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GLASSES : ION EXCHANGE OR DIFFUSION OF
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THE LEACHING OF SODIUM CONTAINING GLASSES : ION EXCHANGE OR DIFFUSION OF MOLECULAR WATER ?

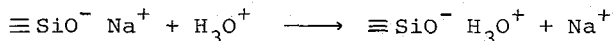
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Résumé. - La corrosion du verre a été étudiée à l'aide de la technique SIMS. La lixiviation des ions de sodium liés aux atomes d'oxygène non-pontants est déterminée par la diffusion de H_2O . Les ions liés aux entités AlO_4^- sont échangés contre H_3O^+ .

Abstract. - The corrosion of glass was studied using SIMS. The leaching of sodium ions bonded to non-bridging oxygen atoms is governed by the diffusion of H_2O . The sodium ions bonded to AlO_4^- -groups undergo an ion exchange with H_3O^+ .

1. **Introduction** - It is generally accepted that the leaching of glass is governed by an ion exchange between oxonium and sodium ions (1-2).



Recently, the authors proposed an alternative mechanism, in which the diffusion of H_2O would be the rate determining step (3-4).



Both mechanisms will be critically reviewed in this paper. The leaching in moderately weak acid solutions (pH = 4-7) will only be considered.

2. **Ion Exchange.** - Leached glasses, when measured with SIMS (fig. 1), exhibit typical S-shaped sodium profiles, indicating a leaching process with an effective diffusion coefficient strongly dependent on concentration. Such behaviour is expected for an ion exchange mechanism :

$$D = D_{Na} D_H / [D_{Na} c_{Na} + (1 - c_{Na}) D_H],$$

where D_H and D_{Na} represent the oxonium and sodium diffusion coefficients respectively and c_{Na} represents the sodium concentration (normalized to the sodium bulk concentration). The experimental results for different glass composition are summarized in table 1. All sodium diffusion coefficients are much greater than the corresponding tracer diffusion coefficients. Arguing that much higher diffusion coefficients would occur in hydrated glasses is contradicted by recent experimental data (5). Essential to an ion exchange mechanism is the presence of anionic sites. The sodium non-bridging oxygen sites, however, are converted into silanol groups, as has been demonstrated using XPS (3). The strongest argument in favour of ion exchange has been given by Lanford et al. (1).

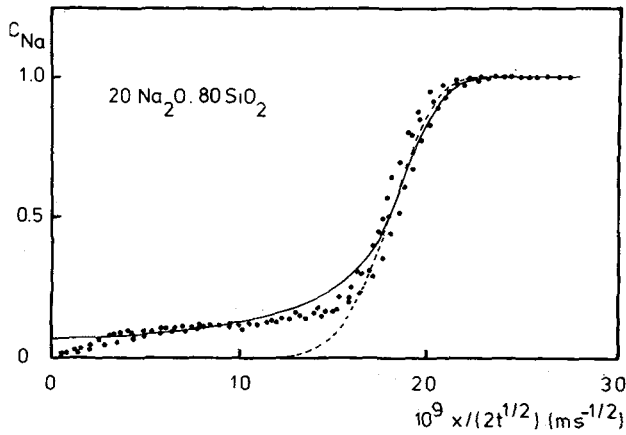


Fig. 1. - The predicted sodium profiles on the basis of H_2O diffusion — ($D_m = 10^{-14} m^2 s^{-1}$, $K=4.10^{-3}$) and on the basis of ion exchange - - - ($D_H = 5.10^{-17}$, $D_{Na} = 5.10^{-11} m^2 s^{-1}$) along with the experimental data for a glass with composition $20 Na_2O.80 SiO_2$.

Using nuclear techniques they demonstrated that each sodium ion was by replaced three hydrogen atoms. Recent data, however, indicate that this ratio, depending on glass composition, varies between 1.7 and 3.2 (2). It has been suggested by Tsong (2) that it is not oxonium ions but protons that are exchanged for sodium, followed by the penetration of H_2O . If the latter process were to occur, the substitution of H_2O by D_2O would result in a 20% decrease in the width of the depletion layer x_1 . This has not been observed experimentally. Indeed, for a glass with composition $20Na_2O.10CaO.70SiO_2$, leached for 16 hrs at $70^\circ C$ in H_2O , x_1 equals 700 ± 40 nm and when leached in D_2O it equals 680 ± 35 nm.

Table 1. D_H and D_{Na} ($70^\circ C$) derived on the basis of ion exchange; sodium tracer diffusion coefficients (7) are indicated in brackets*.

Composition	$D_H (m^2 s^{-1})$	$D_{Na} (m^2 s^{-1})$
$20Na_2O.80SiO_2$	5.10^{-17}	$5.10^{-11} (5.10^{-19})^*$
$20Na_2O.10CaO.70SiO_2$	4.10^{-19}	$4.10^{-15} (5.10^{-20})$
$10Na_2O.10K_2O.10CaO.70SiO_2$	5.10^{-19}	$5.10^{-14} (10^{-23})$

3. H_2O diffusion. - All the data gathered indicates that a mechanism more complex than ion exchange accounts for the leaching of glass, the most likely alternative being the diffusion of H_2O . The diffusing molecules are immobilized at the sodium NBO's by the formation of silanol groups. The sodium ions freed by this reaction are no longer retained by the glass network and may, together with hydroxyl co-ions, diffuse towards the surface. If the H_2O diffusion is considered as being the rate determining step,

$D = K D_m / c_{Na}^2$ (3), where D_m stands for the H_2O diffusion coefficient and K for the 'dissociation constant' of the silanol groups formed. In this case D will also exhibit a pronounced concentration dependence and S-shaped sodium profiles are predicted (3-4). On the basis of this mechanism one can easily account for the fact that 5 to 10% of the sodium ions originally present are retained in the leached layer (fig. 1). On the basis of the ion exchange mechanism one would expect the latter concentration to be less than 1%. The total number of hydrogen atoms in the leached layer is determined both by the number of silanol groups formed and the amount of H_2O contained; the latter quantity will depend on the glass structure. The ratio of H atoms in the leached layer to the sodium ions originally present should not therefore equal three.

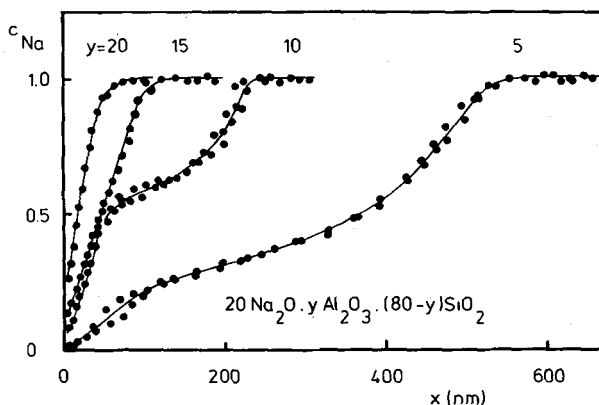


Fig. 2. - The effect of the Al_2O_3 concentration of the sodium depth profile (all samples exposed to H_2O at $70^\circ C$ for 16 hrs).

4. Leaching of aluminosilicate glasses. - Essential to the water diffusion mechanism is the presence in the glass of sodium ions bonded to NBO's. In glasses containing Al_2O_3 some of the ions are bonded to AlO_4 - groups and can not be mobilized by reaction with H_2O . They can only be mobilized by a much slower ion exchange mechanism. For the glasses with $y=5$ and $y=10$ mole % Al_2O_3 the sodium profiles exhibit distinct plateaus (see fig. 2), indicating that about 25% and 50% respectively of the sodium ions are leached more slowly. The latter figures are in fair agreement with the amount of sodium ions bonded to AlO_4 (6). It has to be noted that in this case the D_{Na} value derived, $2 \times 10^{-19} m^2 s^{-1}$, compares favourably with the sodium tracer diffusion coefficients (4). The leaching of sodium ions bonded to NBO's is governed by H_2O diffusion, D being strongly dependent on the Al_2O_3 concentration (see table 2). In silicate glasses water conducting paths exist. With the incorporation of relatively small amounts of Al_2O_3 these paths are closed, resulting in a drastic decrease in D_m . Any further addition of Al_2O_3 will have a less pronounced effect in D_m .

Table 2. The effect of the Al_2O_3 concentration on D_m ($70^\circ C$)
 $20Na_2O \cdot yAl_2O_3 \cdot (80-y)SiO_2$ $D_m (m^2 s^{-1})$ K

$20Na_2O \cdot yAl_2O_3 \cdot (80-y)SiO_2$	$D_m (m^2 s^{-1})$	K
$y=0$	10^{-14}	4.10^{-3}
$y=5$	2.10^{-17}	5.10^{-3}
$y=10$	4.10^{-18}	5.10^{-3}

5. Concluding remarks. - From all the data gathered it is concluded that the leaching of sodium silicate glasses is governed by the diffusion of H_2O . In aluminosilicate glasses the sodium ions bonded to AlO_4 -tetrahedra, however, are leached by ion exchange with H_3O^+ .

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