

Alkaline durability of some silicate glasses containing CaO, FeO and MnO

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In the process of developing an alkali-resistant glass composition to use as reinforcing fibres with cement, seven glasses in the system $\text{Na}_2\text{O}-\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{MnO}-\text{SiO}_2$ with a constant 70 mol % SiO_2 and at least one divalent oxide, were prepared and their intrinsic chemical durability (by the grain test) in aqueous solutions, buffered at different pH values, was examined at 75°C. The durability in this glass system decreased with increasing soda content. The glass composition having the minimum alkali content in this series was 5Na₂O, 12.5 FeO, 12.5 MnO, 70SiO₂ and this glass showed the maximum alkaline durability of this series. Molar substitution of FeO, and particularly of MnO, for CaO in all these glasses increased the durability in the pH range 9 to 12; however, durability in the acid range (pH = 0 to 2) was found to deteriorate when this substitution was made. The thermodynamic stability of the different oxides under present investigation (FeO, Fe₂O₃, MnO, Mn₂O₃ and SiO₂), in aqueous solutions at different pH values has been discussed with standard thermo-chemical data, and it has been shown that the acid and alkaline durability of all these glasses can be satisfactorily correlated with the thermodynamic predictions.

1. Introduction

Glass has a number of important properties which make it potentially attractive for engineering applications. These include reasonably high strength, stiffness, hardness and wear resistance, chemical inertness, low density, and above all cheapness. Unfortunately, however, the most characteristic mechanical property of glass is brittleness, that is a susceptibility to catastrophic failure in the absence of plastic deformation. This severely limits the range of possible engineering applications for glass, and thus materials scientists have attempted in various ways to alleviate this problem. One of the ways of improving the mechanical properties is to make a cement composite containing glass fibres. In fact recently such a glass fibre-reinforced cement, commonly known as GRC (glass fibre-reinforced cement) has been marketed commercially. This owes its origin to the develop-

ment of an alkali resistant glass composition [1]. Commercial production methods for drawing continuous fibres have been developed by, and are available from, Pilkington Brothers Ltd. under the trade name Cem-FIL [2]. The fibres are about 10 μm in diameter and are available in rovings of a few thousand filaments comprising bundles containing a few hundred individual filaments. The filaments are coated with a liquid size which protects them and also binds the filaments in the strands together. Usually 5 to 10% of fibres are incorporated into the cement matrix.

There are a number of important requirements to be met when glass fibres are to be incorporated into cement matrices. These include: (a) a suitable source of fibre at an economically attractive price, (b) fibres that generally are strong and stiff compared with the matrix cement phase, (c) an appropriate fabrication route which does not lead to de-

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gradation of the properties of the matrix or to damage of the fibres, (d) chemical compatibility between the fibres and the cement matrix both during the fabrication and in service, (e) physical compatibility between the fibre and the matrix in terms, for example, of relative coefficients of thermal expansion, and (f) an interface between the fibre and the matrix that induces a fibrous type of structure.

Although GRC is becoming well established for engineering applications, further improvements towards long-term durability of glass fibres in a cement matrix is highly desirable for further exploitation of this new material.

The glass fibres to be used in cement reinforcement must have a very high-alkaline durability otherwise the highly alkaline cement paste (pH ~ 12) will corrode the ultrafine fibres and the desired mechanical properties will be lost. Addition of ZrO₂ to silicate glasses is well known to increase the chemical durability [3, 4], and Cem-FIL contains 16 to 17 wt% ZrO₂. The alkaline durability of Cem-FIL is satisfactory, but it has two main disadvantages: ZrO₂ is costly, and the addition of ZrO₂ to a silicate glass increases the melting and fibre drawing temperatures, thereby increasing the production cost. In the work described below we have succeeded in developing some alkaline-resistant glass compositions with excellent durability from cheap and easily available raw materials like iron and manganese oxides.

In formulating an alkaline-resistant glass, the glass components must be carefully chosen so that each of the component oxides has a low activity in the final glass, and at the same time each oxide should be durable in its own right in an alkaline

medium. In addition consideration may need to be given to the kinetic behaviour of leaching of different ionic species, the accumulation of ionic species on the surface followed by crystallization and consequent breakage of the fibres.

From an exhaustive survey of the available chemical literature it appeared that MnO and Fe₂O₃ are fairly alkaline-resistant, besides being cheap, easily available, and above all having a fairly large glass formation region in silicate systems [5]. Thus a systematic study was undertaken by melting a series of silicate glasses containing a large proportion of MnO and Fe₂O₃ and evaluating their intrinsic chemical resistance towards aqueous solutions of different pH using the grain test method.

2. Experimental

The composition of all the glasses (after chemical analysis) along with their melting history is given in Table I. 500 g of glass was melted in a platinum crucible. Towards the end of melting, the melts were mechanically stirred for 2 h to increase their homogeneity, and thoroughly annealed after casting as slabs. All the glasses were examined with powder X-ray diffraction and replica electron microscopy techniques for possible devitrification or/and phase separation. Grains (-30, +52 mesh, standard B.S. sieve) were prepared under standard conditions [6]. To study their leaching behaviour a 1 g portion of each grain was put in 50 ml aqueous solution buffered at various pH values, and digested at a controlled temperature (75 ± 1° C) in the water bath for 4 h. The composition of the buffer solutions is given in Table II. During digestion the polythene bottles containing the

TABLE I Composition of glasses (after chemical analysis)

Series	Glass No.	Composition (mol%)					Temperature of melting (° C)	Remarks
		SiO ₂	Na ₂ O	CaO	FeO*	MnO†		
A	1	69.8	15.1	-	15.1	-	1400	Glass formed, (Fe ²⁺ /total iron) = 0.145
A	2	70.0	15.0	-	-	15.0	1400	Glass formed, (Mn ³⁺ /total manganese) = 0.012
A	3	69.8	15.1	15.1	-	-	1400	Glass formed,
B	4	69.9	10.1	10.0	10.0	-	1450	Glass formed, (Fe ²⁺ /total iron) = 0.215
B	5	69.8	10.1	10.1	-	10.0	1450	Glass formed, (Mn ³⁺ /total manganese) = 0.0093
B	6	70.0	10.0	-	10.0	10.0	1450	Glass formed, no Mn ³⁺
C	7	70.0	5.0	-	12.5	12.5	1450	Glass formed, no Mn ³⁺
C	8	70.0	5.0	5.0	10.0	10.0	1500	Did not form glass (devitrified)
C	9	70.0	-	15.0	-	15.0	1500	Did not form glass (devitrified)
C	10	70.0	-	-	15.0	15.0	1500	Did not form glass (two immisible liquids even at 1500° C)

*Concentration of total iron is calculated as FeO.

†Concentration of total manganese is calculated as MnO.

TABLE II Composition of solutions used for leaching and controlling pH

pH	Solutions
0	1.0 M HClO ₄
1	0.1 M HClO ₄
2	0.1 M HClO ₄ + NH ₄ OH
9-12	Saturated boric acid solution at 25° C + KOH solution
14	1.0 M KOH solution

grains and the corroding solutions were continuously shaken at a constant speed of 160 strokes min⁻¹. After 4 h the bottles were taken out, the grains removed, and the leached constituents of glass in the solution were determined. Na₂O was estimated with the flame photometer, SiO₂ with molybdc acid, total iron from its ultraviolet absorption in 9 M HCl, and total manganese with the periodate method.

3. Results and discussion

3.1. Series A: glasses 1, 2 and 3

All these glasses contain 70 mol% SiO₂ and 15 mol% Na₂O; the remaining 15 mol% being added as FeO*, MnO or CaO. Thus the relative acid- and alkaline-durability of these glasses will reflect the effectiveness of these three oxides in silicate glasses. The results of leaching of these glasses are shown in Figs. 1 to 3.

3.1.1. Extraction of soda

In this series, glass 2, containing MnO, released the least Na₂O both in the acid and in the alkaline range. Glass 3, containing CaO, was intermediate with respect to Na₂O release. In the case of glass 1, containing iron oxides, the Na₂O release in the acid range was almost double that in the alkaline range. Glasses 2 and 3 released almost the same amount of Na₂O in the acid range, whereas the Na₂O release from glass 1 was about three times more.

As may be seen from Table I, glass 1 contained about 85% of its total iron in the ferric state. In silicate glasses iron (III) is known to be in tetrahedral co-ordination with oxygen (like Al³⁺ in aluminates e.g. NaAlO₂), and probably a significant fraction of the total sodium ions are associated with the ferric iron in glass 1. Glass 1 released a lot of iron in the acid region, and consequently sodium ions came out with it. Also, the leaching of iron (III) from glass in the acid region probably removed the "blocking effect" for the migration of sodium ions associated with silica in this glass.

In the alkaline region, glasses 1 and 2 released more Na₂O with increasing pH, whereas glass 3 did the reverse. This may be due to the fact that the morphology of hydrated silica layers formed on glasses 1 and 2 may be different from that formed on glass 3 [7].

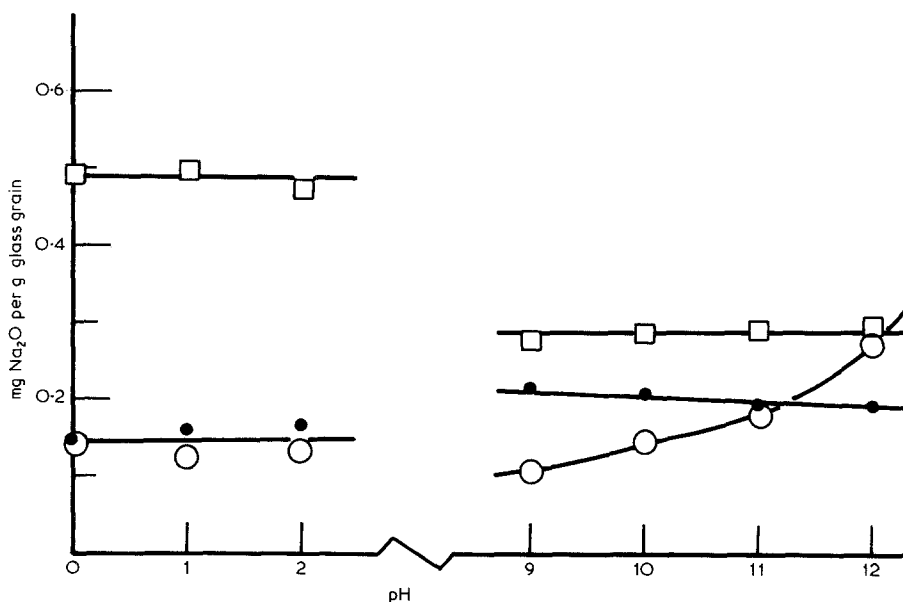


Figure 1 Extraction of Na₂O from glass 1 □, glass 2 ○, and glass 3 ●, at 75° C after 4 h.

*In glass 1, 85% of the total iron was present as iron (III). However, for simplicity of comparison, in expressing composition all the iron was calculated as FeO.

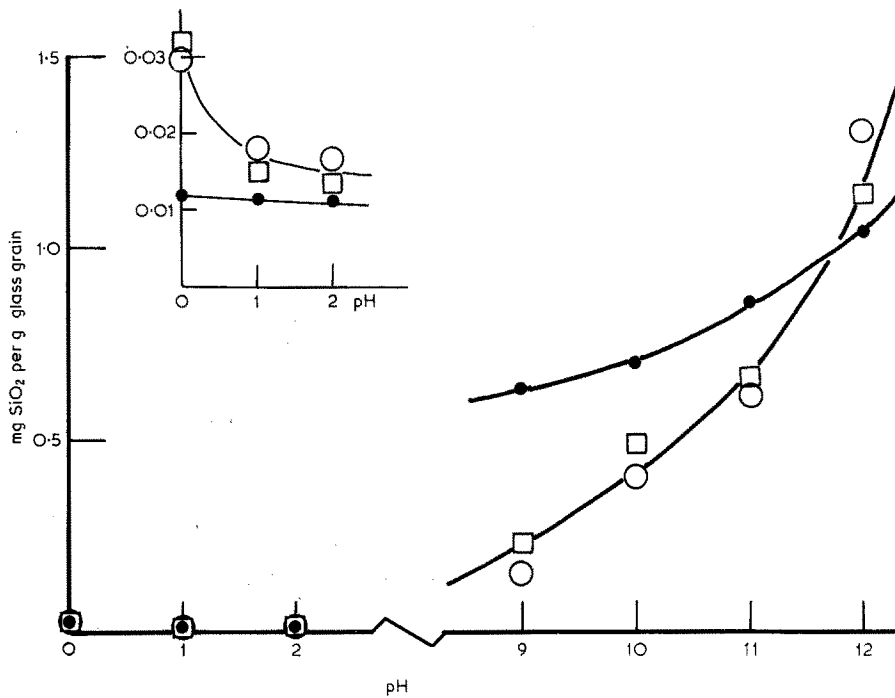


Figure 2 Extraction of SiO_2 from glass 1 \square , glass 2 \circ , and glass 3 \bullet , at 75°C after 4 h.

3.1.2. Extraction of silica

All these three glasses released very small amounts of silica in the acid region; however, the amounts of silica leached out of glasses 1 and 2 were relatively larger than that from glass 3 (see insert in Fig. 2).

In the alkaline region ($\text{pH} = 9$ to 11) the silica released from glass 2 is the least and that from glass 3 is the largest. Thus it appears that, of these three oxides, MnO produces the best protective action in the alkaline region. This may be due either to the greater "passivity" of MnO in the

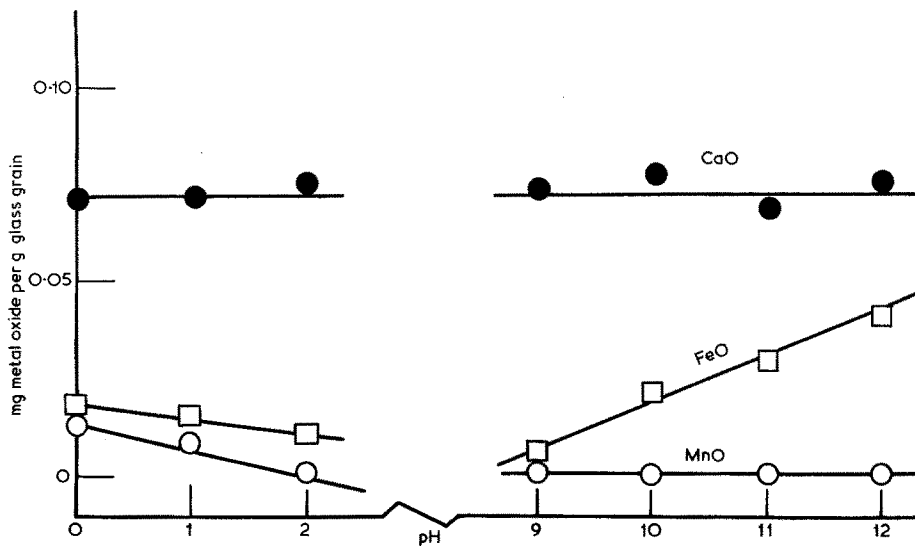


Figure 3 Extraction of divalent metal oxides from glass 1 \square , glass 2 \circ , and glass 3 \bullet , at 75°C after 4 h.

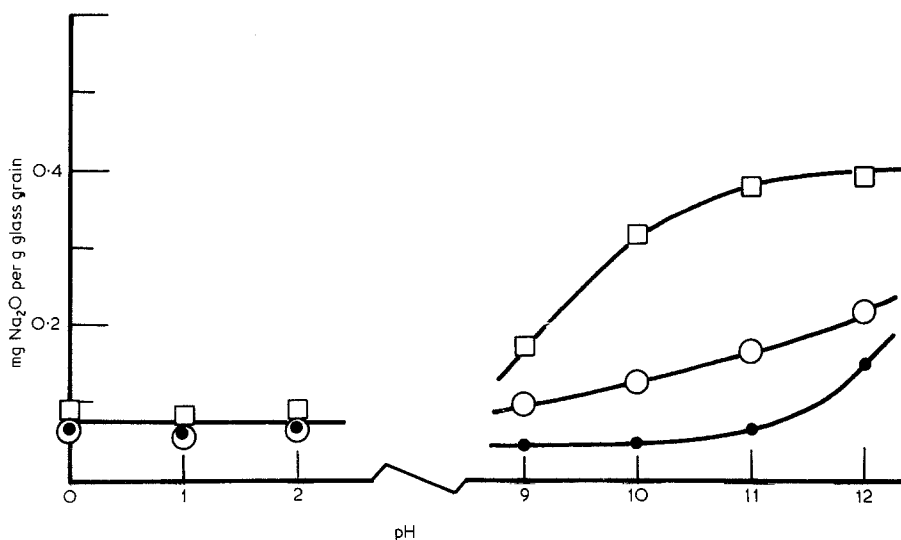


Figure 4 Extraction of Na₂O from glass 4 ○, glass 5 □, and glass 6 ●, at 75° C after 4 h.

alkaline region or SiO₂ having a lower activity in the MnO–SiO₂ system than in either CaO–SiO₂ or FeO–SiO₂ systems [8–10].

3.1.3. Extraction of calcium, iron and manganese oxides

From Fig. 3 it may be seen that in the alkaline region glass 2, containing MnO, releases too little manganese to be estimated with the presently adopted method (less than 0.025 ppm); the amount of CaO release is high and does not alter significantly with pH; the release of iron oxide is also relatively high and increases with increasing pH. In the acid region, again, the CaO release is high; the release of both iron and manganese increases with decreasing pH, the release of manganese being slightly lower than that of iron. From all these leaching results it appears that MnO produces the best alkaline resistivity in silicate systems.

3.2. Series B: glasses 4, 5 and 6

All the glasses of this series are made with an equimolar (10 mol%) mixture of two divalent oxides, and a constant 70 mol% SiO₂ and 10 mol% Na₂O. All these glasses were leached in the same way as in the Series A and the results are shown in Figs. 4, 5 and 6.

3.2.1. Extraction of soda

Soda extraction from all the glasses of this series is qualitatively similar in the acid region; in the

alkaline region the soda extraction increases with increasing pH. Soda extraction is highest in glass 5 and lowest in glass 6. Comparing the results of Figs. 1 to 3 with that of Figs. 4 to 6, it is apparent that all the glasses of Series B (except glass 5) are more durable than those of Series A, both in the acid as well as in the alkaline region. A combination of manganese and iron oxides in glass 6 seems to produce extra durability, particularly in the alkaline region. As will be shown later from thermodynamic considerations, FeO in silicate glasses produces less protective action than Fe₂O₃, and Mn₂O₃ in glass oxidizes FeO to Fe₂O₃, and hence glass 6 probably contains a smaller amount of FeO and thus exhibits extra resistance in the alkaline region [11].

3.2.2. Extraction of silica

Silica extraction from all the glasses of the present series is very small in the acid region. In the alkaline region the silica extraction increases with increasing pH. It is clear from Fig. 5 that the best alkaline resistivity is attained in glass 6 containing manganese and iron oxides. Introduction of CaO in glass 4 and particularly in glass 5 appears to have an adverse effect on the chemical durability.

3.2.3. Extraction of calcium, iron and manganese oxides

The concentration of extracted calcium, iron and manganese oxides in the leach solution is shown in Fig. 6. As with glasses of Series A, very little manganese was extracted in the alkaline region; ex-

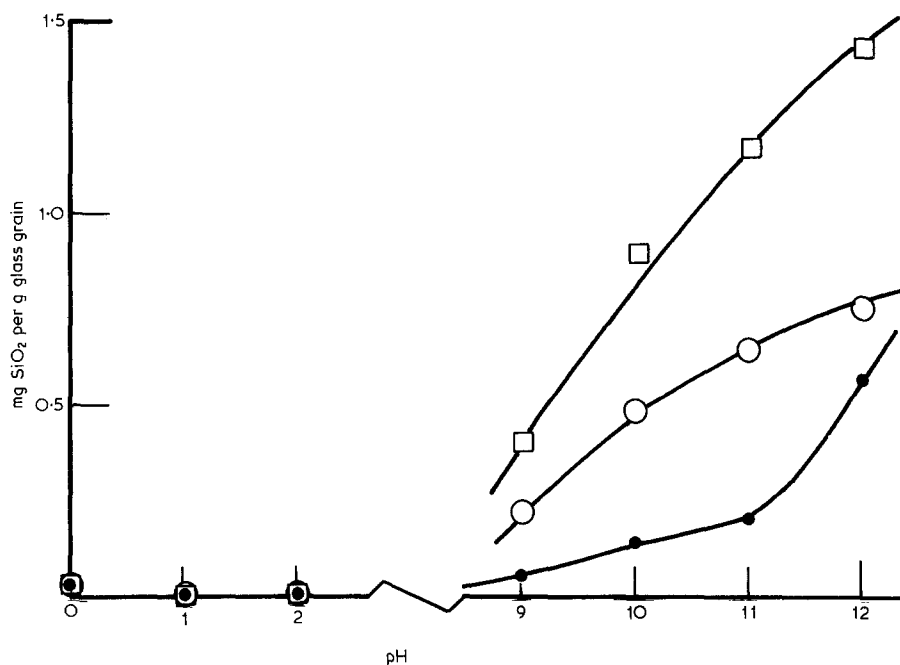


Figure 5 Extraction of SiO₂ from glass 4 ○, glass 5 □, and glass 6 ●, at 75° C after 4 h.

traction of iron increase with increasing pH, and CaO extraction is always larger than that of iron oxide at all pH values.

From all the extraction results of this series of glasses, and those of Series A, glass 6 appears to be the best with respect to the alkaline durability. This extra high durability of glass 6 may be due to any one or a combination of the following factors: (1) a low activity of Na₂O (10 mol% Na₂O com-

pared to 15 mol% Na₂O in glasses of Series A), (2) oxidation of FeO to Fe₂O₃ by Mn₂O₃ in glass, (3) the possibility that glass 6 has the lowest activity of silica.

Finally, an attempt was made to prepare glasses with the minimum possible Na₂O and the maximum amounts of iron and manganese oxides (Series C). A mixture containing 70 mol% SiO₂, 15 mol% MnO and 15 mol% iron oxide (as FeO)

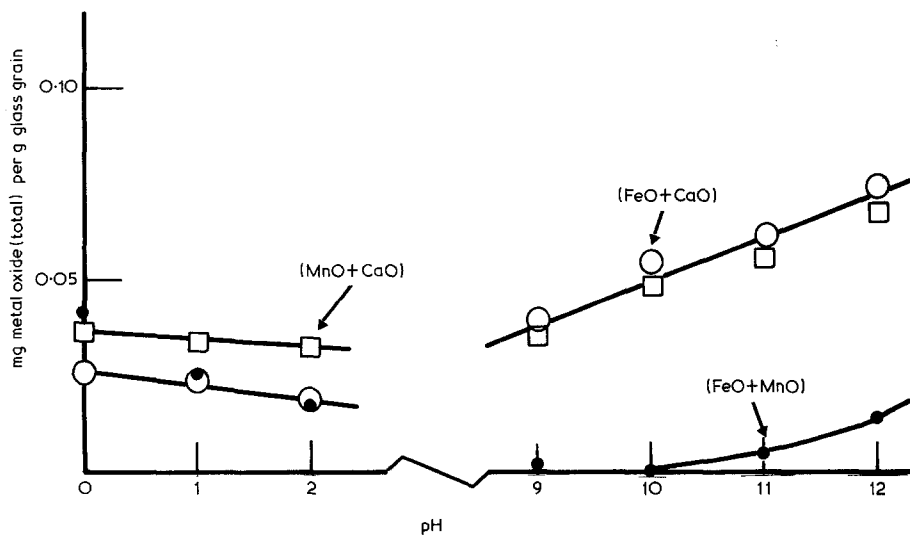


Figure 6 Extraction of total divalent metal oxides from glass 4 ○, glass 5 □, and glass 6 ●, at 75° C after 4 h.

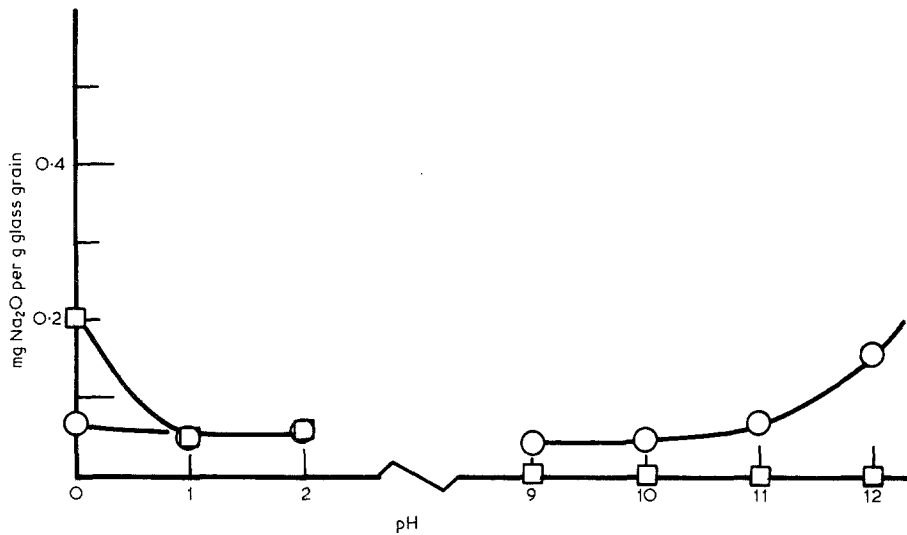


Figure 7 Extraction of Na₂O from glass 6 ○, and glass 7 □ at 75° C after 4 h.

did not produce a single-phase melt even at 1500° C (glass 10). Glass 7, which contains 70 mol% SiO₂, 5 mol% Na₂O, 12.5 mol% iron oxide (as FeO) and 12.5 mol% MnO could be melted at 1450° C and did now show any sign of phase separation on X-ray and electron microscopic examination. The results of extraction on glass 7 is shown in Figs. 7, 8 and 9; these figures also contain the results of glass 6 for easy comparison. As expected, the extraction of soda, silica, iron and manganese oxides from glass 7 is much smaller than that from glass 6 in the alkaline range.

4. Thermodynamic stability of silicate glasses in aqueous solution

In principle the thermodynamic stability of a glass towards aqueous solutions may be considered to be a function of the activity of the component oxides in the glass, and the stability of the individual oxides towards hydration, ionization and complexation in aqueous solution [12]. With the available thermodynamic data it is possible to calculate the various energy changes being associated with these processes, and from it the stability of the glass under various conditions of acidity and

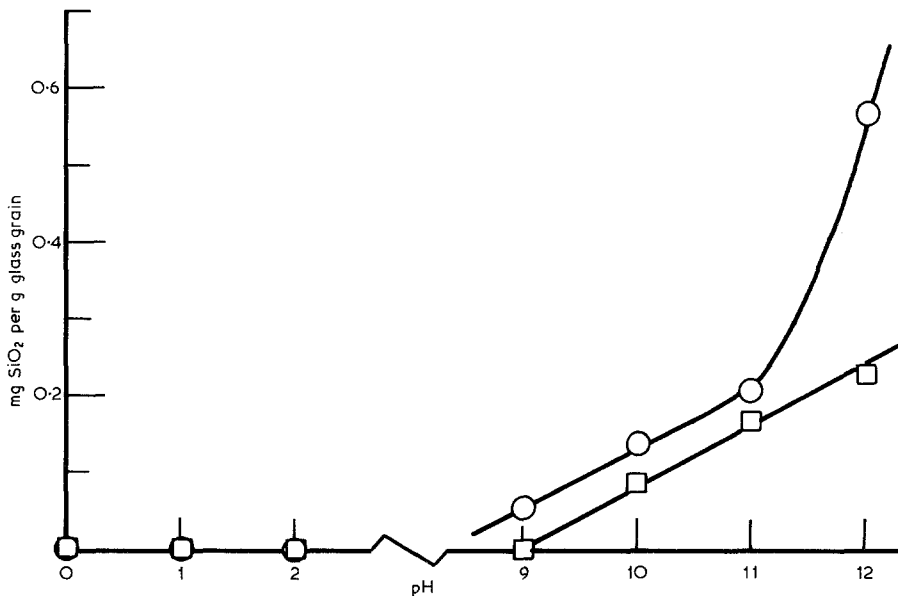


Figure 8 Extraction of SiO₂ from glass 6 ○, and glass 7 □, at 75° C after 4 h.

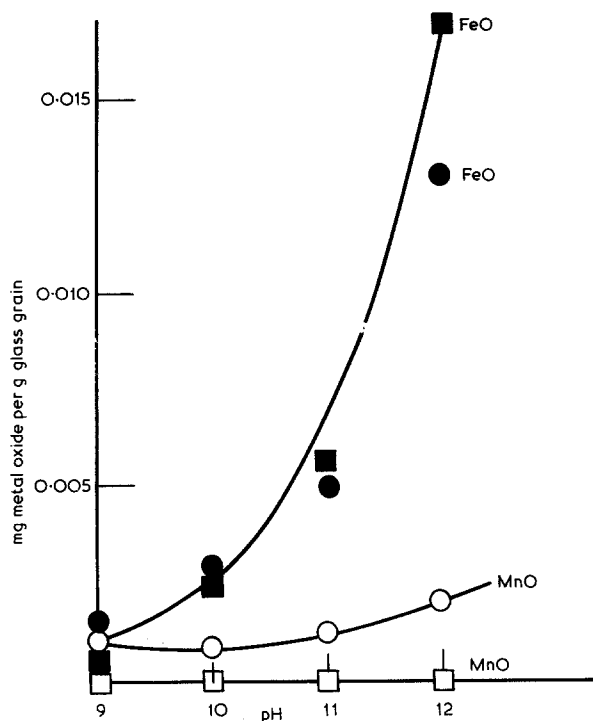


Figure 9 Extraction of FeO (● and ■) and MnO (○ and □) from glass 6 (circles) and glass 7 (squares) at 75° C after 4 h.

alkalinity can be judged. Since these data are available only for 25° C and one atmosphere pressure, the following discussion refers to that temperature and pressure only.

The various aqueous reactions of the major component oxides in the present glasses are listed in Table III, and the stability diagrams for the different oxides, calculated from the standard free energy data (given in Table III), are shown in Figs. 10, 11 and 12.

The very limited solubility of silica in neutral or acidic aqueous solutions (except HF) is one of the

main factors in determining the corrosion resistance of silicate glasses [12]. From Fig. 10 it can be seen that the solubility of silica, in terms of H_2SiO_3 in the solution, is independent of the pH, but that in the presence of alkali when the pH of the solution increases above 9 additional silica in the form of silicate ions ($HSiO_3^-$, SiO_3^{2-}) passes into the solution. In fact if one divides the pH into three zones as is done in Fig. 10, then it is possible to establish the pH range over which particular species are of importance. For example, it can be seen that in the first zone ($pH \leq 10$), the minimum solubility is

TABLE III Thermochemical data for reactions of some major component oxides of glass with water at 25° C

Reaction	ΔG° (kJ mol ⁻¹)	log K	Relationship
SiO_2 (glass) + H_2O (liq) \rightleftharpoons H_2SiO_3	+ 23.389	- 4.11	$\log(H_2SiO_3) = - 4.098$
$H_2SiO_3 \rightleftharpoons HSiO_3^- + H^+$	+ 57.07	- 10.00	$\log(HSiO_3^-) = - 14.098 + pH$
$HSiO_3^- \rightleftharpoons SiO_3^{2-} + H^+$	+ 68.45	- 12.04	$\log(SiO_3^{2-}) = - 26.092 + 2pH$
MnO (cryst) + H_2O (liq) \rightleftharpoons $Mn(OH)_2$	- 14.27	+ 2.51	$\log(Mn(OH)_2) = 2.50$
$Mn(OH)_2 \rightleftharpoons HMnO_2^- + H^+$	+ 108.78	- 19.13	$\log(HMnO_2^-) = - 16.56 + pH$
$Mn(OH)_2 + 2H^+ \rightleftharpoons Mn^{2+}$ (aq) + $2H_2O$ (liq)	- 87.36	+ 15.37	$\log(Mn^{2+}) = 17.81 - 2pH$
Mn_2O_3 (cryst) + $3H_2O$ (liq) \rightleftharpoons $2Mn(OH)_3$	+ 85.23	- 14.99	$\log(Mn(OH)_3) = - 14.934$
$Mn(OH)_3 + 2H^+ \rightleftharpoons Mn^{3+}$ (aq) + $3H_2O$ (liq)	- 36.28	+ 6.38	$\log(Mn^{3+}) = - 8.578 - 3pH$
FeO (cryst) + H_2O (liq) \rightleftharpoons $Fe(OH)_2$	- 2.01	+ 0.35	$\log(Fe(OH)_2) = 0.352$
$Fe(OH)_2 + 2H^+ \rightleftharpoons Fe^{2+}$ (aq) + $2H_2O$ (liq)	- 75.77	+ 13.33	$\log(Fe^{2+}) = 13.629 - 2pH$
$Fe(OH)_2 \rightleftharpoons HFeO_2^- + H^+$	+ 104.36	- 18.36	$\log(HFeO_2^-) = - 17.935 + pH$
Fe_2O_3 (cryst) + $3H_2O$ (liq) \rightleftharpoons $2Fe(OH)_3$	+ 63.47	- 11.16	$\log(Fe(OH)_3) = - 5.561$
$Fe(OH)_3 + H^+ \rightleftharpoons Fe(OH)_2^+ + H_2O$ (liq)	+ 13.01	- 2.29	$\log(Fe(OH)_2^+) = - 7.841 - pH$
$Fe(OH)_3 + 2H^+ \rightleftharpoons Fe(OH)^{2+} + 2H_2O$ (liq)	- 13.77	+ 2.42	$\log(Fe(OH)^{2+}) = - 3.149 + 2pH$
$Fe(OH)_3 + 3H^+ \rightleftharpoons Fe^{3+}$ (aq) + $3H_2O$ (liq)	- 27.57	+ 4.85	$\log(Fe^{3+}) = - 0.72 - 3pH$
$Fe(OH)_3 + H_2O$ (liq) \rightleftharpoons $Fe(OH)_4^- + H^+$	- 77.24	- 13.53	$\log(Fe(OH)_4^-) = - 19.09 + pH$

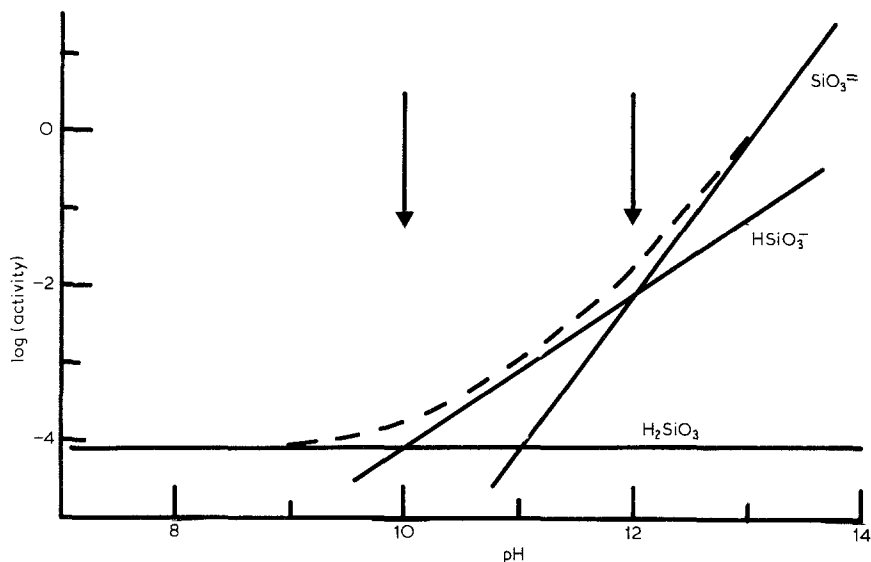


Figure 10 Stability diagram of fused silica in aqueous solution at different pH (25° C).

represented by the undissociated silica (hydrated form), the soluble portion (H_2SiO_3) being $\sim 8 \times 10^{-5}$ molar; this species predominates between $\text{pH} = 0$ and 9 (independent of pH). In the second zone ($\text{pH} = 10$ to 12) most of the silica which passes into the solution is due to the formation of HSiO_3^- . In the third zone ($\text{pH} \geq 12$), the SiO_3^{2-} ion predominates in the solution. The total silica

solubility increases exponentially with alkalinity of the solution.

The stability of MnO and Mn_2O_3 in aqueous solution is shown in Fig. 11. From this figure it is clear that Mn_2O_3 is much more stable than MnO at all pH values in water. Hydration of Mn_2O_3 is energetically less favourable and Mn^{3+} predominates over $\text{Mn}(\text{OH})_3$ only at $\text{pH} \leq 2$. On the

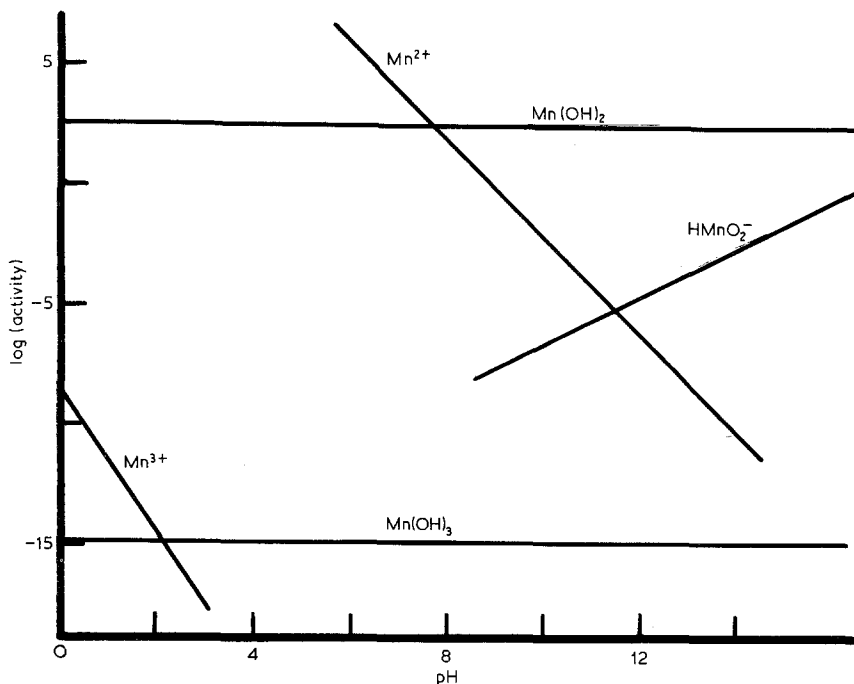


Figure 11 Stability diagram of MnO and Mn_2O_3 in aqueous solution at different pH (25° C).

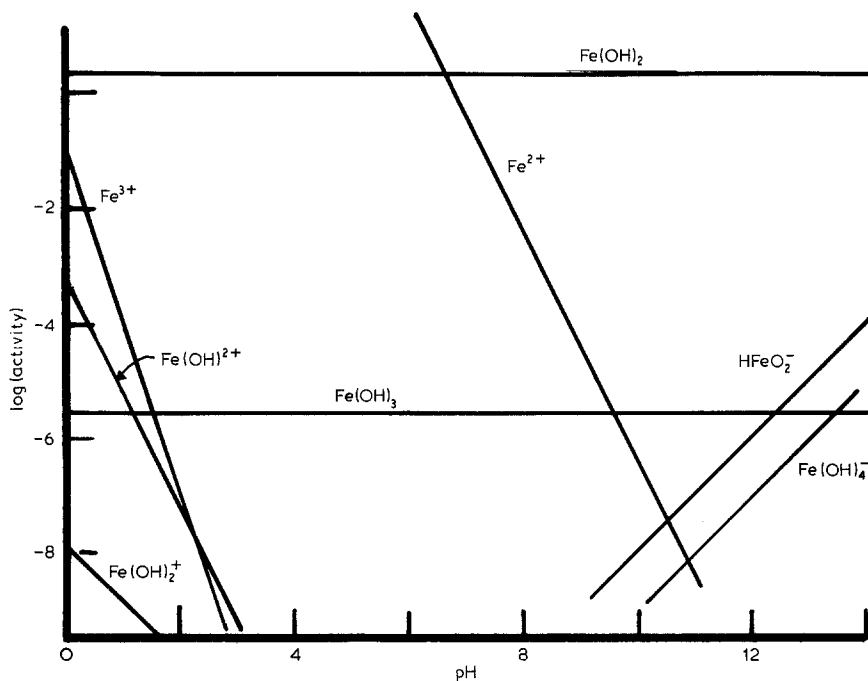


Figure 12 Stability diagram of FeO and Fe₂O₃ in aqueous solution at different pH (25° C).

other hand at $\text{pH} \leq 7.65$ $\text{Mn}(\text{OH})_2$ is the favoured species and Mn^{2+} predominates over $\text{Mn}(\text{OH})_2$. Mn^{3+} does not form any known anionic complex in the alkaline range; the activity of the anionic complex of Mn^{2+} , (HMnO_2^-) is much lower than that of $\text{Mn}(\text{OH})_2$ even at $\text{pH} = 14$. Thus both MnO and Mn_2O_3 are quite stable in the alkaline region.

Most of the manganese (more than 99% of total manganese) in manganese-containing glasses occurs as MnO [13, 14]. Thus manganese-containing glasses are expected to be alkaline-resistant, whereas the acid resistance of these glasses is expected to be poor. This trend is nicely followed by the experimental results for glasses (2, 5, 6 and 7) containing manganese oxides. In all the glasses very small (sometimes below the detection limit, ~ 0.025 ppm) amounts of manganese were released into the solution in the alkaline region, whereas at $\text{pH} 2, 1$ and particularly at 0 much more manganese was released. Further, it may be noted that the passive resistance of manganese oxides in the alkaline region has suppressed the release of SiO_2 and Na_2O from the glass, and thus the overall durability of these glasses in the alkaline region appears quite satisfactory.

From Fig. 12 it can be seen that the hydration of Fe_2O_3 (formation of $\text{Fe}(\text{OH})_3$) is energetically

unfavourable, whereas hydration of FeO (formation of $\text{Fe}(\text{OH})_2$) is very favourable and Fe^{3+} in solution becomes the predominant species only at $\text{pH} \leq 1.6$. It may be noted that at $\text{pH} \sim 2.45$ the nature of the predominant species in solution (except $\text{Fe}(\text{OH})_3$) changes from Fe^{3+} to $\text{Fe}(\text{OH})^{2+}$, but activities of both these species are much smaller than that of $\text{Fe}(\text{OH})_3$. Anionic complexes of ferric iron like HFeO_2^- and $\text{Fe}(\text{OH})_4^-$ become predominant at pH values of 12.4 and 13.45 respectively.

In the case of FeO , Fe^{2+} becomes the predominant species at $\text{pH} \leq 6.6$. No anionic complex of ferrous iron is known in the alkaline region.

From the above discussion it appears that the acid resistance of iron-containing glasses, particularly with more FeO , will be poor. The alkaline resistance of iron-containing glasses is expected to be satisfactory only up to $\text{pH} = 12.4$, and the alkaline resistance of iron-containing glasses will not be as satisfactory as with manganese-containing glasses. These general predictions hold, as may be seen from results with glasses 1, 4, 6 and 7. Comparing the leaching results of glass 1 with that of glass 2, it is at once apparent that the alkaline resistivity of iron-containing glass is inferior to that of manganese-containing glass. The acid resistance of iron-containing glass is also worse than that of

manganese-containing glass; the overall durability of neither of these two types of glasses are satisfactory, particularly at pH ~ 0.

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