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Reaction of zirconium fluoride glass with water: kinetics of dissolution

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When liquid water contacts a zirconium–barium–lanthanum fluoride glass, at least three different processes occur. Barium and zirconium fluoride dissolve into the water, water penetrates into the glass, and zirconium fluoride crystals grow on the glass surface, in static solution. The rate of dissolution, as measured by solution analysis, is possibly controlled by diffusion in the solid surface; surface blockage and surface reactions are other possible kinetic steps involved. Diffusion in solution is not the controlling mechanism. Hydrogen profiles in the glass surface suggest that the penetration rate of water into the glass is controlled by diffusion and a surface reaction.

1. Introduction

The reaction of zirconium fluoride glasses with water is an important consideration in their applications as optical components. These glasses dissolve in water [1–3] and form a white deposit of zirconium fluoride on their surfaces [4]. Some OH groups are introduced into the glass during treatment in liquid water, as shown by infrared absorption [1, 2], and some and possibly all of these groups are in the form of molecular water, as shown by the presence of the 6.1 μm absorption band characteristics of bending of H_2O molecules.

The dissolution of fluoride glass in water is rapid compared to that of durable silicate glasses; the mechanism of dissolution is not certain. The goal of this work was to test and suggest different mechanisms by measuring the rates of dissolution of the components of the glass in water and the profile of hydrogen in the glass surface after hydrolysis. A zirconium–barium–lanthanum fluoride glass was held in either static or stirred water at 24° C, and in unstirred water at 75° C, and the dissolving constituents analysed as follows: fluoride, a fluoride-sensitive electrode; barium, atomic absorption; zirconium, colorimetrically. The hydrogen profile was measured by a resonant nuclear reaction. The results are discussed in terms of different possible mechanisms.

2. Experimental methods

A fluoride glass containing 62 mol % ZrF_4, 33% BaF_2 and 5% LaF_3 was melted with an excess of ammonium bifluoride ($NH_4F \cdot HF$) in an atmosphere of dry nitrogen containing 3% Cl_2. The melt was held in a vitreous carbon crucible for 4 to 5 h about 850° C, and then poured into a brass mould and annealed just above the glass transition temperature of 320° C for 5 min, and cooled slowly.

For leaching, samples 7.5 mm × 7.5 mm × 2.4 mm in dimension were cut and polished on the flat faces with 600 grit SiC paper, then 9 μm diamond, and finally 0.05 μm CeO_2, using ethylene glycol and no water. The samples were cleaned ultrasonically with acetone and finally with hexane. The samples were suspended on nylon filaments and leached in polypropylene jars in 50 ml of solution at 24.2 or 75.5° C.

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Static leaching experiments were carried out by holding a sample in distilled water for a certain time, removing it, and putting it into another 50 ml water for another period of time. Thus the leaching solutions were effectively fresh at certain times throughout the leaching. The solutions from these experiments were analysed for zirconium, barium, and fluorine.

Fluoride ion concentrations were measured in polypropylene beakers with an Orion research model 94-09 fluoride electrode and a Fisher Acumet model 805-MP pH meter. The reference electrode was a Corning model 476022. The fluoride electrode was calibrated with standard sodium fluoride solutions. Calibrating and leaching solutions were diluted with an equal volume of Orion buffer solution TISAB no. 94-09-09 to provide constant ionic strength, a solution pH between 5.0 and 5.5, and to prevent fluoride ions from complexing with cations. Presumably this buffer solution prevents fluoride ions from complexing with zirconium, so all fluoride ions in the leaching solutions are free in solution and measured by the electrode.

Zirconium was analysed by a colorimetric technique in which the zirconium is quantitatively extracted with dibutyl phosphate in chloroform, and the fluoride is complexed with aluminium ion to prevent its interference. The red dye 1-(2pyridylazo)-2 naphthol (PAN indicator) was added in alcoholic solution to give an absorption band at 555 nm whose height is proportional to the zirconium concentration. Details of this method are given by Rolf [5].

Barium was analysed in a Perkin Elmer atomic absorption spectrophotometer model 403 in solutions with 0.1% KCl.

In dynamic leaching experiments the fluoride ion concentration was measured continuously with the fluoride ion electrode in 50 ml of stirred solution containing the sample. The leaching solution was not changed throughout the experiment. The solution contained 7.5% sodium acetate buffer, adjusted to pH 5.1 with concentrated nitric acid.

Hydrogen profiles in the glass surfaces were measured by the $1H(^{15}N, \alpha\gamma)^{12}C$ resonant nuclear reaction (6.405 MeV) with the Dynamitron linear accelerator at SUNY Albany. Profiles of hydrogen concentration in the glass were measured by raising the beam energy in steps above the resonance energy.

Sample surfaces were observed with an AMR Model 1000 scanning electron microscope (SEM). The surface composition was analysed semi-quantitatively with a Kevex-ray Subsystem 4001. Samples were coated with a thin carbon layer to prevent charging.

3. Experimental results

Two different series of static leaching experiments were carried out, one at 24.2° C and the other at 75.5° C. In each series one slab sample was used throughout the experiment. It was put into 50 ml distilled water, held for a time, and then removed and the solution analysed. The same sample was put into a fresh solution and held for a further time. For example, at 24.2° C the sample of area 1.852 cm^2 was held in water for 10 min, then 20 min, then 30 min, giving cumulative times of 10, 30 and 60 min; each new holding period started with fresh distilled water. The analytical results are given in Table I and plotted in Figs. 1 and 2.

If only barium and zirconium fluorides are leached from the glass, the weight fraction of each element expected in solution is fluorine 0.381, zirconium 0.344, and barium 0.275. Lanthanum fluoride is very insoluble, and only small amounts of lanthanum were found in leaching solutions fluoride glasses in a previous study [1]. The actual weight fractions of the elements in solution as a function of time are shown in Figs. 3 and 4. At 24.2° C the amounts

TABLE I Chemical analysis of solution constituents after different holding times of fluoride glass in water

Total leaching time (min)	Total weight of element leached (10^4 g cm^{-2})		
	Fluoride	Zirconium	Barium
	24.2° C		
10	0.0785	0.599	0.252
30	0.5245	1.437	0.904
50	0.9143	2.079	1.400
90	1.447	3.000	2.069
150	2.129	3.970	2.850
210	2.760	4.870	3.560
	75.5° C		
10	3.20	2.63	3.08
20	5.58	4.79	5.06
40	9.68	8.61	7.97
70	14.30	12.88	11.17
130	21.40	20.55	15.80

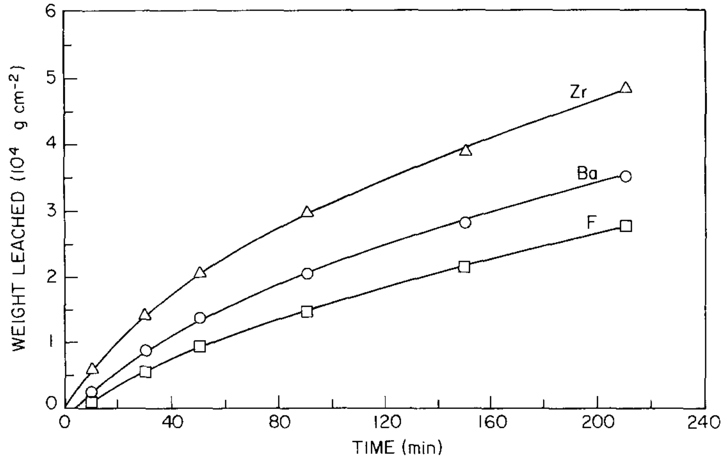


Figure 1 Total amount of elements leached from ZBL fluoride glass as a function of time at 24.2° C, static water solution.

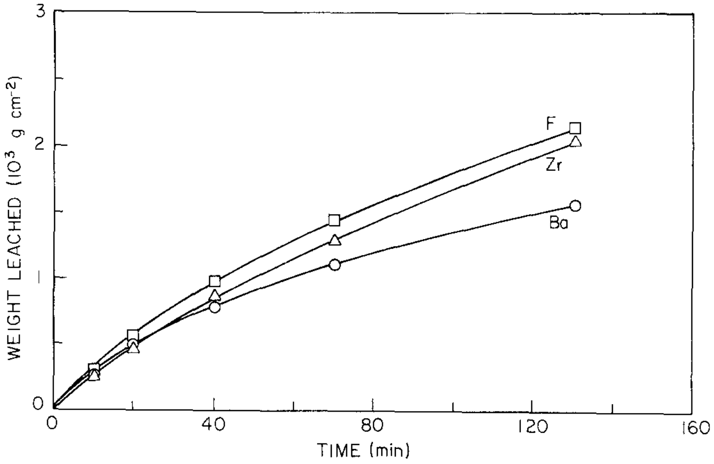


Figure 2 Total amount of elements leached from ZBL fluoride glass as a function of time at 75.5° C, static water solution.

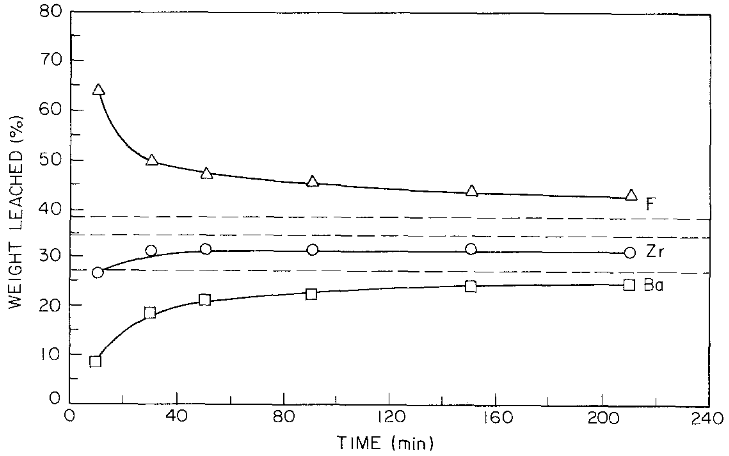


Figure 3 Fraction of each element leached from ZBL fluoride glass as a function of time at 24.2° C.

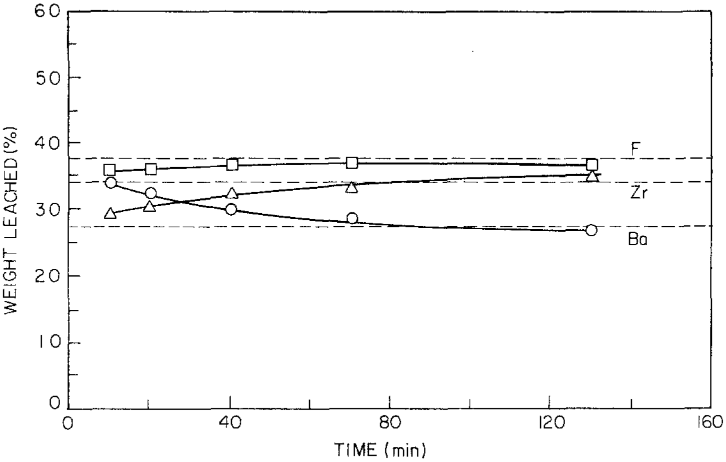


Figure 4 Fraction of each element leached from ZBL fluoride glass as a function of time at 75.5° C.

of barium and fluorine in solution are lower than expected, and for a short initial period hardly any barium and fluorine are leached. At 75.5° C there is no such initial period, and the weight fractions of the elements are close to those in the glass.

Micrographs of the sample surfaces after leaching are shown in Figs. 5 and 6. Individual blade-like crystals formed on the surface at 24.2° C; these crystals form in clumps at 75.5° C. Additional micrographs are given by Doremus *et al.* [4], in which these crystals are identified as zirconium fluoride.

In Fig. 7 hydrogen profiles in the polished surface of a Zr–Ba–La fluoride glass hydrated for different times at 23° C are shown, as measured by the resonant nuclear reaction. The background hydrogen in an unhydrated glass sample was negligible compared to these hydrogen concentrations. The concentration of hydrogen near the glass surface was lower than expected, probably because some hydrogen (in the form of water) was pumped out in the vacuum system used for measuring the profiles.

A sample of fluoride glass was leached continuously with stirring at 27° C in a "dynamic" experiment. The solution contained 7.5% sodium acetate buffer at pH 5, and the fluoride concentration was measured as a function of time without removing the sample from solution. The results are given in Table II and plotted in Fig. 8. The amount of fluoride leached was up to an order of magnitude more than in the static experiment at 24.2° C. A scanning micrograph of the surface of the glass after 115 min leaching is shown in Fig. 9. The surface is highly cracked, and shows no blade-shaped crystals found in the static experiments. Some of the glass has flaked off the surface, perhaps during drying.

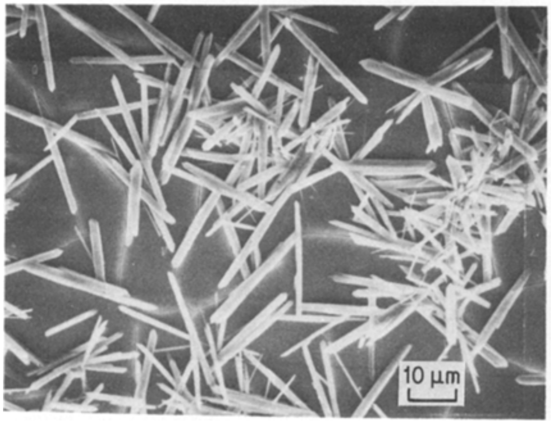


Figure 5 Scanning electron micrograph of ZBL fluoride glass surface after 210 min in water at 24.2° C.

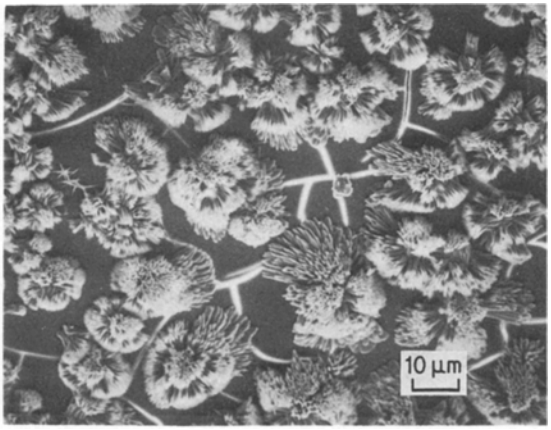


Figure 6 Scanning electron micrograph of ZBL fluoride glass surface after 130 min in water at 75.5° C.

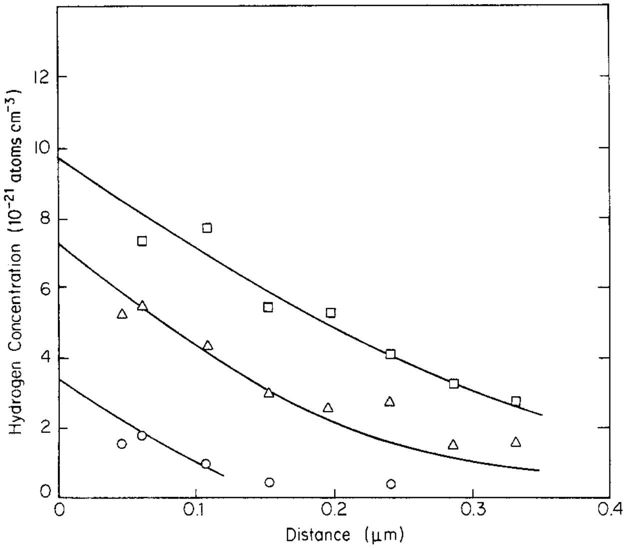


Figure 7 Profiles of hydrogen concentration in ZBL fluoride glass after different times in water at 25° C for □ 60 min, △ 30 min, ○ 5 min. Lines from Equation 8.

4. Discussion

At least three different processes occur during dissolution of the fluoride glass in water. Barium and zirconium fluoride dissolve into the water, water penetrates into the glass, and zirconium fluoride crystals grow on the glass surface, at least in static solution. It is not clear if the first two processes are linked or independent. In this discussion the dissolution experiments are considered first, and then the profile of hydrogen in the glass surface.

TABLE II Fluoride concentration in 50 ml buffered solution (pH 5.1) at 27° C containing a fluoride glass slab of area 1.698 cm^2 as a function of time

Time (min)	Fluorine concentration (mMl^{-1})
1.0	0.119
1.5	0.180
2.0	0.228
2.5	0.265
3.0	0.297
3.5	0.325
4.0	0.35
4.5	0.38
5.0	0.40
6.0	0.43
7.0	0.47
8.0	0.49
9.0	0.53
10	0.55
15	0.68
25	0.86
35	1.04
45	1.18
55	1.25
65	1.43
75	1.48
85	1.60
95	1.67
105	1.74
115	1.80

The rate of dissolution (slope of amount leached against time) decreased with time in all experiments. This decrease occurred throughout the static experiments, even though the solution was periodically changed to fresh water. These results suggest that something occurs on or in the sample surface to decrease the rate, and appear to rule out diffusion in solution as a controlling factor.

The expected values of elemental fractions in solution are compared with actual results in Figs. 3 and 4. At 75.5° C fluoride is close to the expected fraction throughout dissolution and zirconium and barium reach these fractions after about 80 min at 24.2° C; however, the fraction of fluorine is low throughout, as is barium, whereas zirconium is enhanced. A possibility is that zirconium, and to some extent barium, are preferentially leached from the glass.

Plots of the amount leached in static experiments as a function of square root of time are given in Figs. 10 and 11. This kind of dependence of amount leached as a function of time can occur in a diffusion-controlled process if the surface concentration increases as a function of time as a result of a surface reaction. The diffusion equation is

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial X^2} \qquad (1)$$

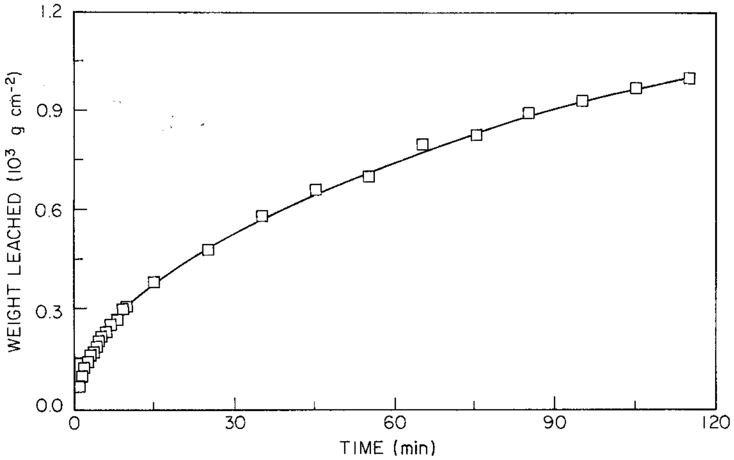


Figure 8 Total amount of fluoride leached from a ZBL fluoride glass as a function of time at 27° C, stirred solution of pH 5.1 buffer.

with c concentration, X distance, t time, and D concentration-independent diffusion coefficient. For semi-infinite geometry the boundary conditions are:

$$c = 0 \text{ when } t = 0, \quad c = 0 \text{ as } X \to \infty,$$

$$-D\frac{\partial c}{\partial X} = \alpha(c_0 - c_s)$$

$$\text{at } X = 0 \qquad (2)$$

where c_0 is the concentration reached at the surface at long times (equilibrium), c_s is the surface concentration at time t, and α is an interface reaction coefficient. The solution of Equation 1 for these boundary conditions for the total amount of material diffused M, per unit surface area is [6]

$$M = \frac{c_0}{h}\left[\exp(h^2 Dt)\ \mathrm{erfc}\ h(Dt)^{1/2} - 1 + \frac{2h(\mathrm{Dt})^{1/2}}{\pi^{1/2}}\right] \qquad (3)$$

where $h = \alpha/D$ and erfc is the conjugate error function. A plot of Mh/C_0 as a function of $h(Dt)^{1/2}$ is given in Fig 12.

The shape of this plot is very similar to those in Figs. 10 and 11, suggesting that the dissolution of zirconium and barium fluoride is controlled by diffusion with surface reaction. However, it is not clear what is the diffusing substance or medium. The static leaching is not influenced by a change of solution, apparently ruling out diffusion in the solution as a controlling mechanism. If diffusion of water into the glass were enhancing the rate of dissolution one would expect the rate to increase with time as more water penetrates into the glass, rather than decrease as it does.

Another possibility is that the crystals on the surface block a part of it for dissolution. An equation for the total amount dissolved is then

$$\frac{\mathrm{d}M}{\mathrm{d}\tau} = k(A_0 - \beta M) \qquad (4)$$

where A_0 is the initial surface area, k is the linear dissolution coefficient and β measures the rate of formation of the blocking crystals. A solution to Equation 4 is

$$\ln\left(1 - \frac{M}{M_f}\right) = -k\beta t \qquad (5)$$

where M_f is the final amount of element dissolved (when the rate of dissolution becomes zero). A plot of Equation 5 in Fig. 12 has a similar shape to Equation 3 at early times and also to the data in Figs. 1 and 2.

The fluoride leaching data of Fig. 8 for the stirred buffer solution are plotted as a function

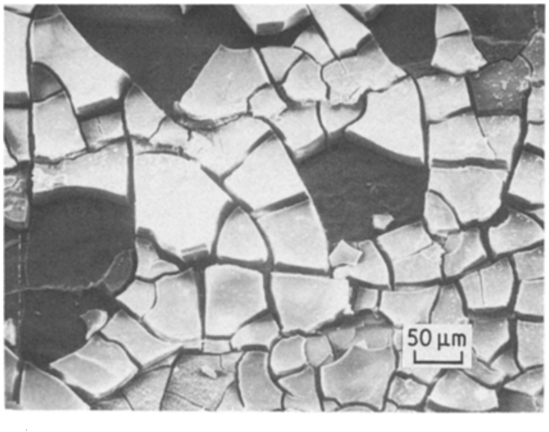


Figure 9 Scanning electron micrograph of ZBL fluoride glass surface after 115 min in stirred solution of pH 5.1 buffer.

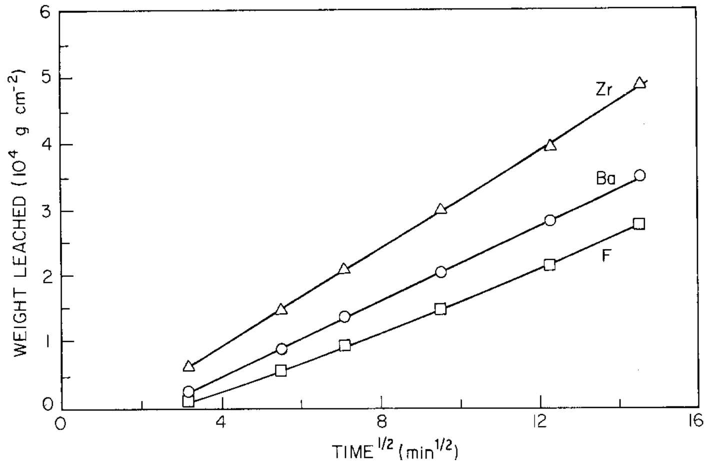
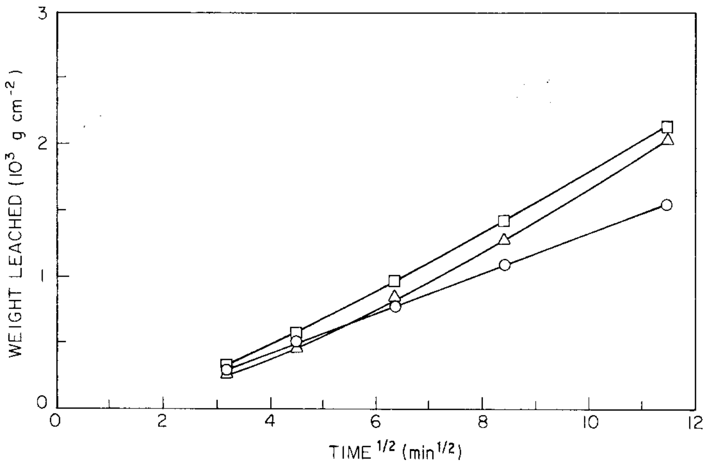


Figure 10 Total amount of elements leached from a ZBL fluoride glass as a function of the square root of time at 24.2° C in static water solution.

Figure 11 Total amount of elements leached from a ZBL fluoride glass as a function of the square root of time at 75.5° C, in static water solution.



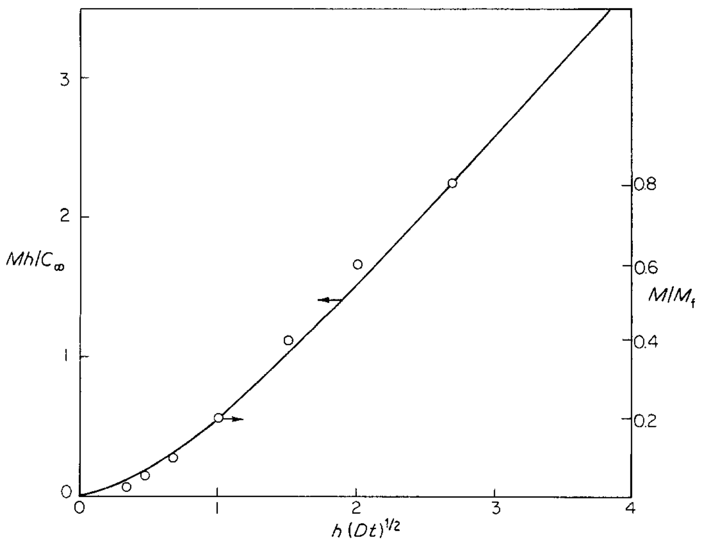


Figure 12 Total amount diffused across an interface with surface reaction as a function of square root of time. Line from Equation 3, points from Equation 5.

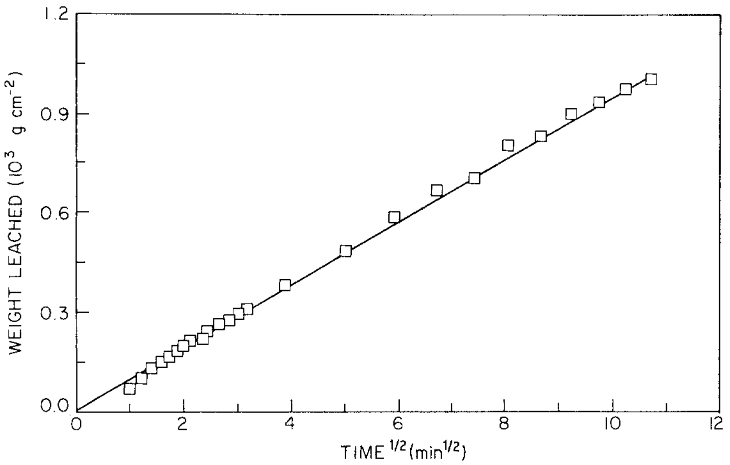


Figure 13 Total amount of fluoride leached from a ZBL fluoride glass as a function of square root of time at 27° C, stirred solution of pH 5.1 buffer.

of square root of time in Fig. 13. The fit is good throughout the dissolution with little or no initial "induction time". Fig. 9 showed no ZrF_4 crystals on the surface of the glass from the stirred solution, so it appears that blocking of the surface cannot explain the reduction of dissolution rate with time for this condition. Perhaps the mechanism for rate reduction in stirred solution is different from that in static solution, although this difference seems unlikely. There are three differences between the experiments recorded in Figs. 1 and 2 and that in Fig. 8:

Static (Figs. 1 and 2)	Stirred (Fig. 8)
No stirring	Stirred
Start with distilled water, pH decreases to between 3 and 4	pH held constant with buffer solution at. 5.1
No added ions in solution	Acetate buffer, acetate ion complexes zirconium

It is not clear what the influence of these various differences is. The rate of dissolution of fluoride glasses increases in acid solution, so the pH rise in the static solution cannot cause the lower rate of dissolution in this solution. Either stirring or complexing of zirconium in solution could cause a faster dissolution rate, and could also perhaps explain the lack of zirconium fluoride crystals on the glass surface in the stirred solution.

When zirconium dissolves in water at intermediate pH, the zirconium ion hydrolyses to form a tetramer [7, 8]:

$$\begin{aligned} &4Zr^{4+} + 24H_2O \\ &= [Zr(OH)_4 \cdot 2H_2O]_4 + 16H^+ \qquad (6) \end{aligned}$$

The tetramer has a roughly square planar shape with zirconium ions at the corners. The zirconium ions have an average coordination number with oxygen of six to eight, so the number of associated water molecules can be two, as shown, to four per zirconium atom. The tetramer has a positive charge, because it migrates to the cathode during electrolysis. The extent of ionization is not known; it is sometimes written as two positive charges per zirconium ion, or

$$\begin{aligned} &[Zr(OH)_4 \cdot 2H_2O]_4 \\ &= [Zr(OH_2) \cdot 2H_2O]_4^{8+} + 8OH^- \qquad (7) \end{aligned}$$

but this is almost certainly too much charge, because the tetramer polymerizes easily as the pH increases. The hydrolysis of Equation 6 explains the increase in hydrogen ion concentration as the zirconium fluoride glass dissolves; it is not necessary to invoke fluoride–hydroxyl exchange to explain this pH decrease. In acetate buffer at pH 5.1 some acetate ions can replace hydroxyl ions in the hydrolysed zirconium complex, stabilizing it. This stabiliziation is a possible reason for the absence of zirconium fluoride crystals on the glass surface dissolving in buffer solution. The solubility of zirconium fluoride in water is not known reliably [4], and is doubtless strongly influenced by complexing of the zirconium ion in solution, solution pH, and concentrations of other ions.

The temperature dependence of the dissolution rate can be roughly judged by comparing initial dissolution rates at 24.2 and 75.5° C. For zirconium this rate is about nine times faster at 75.5 than at 24.2° C. This is much greater than the ratio of ionic mobilities in water of about 2.4 between these two temperatures, again supporting the conclusion that diffusion in solution is not the rate controlling process.

The hydrogen profiles of Fig. 7 indicate that the (extrapolated) surface concentration of hydrogen increases as a function of time, suggesting a surface reaction as assumed in the boundary conditions (Equation 2). The solution of the diffusion Equation 1 for the concentration c as a function of distance with the conditions (Equation 2) is [6]:

$$\frac{c}{c_\infty} = \operatorname{erf}\frac{X}{2(Dt)^{1/2}} - [\exp(hX + h^2 DT)] \times \operatorname{erfc}\left[\frac{X}{2(Dt)^{1/2}} + h(Dt)^{1/2}\right] \qquad (8)$$

where c_∞ is the constant surface concentration at long time ($h(Dt)^{1/2} \gg 5$). The shapes of concentration profiles from this equation, at least for $h \gtrsim 0.1$, are almost the same as the shape of a profile for constant surface concentration except at the lowest concentrations.

In Fig. 7 profiles calculated from Equation 8 with $h(Dt)^{1/2} = 0.35$ at 60 min are compared with experimental profiles for hydrogen in the glass after 30 and 60 min in water at 25° C. The fit gives a diffusion coefficient of 1.8×10^{-13} $\text{cm}^2\,\text{sec}^{-1}$, $h = 1.4 \times 10^4\,\text{cm}^{-1}$, and $\alpha = 2.5 \times 10^{-8}\,\text{cm sec}^{-1}$. These calculations and the above equations assume a constant diffusion coefficient. A possible mechanism is the diffusion of molecular water into the glass. In this case the molecular solubility of water in the glass at 25° C at saturation (c_∞) is 3.2×10^{22} atoms cm^{-3} of hydrogen, or 1.6×10^{22} molecules cm^{-3}, a large number.

The diffusion coefficient of $1.4 \times 10^{-13}\,\text{cm}^2\,\text{sec}^{-1}$ is larger than the extrapolated value for the diffusion of water in vitreous silica of about $8 \times 10^{-17}\,\text{cm}^2\,\text{sec}^{-1}$, but is smaller than the diffusion coefficients of molecular hydrogen ($2 \times 10^{-11}\,\text{cm}^2\,\text{sec}^{-1}$) in vitreous silica at room temperature.

It has been suggested that ion exchange between hydroxyl ions and fluoride ions in the glass introduces hydrogen into the glass:

$$\text{F}^-(\text{g}) + \text{H}_2\text{O} = \text{OH}^-(\text{g}) + \text{HF}$$

where (g) is glass. The decrease of pH during dissolution is sometimes attributed to this reaction. However, there is no evidence from the chemical analysis of solutions that fluoride ion is preferentially leached. The total fluoride ion concentration in the glass is about 5.5×10^{22} atoms cm^{-3}, which is somewhat greater than the saturation value for hydrogen found above.

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