The relative influences of Al_2O_3 and Fe_2O_3 on the chemical durability of silicate glasses at different pH values

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The influence of the pH of aqueous solutions on the chemical durability of two glasses in the system $Na_2O-FeO-Fe_2O_3-SiO_2$ has been compared with that of two glasses in the system $Na_2O-MgO-Al_2O_3-SiO_2$ where equimolar substitution of MgO for FeO and Al_2O_3 for Fe_2O_3 have been made. The presence of Fe_2O_3, and particularly of Al_2O_3, in glass reduces its alkali extraction in the pH range 4 to 9. The extraction results have been discussed and interpreted in the light of the available standard thermochemical data for the component oxides of these glasses.

1. Introduction

The chemical durability of a glass depends on its composition. In silicate glasses the addition of some oxides like Na_2O or K_2O reduces their chemical resistance, whereas the addition of Al_2O_3 or ZrO_2 increases it, when substituted for SiO_2. Different workers have attempted to study the relative influences of the addition of different oxides on the chemical durability of silicate glasses [1-3]. In most cases a satisfactory comparison cannot be made because the substituent metal ions have different charges and sizes from those of the replaced ions. Even in the case of simple ionic diffusion through a rigid matrix, and involving no chemical reaction, the diffusion rate depends on the charge and size of the diffusing ion. As the ionic sizes and coordination numbers of Fe^{3+} and Fe^{2+} ions are close to those of Al^{3+} and Mg^{2+} ions respectively when present in glass [9-11, 13], in the present investigation we have studied the chemical durability of a series of four silicate glasses where equimolar substitution of Al_2O_3 for Fe_2O_3 and MgO for FeO have been made.

2. Experimental

The compositions of the glasses (after chemical analyses) are given in Table I. Acid washed quartz (iron content less than $0.01\,wt\%$ as Fe_2O_3), AnalaR grades of Na_2CO_3, Al_2O_3, and laboratory grade Fe_2O_3 (purity $\geqslant 99\%$) were used as batch materials. Batch materials to produce $500\,g$ of glass were accurately weighed, thoroughly mixed in a porcelain mortar, and melted in a platinum crucible at $1450°C$ for $5\,h$ with mechanical stirring for homogeneity. The ferrous/ferric ratio in the iron-containing glasses was varied by changing the oxygen pressure in the furnace atmosphere. After melting, the glass was cast as rods and thoroughly annealed. Grains (-30, $+52$ BS mesh) were made from all these glasses under standard conditions [4]. To study the chemical durability a $1\,g$ portion of grain was put in a $50\,ml$ aqueous solution buffered at various pH values, and digested at a controlled temperature ($70 \pm 1°C$) in the water bath for $5\,h$. The compositions of the

TABLE I Compositions of the glasses (after chemical analysis)

Glass number	Composition (mol%)					
	Na_2O	SiO_2	$\frac{1}{2}Fe_2O_3$	FeO	$\frac{1}{2}Al_2O_3$	MgO
1	12.53	73.42	12.55	1.50	–	–
2	12.56	74.32	11.26	1.87	–	–
5	12.53	73.42	–	–	12.55	1.50
6	12.56	74.32	–	–	11.26	1.87

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Figure 1 Extraction of silica from the glasses at various pH values.

buffer solutions are given in Table II. During digestion the polythene bottles containing the grains and the corroding solutions were continuously shaken at a constant speed of 160 strokes per minute. After 5 h the bottles were taken out, the grains removed, and the leached constituents of glass in the solution were determined. Na_2O was estimated with the flame photometer, SiO_2 with molybdic acid, total iron from its ultra-violet absorption in 9N HCl, magnesium with atomic absorption, and aluminium colorimetrically with Solochrome cyanine R.

3. Results and discussion

The amounts of silica, soda, alumina and iron extracted from these glasses at various pH values are shown in Figs. 1 to 3. All these glasses contain 73 to 74 mol % SiO_2 and 12.5 mol % Na_2O; the remainder is mainly made up of Al_2O_3 or Fe_2O_3. Thus the acid- and alkaline-durability of these glasses will reflect the relative effectiveness of these two oxides (Al_2O_3, Fe_2O_3) in protecting silicate glasses.

3.1. Extraction of silica

All these glasses release very similar and small amounts of silica in the acid region ($\leqslant$ 0.2 mg/g glass grain). In the alkaline region (pH$\geqslant$8) the extraction of silica increases rapidly with increasing pH of the solution. There is no significant difference in silica extraction from the two iron-containing glasses (glass nos. 1 and 2); and silica extractions from the two aluminium-containing glasses (glass nos. 5 and 6) are also not significantly different from each other. However, in the alkaline region the silica extraction from glasses 1 and 2 is much higher than that from glasses 5 and 6. This may be due either to the greater "passivity" of hydrated Al_2O_3 in the alkaline region or to SiO_2 having a lower activity in the Al_2O_3–SiO_2 system than in the Fe_2O_3–SiO_2 system [5].
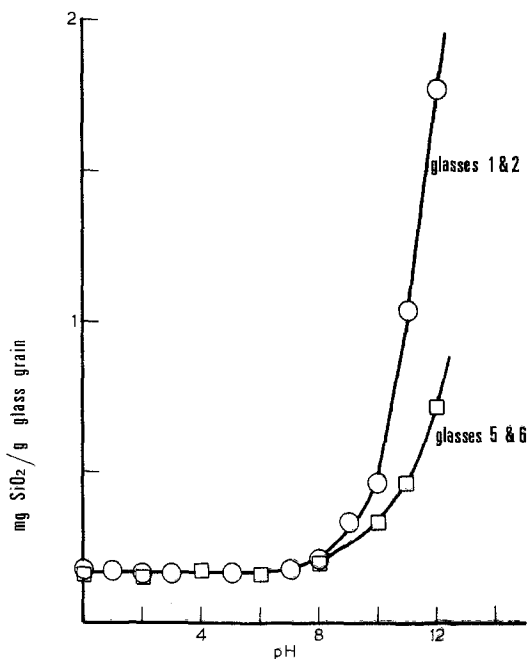
The very limited solubility of silica in neutral or acidic aqueous solutions (except HF) is one of the main factors in determining the corrosion resistance of silicate glasses. From thermochemical considerations it can be shown [6] that the solubility of silica in aqueous acid solutions is due to the formation of H_2SiO_3, and is very small. However, 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. Thus an enhanced extraction of silica at pH $\leqslant$ 9 is a common feature of all silicate glasses, and this has also been found to be so in the present study (Fig. 1).

As will be shown shortly, in the alkaline region hydrated alumina is stable up to pH = 10.7; when the pH of the solution increases further soluble AlO_2^- species are formed. Thus Al_2O_3 in a silicate glass is expected to reduce the silica extraction in the alkaline region, as indeed has been found in the present investigation. Hydrated ferric oxide is also stable in the alkaline region (Fig. 5). Anionic species of ferric iron like $HFeO_2^-$ and $Fe(OH)_4^-$ become predominant at pH values 12.4 and 13.5 respectively. However, the free energy of mixing of Fe_2O_3 with SiO_2 is much less negative than that of Al_2O_3 with SiO_2 [7]. Thus the activity of silica in glasses 1 and 2 is expected to be much higher than that in glasses 5 and 6. Besides, the mor-

phology of the hydrated Al_2O_3 layer may be quite different from that of the hydrated Fe_2O_3 layer, and this could alter the rate of extraction significantly.

Glass 1 contains slightly more Fe_2O_3 than glass 2. As may be seen from Fig. 5, Fe_2O_3 is more stable, both in the acid and in the alkaline medium, than FeO. Thus glass 1 is expected to be relatively more durable than glass 2. However, the free energy of mixing in the system $FeO-SiO_2$ is more negative than that of $Fe_2O_3-SiO_2$ [7]. Thus the activity of silica in glass 2 is smaller than that in glass 1. It is therefore probable that the very similar silica extraction from glasses 1 and 2 is due to these two factors (lower stability of hydrated FeO and lower activity of silica in the $FeO-SiO_2$ system) counter-balancing one another. Besides, the FeO contents of glasses 1 and 2 are only slightly different, and may not be large enough to produce a noticeable effect on the silica extraction.

3.2. Extraction of soda
The results of extraction of soda from these glasses are shown in Figs. 2a and b. Fig. 2a also contains, for comparison, the results of soda extraction from a glass of molar composition: $74.5\,SiO_2$, $12.5\,Na_2O$, $11.0\,CaO$, $2.0\,MgO$ (which is very similar to glass 6 where Fe_2O_3 has been replaced by CaO). In the case of the lime glass the extraction of soda remains almost constant from pH 1 up to pH 9 to 10; at higher pH values the extraction of soda drops. This is usually explained on the basis of a decrease in the amount of exchangeable proton in the solution as the pH increases [8]. The soda extraction behaviours of iron- and aluminium-containing glasses are very different. Up to pH 3, extraction of soda from these glasses is high and qualitatively similar to that from the CaO-containing glass; with further increase of pH extraction of soda drops very steeply in the case of Al_2O_3-containing glasses, and less steeply in the case of Fe_2O_3-containing glasses. Soda extraction from all four glasses goes through a minimum plateau around pH $\sim 5-11$, and then increases very steeply with further increase of pH of the solution. In the acid range (pH $\leqslant 3$), more soda is extracted from the glasses containing Al_2O_3 whereas at pH $\geqslant 4$ more soda is extracted from the glasses containing Fe_2O_3.

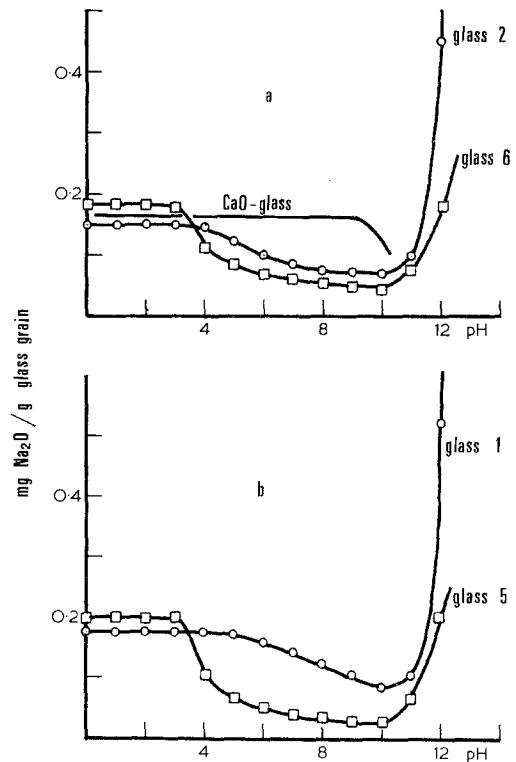In sodium silicate glasses, iron(III) [9] and aluminium(III) [10, 11] occur in tetrahedral co-

Figure 2 Extraction of soda from the glasses at various pH values.

ordination (FeO_2Na, AlO_2Na) and probably a significant fraction of the sodium ions is closely associated with the ferric and trivalent aluminium ions in these glasses. In the acid range (pH $\leqslant 3$) both hydrated Fe_2O_3 and hydrated Al_2O_3 are unstable and form soluble Fe^{3+} (aq) and Al^{3+} (aq) ions; thus large amounts of iron and aluminium are extracted at pH values less than 3, and consequently sodium ions come out with them. Also, the leaching of iron(III) and aluminium(III) from glass in the acid region probably removes the "blocking effect" for the migration of sodium ions associated with silica in these glasses.

Above pH 3 hydrated Al_2O_3 is stable and is well known to chemisorb sodium ions [12]. This is why an Al_2O_3-containing silicate glass electrode can be used to estimate the activity of sodium ions in aqueous solution at pH $\geqslant 3$. From the results of Figs. 2a and b it appears that hydrated iron oxides are also capable of chemisorbing sodium ions, although not as effectively as hydrated aluminium oxide. Comparing extraction of soda from glasses 5 and 6 it appears that hydrated FeO is probably a more preferable site for Na^+ adsorption than hydrated Fe_2O_3.
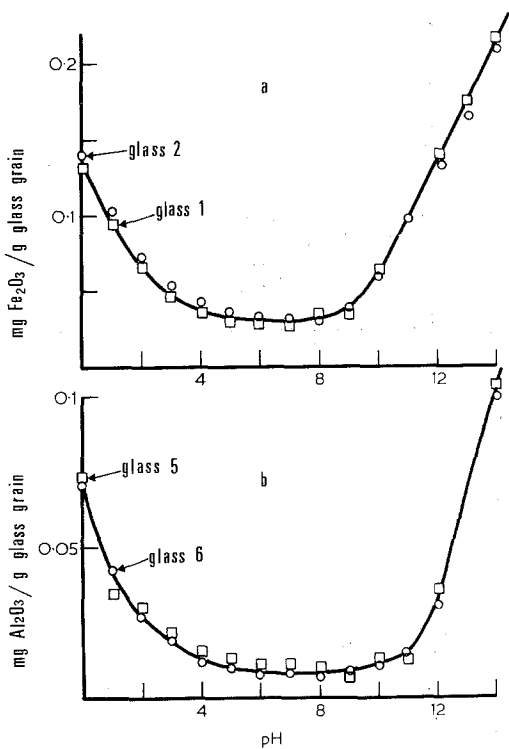
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Figure 3 (a) Extraction of iron from glasses 1 and 2 at various pH values. (b) Extraction of alumina from glasses 5 and 6 at various pH values.

3.3. Extraction of iron and aluminium

The results of extraction of iron and aluminium from these glasses are shown in Figs. 3a and b respectively. The stability diagrams of Al_2O_3, FeO and Fe_2O_3 in aqueous solution at different pH values are shown in Figs. 4 and 5. As is clear from these figures, iron and aluminium oxides are unstable at pH $\leqslant 3$, and consequently large amounts of iron and aluminium are extracted from all these glasses in the acid region. In the alkaline region (pH $\geqslant 10.7$) hydrated Al_2O_3 becomes sus-
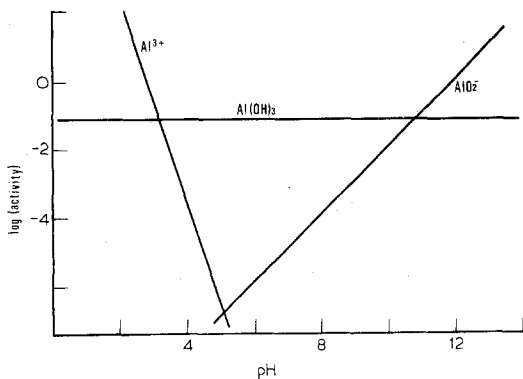

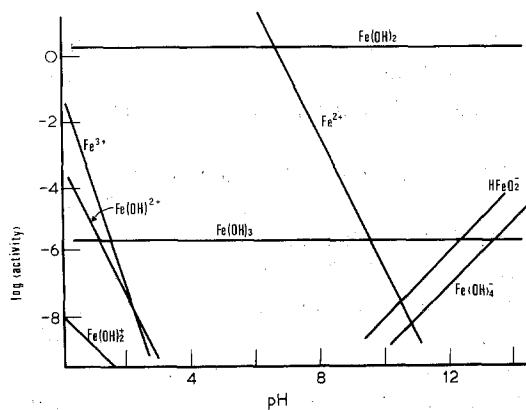*Figure 4* Stability of Al_2O_3 in aqueous solution at various pH values (25° C).

Figure 5 Stability of FeO and Fe_2O_3 in aqueous solution at various pH values (25° C).

ceptible to dissolution due to the formation of AlO_2^- species. From Fig. 3b it can be seen that indeed the extraction of aluminium increases rapidly around pH ~ 11 with increasing alkalinity of the solution. Hydrated Fe_2O_3 does not form any known anionic species up to pH ~ 13, and the anionic species of FeO does not form at all in the alkaline range. From Fig. 3a it is clear that extraction of iron from these glasses also increases with increasing alkalinity above pH ~ 9. This may be due to the fact that silica, the backbone of glass, becomes susceptible to dissolution at pH $\geqslant 9$, and hydrated iron oxide then enters the solution not as a soluble species but as an insoluble colloidal suspension, as the silicate surface disintegrates.

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