosion.

Fig. 2 shows the $\log(v_e)$ versus $1/T$ curves plotted for some typical glasses in the 1–50°C temperature range. Table I gives the dissolution rate at 20°C ($v_e(20^\circ\text{C})$) and the activation energy of the dissolution reaction, E_a . The E_a values were obtained by fitting the relation $v_e = v_0 \exp(-E_a/RT)$ to the dissolution rate versus temperature data as in Fig. 2.

The main effects which are also illustrated in Figs 3 and 4, are as follows:

1. Fig. 3 shows that the introduction of Na_2O into the vitreous SiO_2 strongly increases the glass dissolution rate.
2. The substitution of CaO for Na_2O has a relatively small influence (Fig. 4).

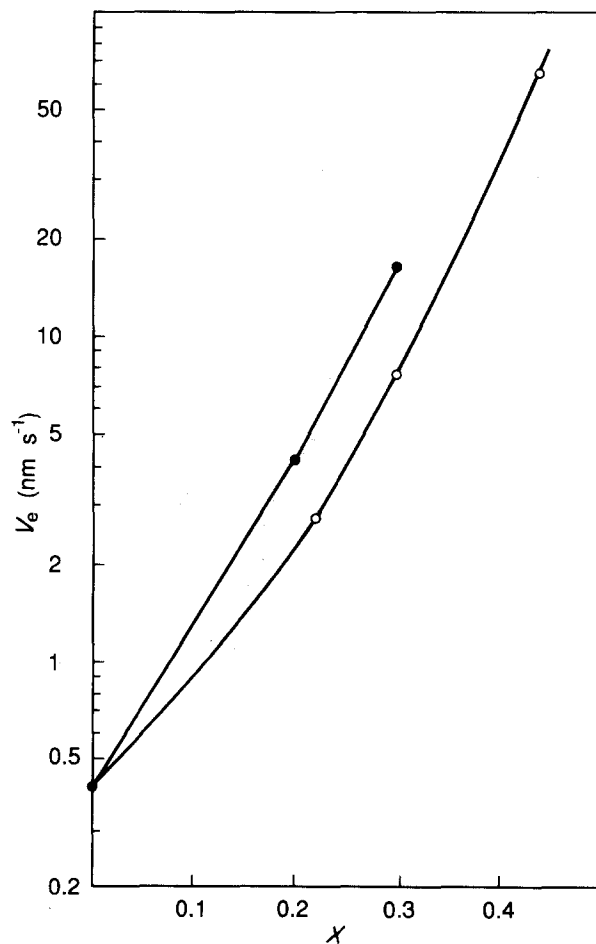


Figure 3 The dissolution rate v_e at 20°C for glasses in the systems (●) $x\text{Na}_2\text{O}\cdot (1-x)\text{SiO}_2$ and (○) $0.5x\text{Na}_2\text{O}\cdot 0.5xB_2\text{O}_3\cdot (1-x)\text{SiO}_2$.

TABLE 1 The activation energy E_a , dissolution rate at 20°C $v_e(20^\circ\text{C})$, the SiO_2 concentration $[\text{SiO}_2]$ and connectivity of the silicate network D_1 of the glasses investigated

Glass	E_a kJ mol^{-1}	$v_e(20^\circ\text{C})$ nm s^{-1}	$[\text{SiO}_2]$ mmol cm^{-3}	D_1
System 1: $x\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$				
$x = 0$	38.6	0.41	36.9	1
0.20	36.0	4.2	31.6	0.833
0.30	49.6	16.5	28.5	0.713
System 2: $(0.30-y)\text{Na}_2\text{O} \cdot y\text{CaO} \cdot 0.70\text{SiO}_2$				
$y = 0$	49.6	16.5	28.5	0.713
0.05	38.3	16.8	28.9	0.713
0.10	37.1	22.4	29.4	0.713
0.15	36.4	24.1	30.0	0.713
System 3: $(0.30-y)\text{Na}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot 0.70\text{SiO}_2$				
$y = 0$	49.6	16.5	28.5	0.713
0.05	38.1	10.0	27.3	0.833
0.10	38.5	14.5	26.3	0.926
System 4: $(0.30-y)\text{Na}_2\text{O} \cdot y\text{B}_2\text{O}_3 \cdot 0.70\text{SiO}_2$				
$y = 0$	49.6	16.5	28.5	0.713
0.05	37.8	7.9	28.5	0.833
0.10	37.2	8.3	28.5	0.920
0.15	38.4	7.6	28.1	0.977
System 5: $0.5x\text{Na}_2\text{O} \cdot 0.5x\text{B}_2\text{O}_3 \cdot (1-x)\text{SiO}_2$				
$x = 0$	38.6	0.41	36.9	1
0.11	38.3	2.75	30.7	0.997
0.15	38.4	7.6	28.1	0.977
0.22	54.5	65.6	22.3	0.930
System 6: $0.10\text{Na}_2\text{O} \cdot 0.10\text{B}_2\text{O}_3 \cdot (0.10-z)\text{CaO} \cdot z\text{Al}_2\text{O}_3 \cdot 0.70\text{SiO}_2$				
$z = 0$	38.9	10.1	29.6	0.920
0.025	39.7	7.5	28.7	0.960
0.05	40.3	8.5	27.5	0.997
0.10	36.8	3.2	24.8	1.000
System 7: $0.10\text{Na}_2\text{O} \cdot 0.10\text{B}_2\text{O}_3 \cdot (0.10-x)\text{ZnO} \cdot x\text{Al}_2\text{O}_3 \cdot 0.70\text{SiO}_2$				
$x = 0$	38.6	6.2	29.6	0.920
0.025	39.2	6.4	28.7	0.960
0.05	39.8	8.2	27.5	0.997
0.10	36.8	3.2	24.8	1.000
$0.125\text{Na}_2\text{O} \cdot 0.125\text{ZnO} \cdot 0.125\text{Al}_2\text{O}_3 \cdot 0.625\text{SiO}_2$	41.5	51	24.3	1.000
$0.20\text{K}_2\text{O} \cdot 0.10\text{CaO} \cdot 0.70\text{SiO}_2$	40.4	65.5	26.3	0.713
$0.20\text{Na}_2\text{O} \cdot 0.10\text{MgO} \cdot 0.70\text{SiO}_2$	34.5	18.2	29.6	0.713
$0.20\text{Na}_2\text{O} \cdot 0.10\text{ZnO} \cdot 0.70\text{SiO}_2$	35.7	18.5	29.4	0.713

3. With 5 mol % Al_2O_3 or B_2O_3 , v_e decreases sharply (Fig. 4). At 10% Al_2O_3 , v_e increases again. With B_2O_3 , v_e remains at a constant level.

4. The substitution of $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ for SiO_2 also shows a significant increase of v_e with x , which is only a factor of two smaller than measured for the substitution of Na_2O (Fig. 3).

5. In the structurally more complex borosilicate glasses of systems 6 and 7 the replacement of MO by Al_2O_3 results in complex v_e -composition relations. In the structurally complex glasses as in systems 5-7 the effects can only be described qualitatively.

5. Discussion

For many physical properties of silicate glasses there exist well established relations, often linear in first approximation, between the chemical composition of the glass and the value of the particular property. This is the case for such diverse properties as refractive

index, viscosity and elastic modulus, over wide compositional ranges [18]. For chemical properties such as chemical durability [18] and, as is shown in this study, the dissolution rate in HF solutions, such linear relations are clearly not observed.

For a silicate glass to dissolve in a solvent, it is necessary that the silicate network structure is broken down. In the glasses studied here this network is built up from interconnected SiO_4 , AlO_4^- , BO_4^- and in some glasses ZnO_4^{2-} tetrahedra. The network-building tetrahedra are connected with $X-O-X$ bonds in which at least one of the XO_4^- units is a SiO_4 unit [15]. The breaking of these bonds occurs by the attack of the active fluoride species. From studies on the dissolution rate of vitreous SiO_2 [2, 3, 5, 10, 19, 20], alkali lime-silicates [9] and crystalline silicates such as feldspars [21-24], the following model of the mechanism of the dissolution process can be constructed. The dissolution reaction is surface reaction rate controlled [9, 10, 19] and in principle proceeds in three steps:

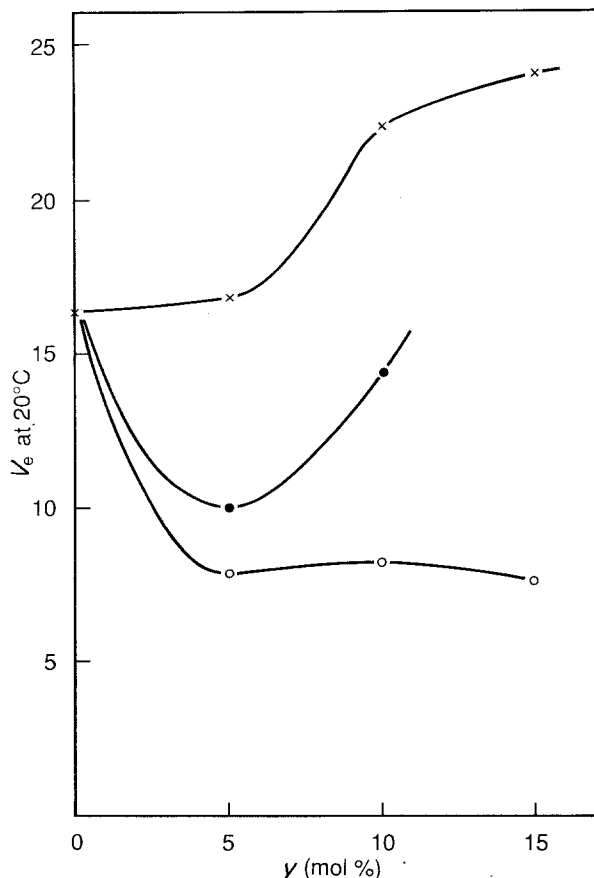


Figure 4 The dissolution rate v_e at 20 °C for glasses in the systems $(0.30 - y)\text{Na}_2\text{O} \cdot y\text{M}_x\text{O}_y \cdot 0.70\text{SiO}_2$ with $M = (\times)$ Ca, (\bullet) Al, (\circ) B.

1. The adsorption of the active fluoride species on the surface. These are considered to be either HF and HF_2^- or both [2, 9, 10]. This step is usually considered to be fast compared with the dissolution rate [19]. The coverage of the surface with reactive species is given by a Langmuir isotherm [9] which, at low HF concentrations, results in a linear dissolution rate dependence on the concentration.

2. The rupture of all the Si–O–Si and X–O–Si bonds surrounding the tetrahedra units which form the glass network structure. This process is catalysed by the presence of H^+ ions.

3. The desorption of the soluble reaction product. When poorly soluble reaction products are formed, it has been proposed that this step becomes dissolution rate determining [25]. Liang and Readey [19] consider this step to be rate determining, because it involves coordination changes.

As an additional important effect in this respect, Kline and Fogler [22, 23] found that in the dissolution process of feldspars (e.g., MAlSi_3O_8 with $M = \text{Na, K, Li}$) and related crystalline silicates leaching of alkali ions precedes the actual dissolution of the silicate network. Because in a previous paper [9] it was argued that the dissolution reaction mechanism of crystalline silicates and multicomponent silicate glasses are similar, alkali leaching can effect the dissolution rate of these glasses.

The dissolution of the structurally simplest vitreous SiO_2 involves the subsequent rupture of all four

Si–O–Si bonds surrounding each SiO_4 tetrahedron. The introduction of a network modifier oxide such as Na_2O and CaO also breaks one Si–O–Si bond to form two SiO_4 tetrahedra each having one NBO, breaking down the three dimensional network present in vitreous SiO_2 . This substitution clearly does lead to a significant increase in the dissolution rate as is found in system 1 (Fig. 3). This observation strongly suggests that the connectivity in the silicate network is an important factor in determining the dissolution rate. In vitreous silica each SiO_4 tetrahedra is connected to four others and no NBOs are present and its network can be considered to be three dimensional. In a glass with composition $0.33\text{NaO} \cdot 0.67\text{SiO}_2$ each SiO_4 tetrahedron contains two NBOs the network will be chain-like or one dimensional. In analogy a network formed by tetrahedra with one NBO can be called two dimensional. If we define a number D_1 as the degree of connectivity, referred to as D , and proportional to the network dimension can then be defined as

$$D_1 = \frac{3 - \{\text{NBO}\}}{3} \quad (1)$$

where $\{\text{NBO}\}$ is the main number of NBOs per network tetrahedron, a number which can be calculated from the chemical composition of the glass.

Glasses with a general composition $0.30(\text{Na}_2\text{O} + \text{MO}) \cdot 0.70\text{SiO}_2$ in systems 1, 2 and 8, all have a similar network structure with $D_1 = 0.713$. In the first approximation these glasses all have dissolution rates which are of the same magnitude, varying between 16.5 to 24.1 nm s^{-1} (Table I). It appears that the type of network modifier does not effect the dissolution rate to a large degree. One way to explain this phenomenon is by assuming that the removal of the alkali and alkaline-earth cations precedes the dissolution of the silicate network. This process can be considered as leaching and is not rate determining.

The formation of a leached layer on a dissolving, and therefore moving, interface has been described by Boksay *et al.* [26]. The mole fraction n of the leached ion in the depletion layer as a function of the distance to the interface y , where $y = 0$ indicates the moving interface, is given by

$$n = \exp\left(\frac{-a}{D}y\right) \frac{1}{\pi^{1/2}} \int_{-\infty}^s \exp(-p^2) dp - \frac{1}{\pi^{1/2}} \int_{-\infty}^r \exp(-p^2) dp + 1 - \exp\left(\frac{-a}{D}y\right) \quad (2)$$

in which $s = \frac{y - at}{(4Dt)^{1/2}}$ and $r = -\frac{y + at}{(4Dt)^{1/2}}$, a is the rate of network dissolution, t is the time of etching and D is the diffusion constant of the leaching ion in the glass (p is the integration, parameter). For two of the glasses studied here ($0.20\text{Na}_2\text{O} \cdot 0.80\text{SiO}_2$ and $0.20\text{Na}_2\text{O} \cdot 0.10\text{CaO} \cdot 0.70\text{SiO}_2$), the diffusion coefficient of Na^+ is available [27, 28]. These values (re-calculated for 20 °C using the activation energy of 90 kJ mol^{-1}) are $D = 6.10 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for the $0.20\text{Na}_2\text{O} \cdot 0.80\text{SiO}_2$ glass and $D = 4.9 \cdot 10^{-17} \text{ m}^2 \text{ s}^{-1}$ for the $0.20\text{Na}_2\text{O} \cdot 0.10\text{CaO} \cdot 0.70\text{SiO}_2$ glass. If we take

$y_{0.5}$ as the value of y where $n = 0.5$ as a characteristic thickness of the depletion layer and using Equation 2 we obtain $y_{0.5} = 99 \mu\text{m}$ for the former glass and $y_{0.5} = 1.5 \text{ nm}$ for the latter. Although both thicknesses are very different, it is important to note that in both cases surfaces depleted in alkali ions are present during dissolution. So it can be concluded that at the moment of dissolution the surface of the glass is transformed into a hydrated layer of which the composition can be represented as $\text{Si}_7\text{O}_{11}(\text{OH})_6$, at least when it is assumed that the alkaline earth ions are also leached out. The dissolution rate of this layer is then the rate determining factor.

For the $0.30\text{K}_2\text{O} \cdot 0.70\text{SiO}_2$ glass with potassium instead of sodium a much higher dissolution rate is observed. This indicates that other structural factors are also important in determining the glass dissolution rate. Although the leaching rate of the potassium glass is higher than that of the sodium glass the hydrated silica layer has the same composition. The only major difference is the fact that the molar volume of this layer is significantly smaller for the potassium glass. After leaching this will result in a more open hydrated silica layer. The accessibility of Si–O–Si bonds further away from the surface for the adsorbed fluorine reactant can then be expected to increase resulting in the observed higher dissolution rate. So the dissolution rate of the hydrated layer will depend on its density, which is dependent on the molar concentration of SiO_2 referred to as $[\text{SiO}_2]$ in the original glass.

On the introduction of the other network-forming oxides XO_4^- tetrahedra are present which are taken up by the silicate network in which X–O–Si are formed. This is the case for Al_2O_3 and in some glasses ZnO. For B_2O_3 the structural changes are more complex. Part of the B_2O_3 will be taken up by the silicate network but the other part will form a separate borate-based network (see Section 4).

It can be expected in view of the low corrosion resistance of borate glasses that the connectivity of the silicate-based network determines the dissolution rate. The way the presence of other bonds in the silicate-based glass network affects the dissolution rate of the glass depends on the difference in rupture rate of the various bonds. If the rate of rupture of the bonds is the same, the dissolution rate would primarily depend on the number of NBOs in the silicate-based network of the glass indicated by D_1 . However, this is not observed, as evinced by the observation that an increase above 5% of the Al_2O_3 and B_2O_3 contents in systems 3 and 4 does not continue to lower the dissolution rate. The observation that the $0.125\text{Na}_2\text{O} \cdot 0.125\text{ZnO} \cdot 0.125\text{Al}_2\text{O}_3 \cdot 0.625\text{SiO}_2$ glass, which contains no NBOs has a high dissolution rate also contradicts this assumption.

The latter glass does have a relatively low SiO_2 content. This indicates that in glasses containing more than one network-forming oxide the SiO_2 concentration $[\text{SiO}_2]$ is an important factor in determining the dissolution rate. Consequently the rate of rupture of the other bonds must be higher. The dissolution process can be even more complex because the leached surface layer will contain H^+ ions. In the first place

these will catalyse the rupture reaction of a Si–O–Si bond [9, 21]. Furthermore, these could cause a preferential depletion of Al^{3+} ions in the surface layer as was observed in the reaction of albite $\text{NaAlSi}_3\text{O}_8$ in mild acidic aqueous solutions [29].

We have seen in the preceding discussion that the dissolution rate is influenced by two structural and/or compositional factors: The connectivity of the silicate network D_1 and the SiO_2 concentration $[\text{SiO}_2]$. This dependency can be represented by the equation

$$v_e = \frac{c}{D_1^p [\text{SiO}_2]^q} \quad (3)$$

in which it is assumed that v_e is inverse proportional to D_1 to the power p and $[\text{SiO}_2]$ to the power q , c is a constant. All the dissolution rate data at 20°C were fitted to this equation using a multiple linear regression technique. The values of D_1 and $[\text{SiO}_2]$ used in this calculation are given in Table I. $[\text{SiO}_2]$ is calculated from the composition of the glass and its calculated molar volume [18]. D_1 is calculated from the composition of the glass. The composition of the glass determines its structure, and the mean number of NBOs in each tetrahedra in the silicate-based network can be determined in this way. The structural information as presented in a condensed form in Section 1.4 is used. For B_2O_3 -containing glasses the model of Bray [14] is used to estimate the quantity of boron taken up in the silicate network as a reedmergnerite unit and the part present as a separate borate network. Fig. 5 shows the best fit obtained in the linear regression analysis with $p = 4.1$ and $q = 9.5$. All the measured dissolution rates except one, are within a factor of 2 from the mean curve. The deviating glass is $0.10\text{Na}_2\text{O} \cdot 0.10\text{B}_2\text{O}_3 \cdot 0.10\text{Al}_2\text{O}_3 \cdot 0.70\text{SiO}_2$, a glass which has a composition and structure which is different from all the other glasses because the sum of

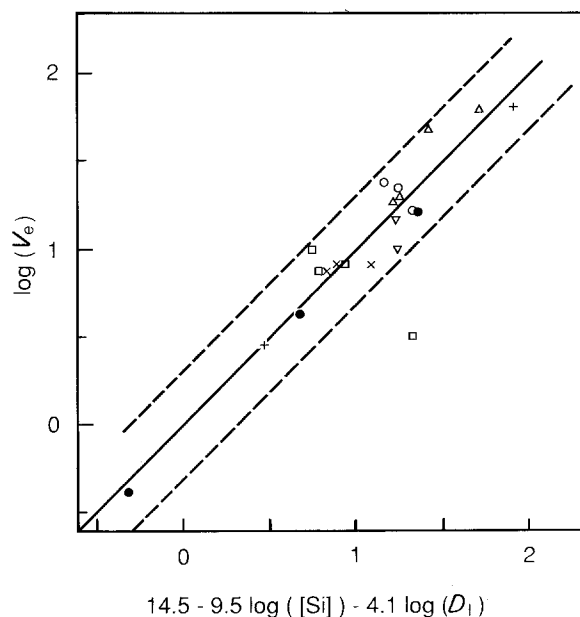


Figure 5 The dissolution rate at 20°C versus $3.5 \cdot 10^{14} [\text{SiO}_2]^{-9.5} D_1^{-4.1}$. The best fit curve is shown (—), together with the region between the hatched lines in which the dissolution rate varies within a factor 2 from the best fit curve. Glasses in system (●) 1, (○) 2, (▽) 3, (×) 4, (+) 5, (□) 6 and (△) 8.

network-forming oxides B_2O_3 and Al_2O_3 exceeds the sum of network modifier.

However, disregarding this last glass, the variations around the mean fitted curve are sufficiently small to support the model of dissolution of a multicomponent silicate based glass presented here, taking into account that many other factors will have an influence. Some of these are:

1. Variations in adsorption behaviour of the fluorine species.
2. Diffusion rate of catalytic H^+ ions into the leached layer.
3. Formation of insoluble boro-, silico- or aluminofluorates.
4. Effects of differences in leaching behaviour of the various cations.
5. Smaller structural effects of substitutions such as preferent orientations, preferent positions of groups in the silicate network, phase separation, etc.

In view of all these parameters it is somewhat surprising to find the relation as is illustrated in Fig. 5. The high values of p and q indicate that the dissolution rate is very sensitive towards the density of the hydrated silicate surface layer obtained after leaching. The lower density and pores in the hydrated surface layer allows the adsorbed fluorine species to attack a Si-O bond further away from the surface of the glass. Presumably there exists diffusion of the adsorbed fluorine molecules into the leached layer. This is possible because the adsorption rate is fast compared with the dissolution rate. The model presented here agrees very well with the data presented by Honigmann [11]. The introduction of the network modifiers Na_2O , K_2O , CaO , MgO , ZnO in a $0.18Na_2O \cdot 0.82SiO_2$ glass results in an increase in dissolution rate which is similar for all these substitutions. The introduction of Al_2O_3 and B_2O_3 in this glass results in a much smaller increase. The data presented for calcium aluminosilicate glasses [4] show an increase in dissolution rate when CaO as well as Al_2O_3 are introduced. Both investigations support the role of both the silicon concentration and the network connectivity as proposed in this paper.

The activation energy of the dissolution reaction is given in Table I. For most of the glasses the activation energy lies in the range of 35–42 $kJ mol^{-1}$. This strongly supports the conclusion that the reaction mechanism of dissolution in all these glasses is the same as in vitreous SiO_2 and therefore involves only the rupture of the Si-O-Si bond. The glasses $0.30Na_2O \cdot 0.70SiO_2$ and $0.22Na_2O \cdot 0.22B_2O_3 \cdot 0.56SiO_2$ have a significant higher activation energy of 50 and 55 $kJ mol^{-1}$. These two glasses are also the only ones to show a large tendency towards corrosion by atmospheric water. The higher value is also near to the estimated activation energy of the leaching of sodium ions from a $0.30Na_2O \cdot SiO_2$ glass which is 55–60 $kJ mol^{-1}$ [30]. This similarity in activation energy indicates that the higher value is related to the formation of the leached layer. It indicates that for these two glasses the dissolution rate of the leached layer becomes so high that the leach rate of the alkalis becomes rate determining.

6. Conclusions

The dissolution rate of a multicomponent silicate glass in an aqueous HF solution strongly depends in a complex way on its chemical composition. In the type of silicate glasses investigated in this study the dissolution rate is predominantly determined by two factors: The connectivity of the silicate-based network and the silicon concentration in the glass. The alkali and alkali earth oxides are leached from the glass prior to its dissolution and the rupture rate of bonds other than Si-O, such as Al-O and B-O present in the silicate-based network is much higher than that of the Si-O bond. The following mechanism of the dissolution of a multicomponent silicate glass is proposed:

1. The adsorption of the active fluorine species on the surface.
2. The leaching from the alkali and alkaline earth cations to form a porous layer.
3. Fast rupture of the X-O-Si bonds with $X = B, Al$ or Zn .
4. The rate determining rupture of the Si-O-Si bonds, also of bonds further away from the interface, possibly through diffusion of HF molecules and/or HF_2^- ions into the leached surface layer.
5. Desorption of fluorosilicates.

In first approximation the kinetics of the dissolution reaction can be presented as:

$$v_e = 3.54 \times 10^{14} \times D_1^{-4.1} \times [SiO_2]^{-9.5} \text{ nm s}^{-1}$$

A more detailed study incorporating heat of dissolution, adsorption and other surface phenomena is necessary, in order to evaluate which factors or combination of factors are determining the dissolution rate in HF solutions of a particular glass composition.

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