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The absence of a mixed-alkali effect in the leaching of corrosion-resistant glasses

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Alkali depth profiles in water-leached glasses with molar composition $16A_2O \cdot 8CaO \cdot 2MgO \cdot 1Al_2O_3 \cdot 73SiO_2$ (A = Na, K and Na + K) were determined using secondary ion mass spectroscopy (SIMS). In the glass containing only sodium an apparent correlation exists between the alkali diffusion coefficient derived from the leaching kinetics, assuming this process is governed by ion exchange, and that determined via electrical conductivity measurements in the dry glass. In the other two glasses the diffusion coefficients derived on the basis of ion exchange are much higher than the ones found in the dry glasses. These data can be interpreted in terms of a model for the leaching of glass where the rate-determining step is the diffusion of molecular water.

1. Introduction

When a glass sample is exposed to water two processes will occur: the leaching of alkali ions and the dissolution of the glass network. Initially the leaching process will predominate, the alkali release being proportional to the square root of time. Until a few years ago it was generally accepted that this process is governed by the ion exchange between the alkali ions in the glass and oxonium ions in the liquid [1].

The validity of this assumption has been questioned by one of us [2, 3] as well as by Bunker *et al.* [4]. The alkali diffusion coefficients calculated from the leaching data are inconsistent with the diffusion coefficients measured in the dry glasses. If glass leaching is governed by ion exchange one would expect on the basis of the mixed-alkali effect that the replacement of part of sodium ions in the glass by potassium ions results in an improved corrosion resistance. This is not, however, observed in glasses with composition $20Na_2O \cdot 10CaO \cdot 70SiO_2$ [2] and $25Na_2O \cdot 75SiO_2$ [4]. On the basis of these as well as other observations both groups came to the conclusion that the diffusion of molecular water is the rate-determining step in glass leaching.

In a recent paper Doremus *et al.* [5] have argued that the discrepancy in the diffusion data for such laboratory glasses is caused by the formation of a transformed surface layer, in which layer alkali diffusion would proceed much faster. A transformed layer would not be expected to develop, however, when more durable glasses such as a commercial soda-lime glass are exposed to water. In the latter glass a good correlation is indeed found between the sodium diffusion coefficient derived from the leaching data and the diffusion coefficient in the dry glass.

Therefore it is interesting to investigate whether or not a mixed-alkali effect is observed in more durable glasses. If ion interdiffusion is the rate-determining step an improved corrosion resistance is to be expected. If, on the contrary, the diffusion of molecular water is the rate-determining step, such an improvement will not be found.

2. Experimental details

Glasses 1 to 3 (see Table I) were prepared from reagent grade chemicals by melting at 1500 to 1600° C in a 90 Pt/10 Rh crucible in air. Oxygen was bubbled through for 1 h in order to homogenize the melt. After the melts had been allowed to become bubble-free they were cooled down in the furnace. Small discs (diameter = 15 mm, $l = 2$ mm) were cut with a low-speed diamond saw and both sides were ground with SiC paper to 800 grit and subsequently polished with a colloidal silica solution.

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TABLE I Batch composition of glasses (mol%)

Oxide	Glass number		
	1	2	3
Na_2O	16	8	–
K_2O	–	8	16
CaO	8	8	8
MgO	2	2	2
Al_2O_3	1	1	1
SiO_2	73	73	73

Before leaching, the samples were rinsed in a degreasing agent and the contaminated surface layer was removed by etching the samples for 5 min with a 4% HF solution. The discs were clamped horizontally in a PTFE holder and immersed in a quartz glass reservoir containing 250 ml of deionized water. The resevoir was held at a constant temperature of 70 ± 1° C. The samples were rotated at 150 r.p.m., the direction of rotation being reversed every five cycles. All samples were exposed for 4 and 16 h, respectively, and analysed immediately afterwards.

Depth profiles of the glass components were measured with a single-focusing secondary ion mass spectrometer. A rastered beam (1 x 1.5 mm) of 6 keV O_2^+ ions was used. The primary ion current ranged from 0.1 to 1.0 μA. A tantalum diaphragm with a 600 μm orifice was place on top of the sample surface and reduced the charging during ion bombardment to a low and stable value of 50 V [6]. Only ions originating from the central 300 μm of the sputter crater were analysed. After bombardment the depth of the sputter crater was determined using a stylus instrument. The sputter rate, which is directly proportional to the impinging ion density, equalled about 0.5 nm sec^{-1} for a primary ion current of 1 μA. The quantification of the data was based on relative sensitivity factors, using silicon as an internal standard.

TABLE II Leaching depth of sodium and potassium after hydration in water (70° C)

Time of exposure (h)	Depth (nm)	
	Sodium	Potassium
Glass 1		
4	60 ± 10	
16	130 ± 10	
Glass 2		
4	70 ± 5	55 ± 5
16	150 ± 10	125 ± 10
Glass 3		
4		360 ± 20
16		750 ± 40

The electrical resistivity of the glass samples was measured by means of a pulsed d.c. procedure. A 100 V pulse was applied across the sample for 1 sec and the resulting current averaged over this period of time. Subsequently the same procedure was followed after reversing the polarity of the power supply. With this experimental set-up resistivities up to 10^8 Ωm can be accurately measured in the temperature range 30 to 900° C.

3. Results

Table II gives the half-widths of the alkali depletion layers as determined using secondary ion mass spectroscopy (SIMS). For exposure times up to 16 h a square root time dependence of the alkali depletion is observed for all glass compositions. The effect of network dissolution can therefore be neglected under the experimental conditions used. The experimental SIMS profiles are given in Figs. 1 to 3. The data are plotted on a normalized depth scale, so that the time dependence cancels out. Typical S-shaped profiles are observed for all alkalis.

The data of glass no. 1 are in good agreement

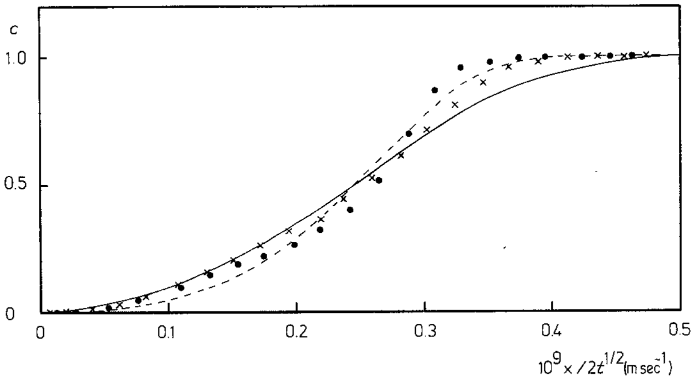

Figure 1 Sodium distribution in glass no. 1 after 4 h x and 16 h • exposure to H_2O at 70° C, together with the predicted behaviour on the basis of ion exchange with $D_{Na} = 6.1 \times 10^{-19}$ and $D_H = 6.1 \times 10^{-20}$ ——, and with $D_{Na} = 3.1 \times 10^{-18}$ and $D_H = 3.1 \times 10^{-20}$ m² sec^{-1} – – – respectively.

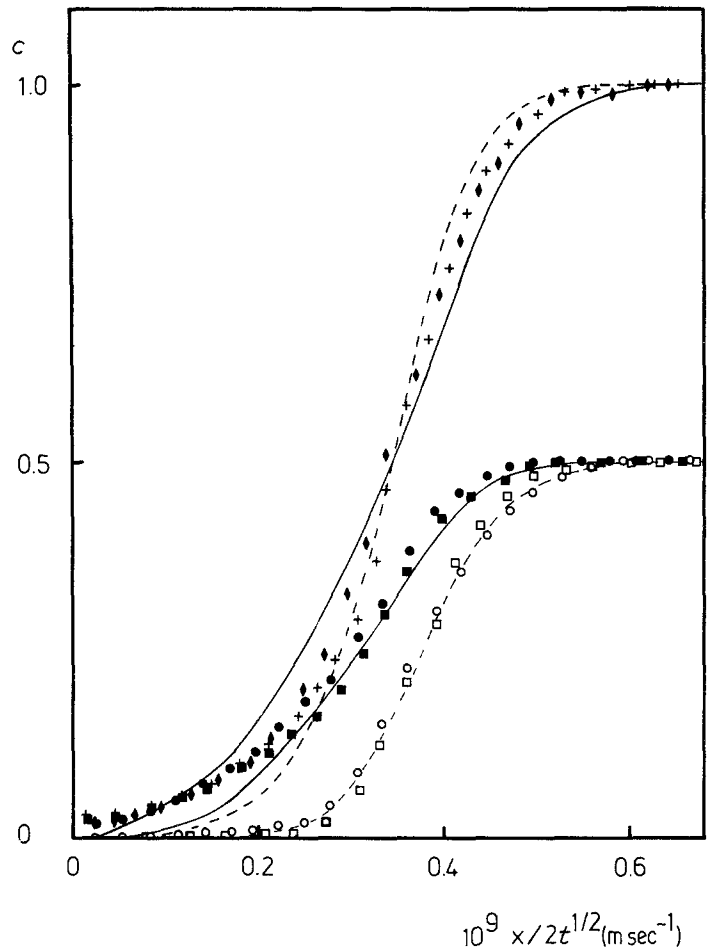

Figure 2 Sodium distribution after 4 h ○ and 16 h □, potassium distribution after 4 h ● and 16 h ■ and the total alkali distribution in glass no. 2 after 4 h ◇ and 16 h + exposure to H_2O at 70° C, together with the predicted behaviour on the basis of ion exchange with $D_A = 5.6 \times 10^{-18}$ and $D_H = 5.6 \times 10^{-20}$ ——, and with $D_A = 3.6 \times 10^{-17}$ and $D_H = 3.6 \times 10^{-20}$ m^2 sec^{-1} – – – respectively.

with those given by Lanford *et al.* [1] for a glass with a similar composition. They quote for a commercial soda-lime glass a half-width of the sodium depletion of 0.11 μm after 14 h of water exposure at 90° C.

In the mixed-alkali glass no. 2 the half-width of the potassium depletion is somewhat smaller than the one found for sodium. Similar results were previously obtained for a glass with composition $10Na_2O \cdot 10K_2O \cdot 10CaO \cdot 70SiO_2$ [2]. The total alkali depletion in glass no. 2 hardly deviates from the depletion found in glass no. 1.

A much larger potassium depletion is found in glass no. 3. This is in full agreement with the lower corrosion resistance found in different potassium glasses as compared with their sodium-containing

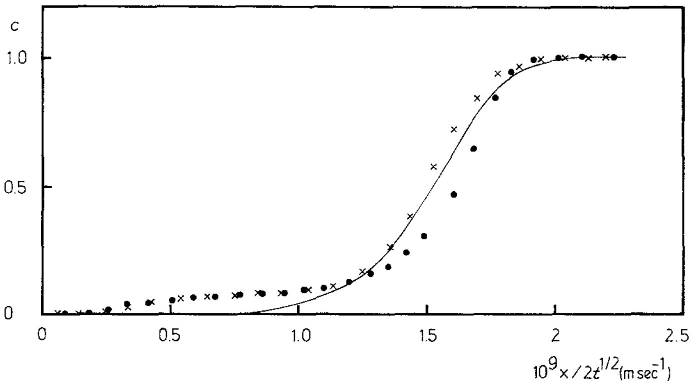

Figure 3 Potassium distribution in glass no. 3 after 4 h x and 16 h ● exposure to H_2O at 70° C, together with the predicted behaviour on the basis of ion exchange with $D_K = 4.5 \times 10^{-15}$ and $D_H = 4.5 \times 10^{-19}$ m^2 sec^{-1} ——.

TABLE III Electrical resistivity and alkali diffusion coefficient for the glasses studied

Glass	$\rho_{70^\circ C}$(Ω m)	$\bar{c}$(mol m^{-3})	D(m^2 sec^{-1})
1	1.5×10^{8}	1.4×10^{4}	1.0×10^{-19}
2	1.0×10^{12}	1.3×10^{4}	1.4×10^{-23}
3	1.6×10^{9}	1.2×10^{4}	7.9×10^{-21}

counterparts [7, 8]. The shape of the potassium profile deviates markedly from the one found in the less durable potassium silicate glasses by Dobos [9]. In the latter case the maximum slope of the potassium profile is found at the glass surface.

The electrical resistivity, ρ, of all glasses was determined in the temperature range 150 to 350° C. The extrapolated resistivity is given in Table III. The electrical resistivity is linked to the diffusion coefficient D_A of the mobile alkali ion by the following relation [10]:

$$1/\rho = f\frac{Z^2F^2D_A\bar{c}}{RT}$$

where z equals the charge of the diffusant, F is Faraday's constant, R the Boltzmann constant, T the absolute temperature and $\bar{c}$ the molar concentration of the mobile species. The $\bar{c}$ values used are based on the data given by Scholze [11]. For most glasses the Haven ratio, f, equals 0.2 to 1 [10]. The alkali diffusion coefficients given in Table III are derived from the electrical resistivity, assuming that the Haven ratio equals one. If the Haven ratio equalled 0.1 the diffusion coefficient would be ten times larger than the value quoted. For the mixed-alkali glass no 2 it is assumed that $D_{Na} = D_K$. If the mobility of one of the alkali ions is much higher than that of the other its D value will of course be twice as high.

4. Discussion

As pointed out above, the leaching of a glass with a composition similar to glass no. 1 can be described, according to Doremus *et al.* [5], by an ion exchange between the hydronium and the sodium ion. The interdiffusion coefficient, D, is given as [12]

$$D = \frac{D_H D_A}{c_A D_A + c_H D_H} \qquad (2)$$

where D_H and c_H are the diffusion coefficient and concentration of the hydronium ion, and D_A and c_A the diffusion coefficient and concentration of the alkali ion, respectively. For the sake of convenience all concentrations are normalized to the alkali bulk concentration. For $D_H > D_A$ S-shaped alkali profiles are predicted.

Fig. 1 gives the best fits to the experimental data of glass no. 1. From these fits it follows that $D_H = 3$ to 6×10^{-20} and $D_{Na} = 3.0$ to 0.6×10^{-18} m^2 sec^{-1}. The D_{Na} value derived on the basis of the electrical conductivity data (see Table II) equals 1.0 to 0.1×10^{-18} m^2 sec^{-1}, taking into account the uncertainity in the Haven ratio. For glass no. 1 the diffusion coefficient derived from the corrosion data correlates fairly well with the value derived from the electrical conductivity data, and the corrosion data could reasonably be explained by ion exchange.

In the mixed-alkali glass no. 2 the situation becomes more complicated. The problem of the interdiffusion of three compounds does not easily lend itself to a mathematical treatment and we will therefore follow another approach. The alkali diffusion coefficient can be estimated from the corrosion data by considering the total alkali concentration. In this way it is assumed that $D_{Na} = D_K = D_A$. The best fits to the alkali profiles result in $D_A = 6.0$ to 0.4×10^{-17} m^2 sec^{-1}. It follows from the electrical conductivity data that D_A should equal 10^{-23} to 10^{-24} m^2 sec^{-1}. A large discrepancy exists between the D_A value derived from the corrosion data and the one derived from the electrical conductivity data, making the interpretation of the leaching kinetics on the basis of ion exchange rather doubtful. When glass no. 2 is compared with glass no. 1 it is found to have a quite similar corrosion behaviour. The much lower ion mobility in the former glass is apparently not reflected in the corrosion data.

An S-shaped potassium profile is also observed in glass no. 3, indicating that $D_K > D_H$. A best fit to the experimental data is given in Fig. 3. For high values of the D_K/D_H ratio the quality of the fit becomes less sensitive to the exact ratio chosen. The D_K value derived (5×10^{-15} m^2 sec^{-1}) is therefore estimated to be accurate within one or two orders of magnitude. Even when this large error is taken into account the D_K value based on the corrosion data cannot be reconciled with the value derived from the electrical conductivity data ($D_K = 10^{-19}$ to 10^{-20} m^2 sec^{-1}). This contrasts with the experimental data on some potassium silicate glasses [7]. In these glasses the potassium depletion can be explained by assuming

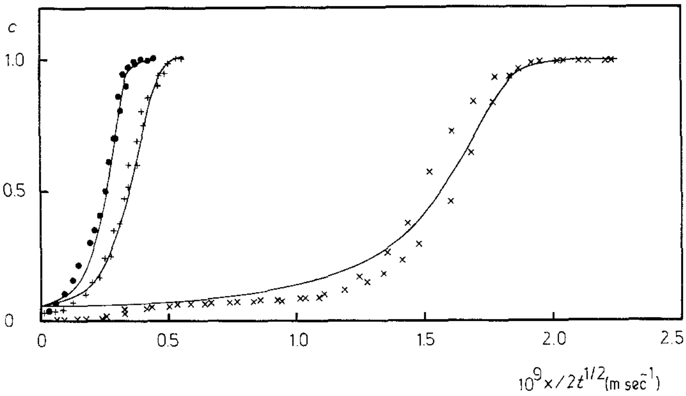

Figure 4 Total alkali distribution in glass no. 1 ●, glass no. 2 + and glass no. 3 x after exposure to H_2O at 70° C, together with the predicted behaviour on the basis of H_2O diffusion, where $c^0_{H_2O} = 1$, $K = 5 \times 10^{-2}$ and $D_{H_2O} = 1.7\ 10^{-19}$ in glass no. 1, 3.1×10^{-19} in glass no. 2 and $D_{H_2O} = 6.2 \times 10^{-18}$ m^2 sec^{-1} in glass no. 3 respectively.

that $D_K = D_H$. According to Lanford *et al.* [1] the similar ionic radius of the potassium and hydronium ion justifies why their mobilities should be the same. The data of glass no. 3 show that such a relation is not always found for glasses containing potassium.

Although glass no. 1 shows a fair correlation between the alkali diffusion coefficient derived from the corrosion data and the diffusion coefficient in the dry glass, such a correlation is not found in glasses no. 2 and no. 3. The fact that higher diffusion coefficients have to be invoked to explain the corrosion data for a large number of glasses is attributed by Doremus *et al.* [5] to the formation of a transformed layer. Phase separation is assumed to be the driving force for the formation of such a layer. However, the substitution of sodium by potassium will result in a decreased tendency towards phase separation. This tendency is indeed found to be smaller in the K_2O–SiO_2 than in the Na_2O–SiO_2 system [13]. Therefore no basis exists for invoking the formation of a transformed layer in the glasses containing potassium.

We will now examine the extent to which the experimental data can be explained by H_2O diffusion. The diffusing molecules are assumed to become trapped at the non-bridging oxygen atoms bonded to the alkali ions. In this reaction the negatively charged oxygen atoms are converted into silanol groups, resulting in the mobilization of the alkali ions. A mathematical description of such a process has been given [14, 15]. The width of the alkali depletion layer is thought to be determined by the water diffusion coefficient D_{H_2O} and to some extent also by the water content of the leached layer ($c^0_{H_2O}$). The shape of the profile and especially the amount of alkali retained in the leached layer is thought to be determined by K, the "dissociation constant" of the silanol groups.

With the experimental technique used it is not possible to determine quantitatively the hydrogen or H_2O content of the leached layer. In a leached glass with similar composition, Lanford *et al.* [1] have determined that the hydrogen concentration equals three times the sodium concentration originally present. Because each alkali is replaced by one hydrogen atom belonging to a silanol group, $c^0_{H_2O}$ will equal one. The best fits to the experimental data, using $c^0_{H_2O} = 1$, are given in Fig. 4. The much larger D_{H_2O} value found in glass no. 3 (6.2×10^{-18} m^2 sec^{-1}) as compared with the value found in glass no. 1 (1.7×10^{-19} m^2 sec^{-1}) can be explained on the basis of the higher porosity of the leached layer formed. Owing to the larger ionic size of the potassium ions the voids formed in the leached layer of glass no. 3 will be larger, thus enhancing the water mobility. The substitution of potassium for half the sodium has only a small effect on D_{H_2O}. Only a doubling of the diffusion coefficient is observed. It seems, therefore, that the smaller voids, originally occupied by the sodium ions, limit the water diffusion in glass no. 2.

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