Durability of Na_2O–RO–SiO_2 glasses in water

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The effect of divalent cation ions on chemical durability was studied in the base glasses $16Na_2O$–$10RO$–$74SiO_2$. In order to keep the same surface area, a fixed volume of glass powder was exposed to the corroding action of water. The amount of SiO_2 and alkali extracted was determined. The chemical durability of glass was found to increase with increasing bond strength between the divalent cation and the non-bridging oxygen ion.

1. Introduction

During the past, many systematic investigations [1–14] have been carried out to study the effect of various glass constituents on the chemical durability of glasses. In most of these studies [5–13] a fixed weight of glass grains was reacted with water or other solutions and the quantities of alkali and other glass constituents extracted per gram of glass grains were reported and the mechanism of chemical corrosion of glass was discussed.

As the chemical durability of glass is a surface phenomenon, the quantity of glass constituents extracted by a reacting liquid from a glass of constant composition in a definite time at a fixed temperature depends on the surface area exposed to the corroding liquid. When the composition of glass is varied over a wide range, the surface area of a fixed weight of glass grains of specified particle size may vary considerably due to change in its density. Hence the results given by previous workers in terms of the quantity of glass consituents extracted per gram of glass grains per unit time may not necessary give the correct picture of the relative effect of different glass constituents on the chemical durability of glasses.

The objective of the present investigation was to study the effect of divalent cations on chemical durability of glasses by exposing a fixed surface area of glass grains to the corroding action of water.

2. Experimental details

In a base glass $16Na_2O \cdot 10RO \cdot 74SiO_2$ (mol%) composition), RO was provided by MgO, CaO, SrO, BaO, PbO and ZnO on a molar basis. Acid-washed quartz was used as a source of SiO_2 and other oxides were introduced as their respective carbonates or oxides of analytical reagent grade. The glasses were melted in a Pt–2% Rh crucible kept in an electric furnace at $1425 \pm 20°C$, in air. After 6 h melting the glasses were poured on a plate, crushed and remelted for another 2 h. The molten glass was cast and annealed in an electric muffle. The glasses were tested according to the ASTM powder test [15] and the ISI test [16] taking a fixed volume of glass grains.

2.1. ASTM powder test

The glass powder (− 40 + 50 mesh) was washed with acetone and dried. According to specification, 10 g glass grains (− 40 + 50 mesh) are exposed to the corroding action of 50 ml double distilled water as per schedule of the test. The surface area of these powders was earlier assumed to be equal to $375 \, cm^2 \, cm^{-3}$ total glass volume [17]. Thus 10 g soda-lime silica glass having the density 2.475 (Table I) will have $1515 \, cm^2$ surface area. In order to keep the surface area of the glass grains constant, varying weights of the glass grains (10/2.475 × density) were taken and the test was performed as per specification. After the test, alkali (Na_2O) in the extract was determined

TABLE I Density, surface area and amount of Na_2O and SiO_2 extracted per cm^3 glass grain (glass composition 16 $Na_2O \cdot 10RO \cdot 74SiO_2$)

Group	Stabilizing ions	Density ($g\ cm^{-3}$)	Surface area per glass grain ($cm^2\ g^{-1}$)	Co-ordination number	Coulombic force (Pauling's radius)	SiO_2 extracted ASTM powder test (mg)	Na_2O extracted (mg)	
							ISI test	ASTM powder test
I	Mg^{2+}	2.441	153.63	6	0.476	0.0277	0.774	2.977
	Ca^{2+}	2.475	151.52	8	0.350	0.0294	1.000	3.772
	Sr^{2+}	2.674	140.24	8	0.313	0.0381	1.504	5.524
II	Ba^{2+}	2.831	132.46	8	0.265	0.0569	1.920	9.317
	Zn^{2+}	2.610	143.68	4	0.440	0.0096	0.737	1.505
	Pb^{2+}	3.020	124.17	4	0.294	0.0321	1.152	4.390

by titrating a part of it against $0.02\,N$ H_2SO_4. From another aliquote portion, the SiO_2 was estimated by silico-molybdenum blue method on a photo-electric colourimeter.

2.2. ISI test

In this test 5 g glass powder ($-25 + 36$ mesh) is reacted with 100 ml double distilled water at $100°C$ for $\frac{1}{2}$ h in a chemically resistant conical flask of 250 ml capacity fitted with reflux condenser. To keep the surface area of the glass powders constant, varying weights of glass powders ($5/2.475 \times$ density) were taken and the test was performed as per schedule. The alkali extracted was titrated against $0.01\,N$ HCl.

3. Results and discussion

The density of the glasses determined by Archimedes principle are given in Table I. The density of the heaviest glass of this series is about 18% higher than the density of the lightest glass as given in Table I. A curve showing the surface area of 1 g glass grains ($-40 + 50$ mesh) as a function of density is presented in Fig. 1.

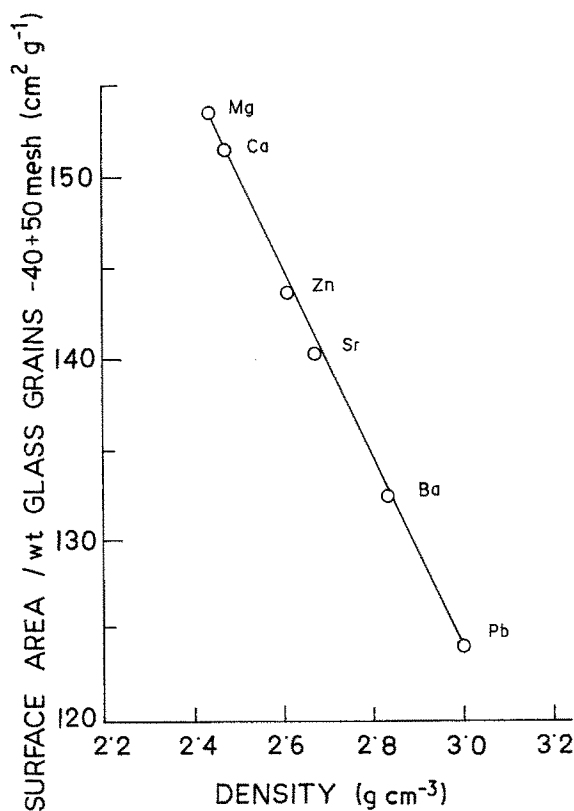The results summarized in Table I show that in each group, the quantity of alkali extracted

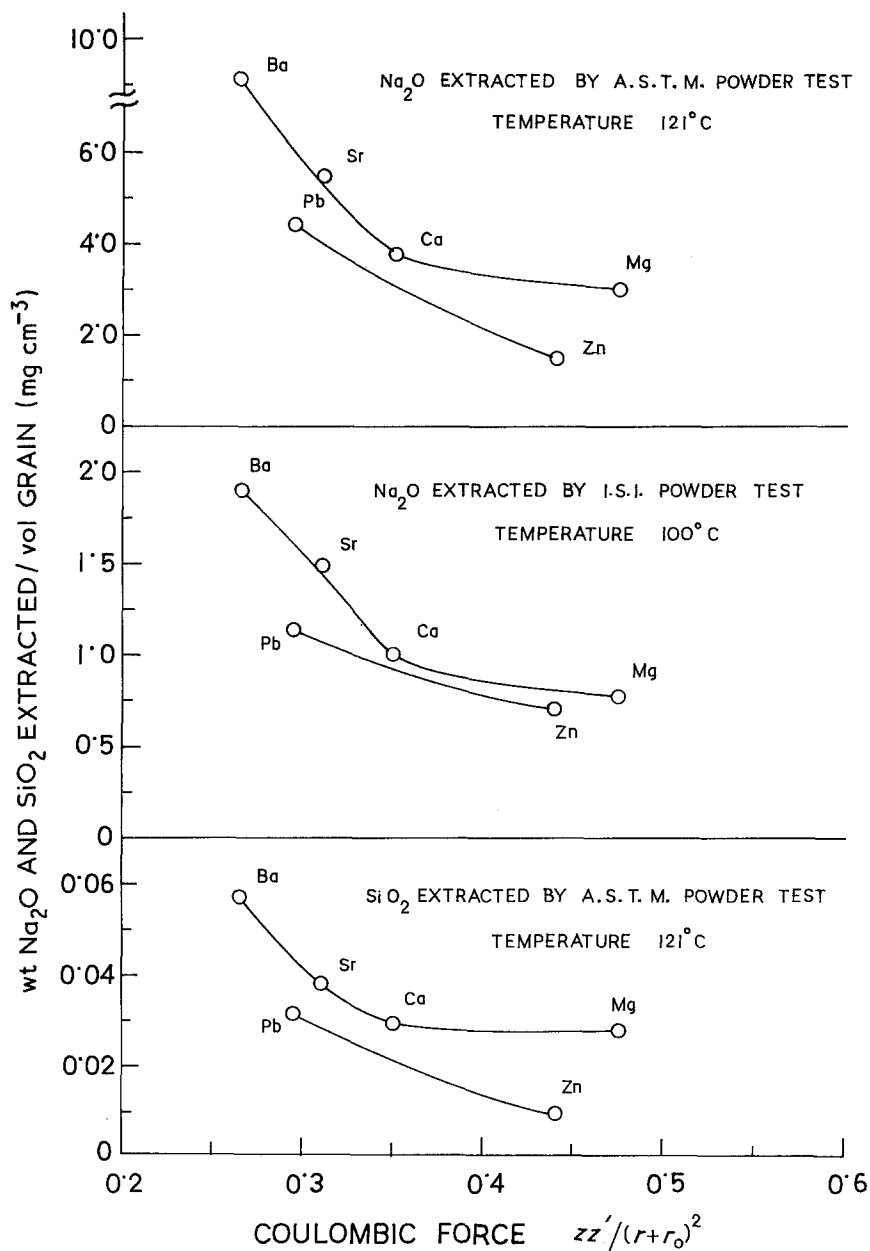Figure 1 Relation between density and surface area (cm^2) per g glass grains in 16 $Na_2O \cdot 10RO \cdot 74SiO_2$ glasses.

Figure 2 Effect of coulombic force on extraction of mg Na_2O and SiO_2 per cm^3 grain in $16\,Na_2O \cdot 10RO \cdot 74SiO_2$ glasses.

decreases with increasing coulombic force* between the divalent cations and non-bridging oxygens. The quantity of SiO_2 extracted also increased in the same order. The reaction between water and glass [1] is a highly complex one involving the penetration of glass by water and subsequent decomposition of the complex silicate mixture with formation of substances wholly different from those originally present. Various workers [5, 18—25] have discussed the mechanism of this reaction. It is now more or less established that the reaction between water and glass is due to a diffusion process as shown by Isard and Douglas [5] and Beattie [23] as well as due to the breakdown of the glass network. Das and Douglas [8] observed the extraction of SiO_2 from ternary silicate glasses even during the "first mechanism" in which ion exchange plays

*The coulombic forces were calculated using the formula $zz'/(r + r_0)^2$ where z, z' are the electrostatic charge on the divalent cations and non-bridging oxygen ions, and r and r_0 represent their ionic radii, respectively.
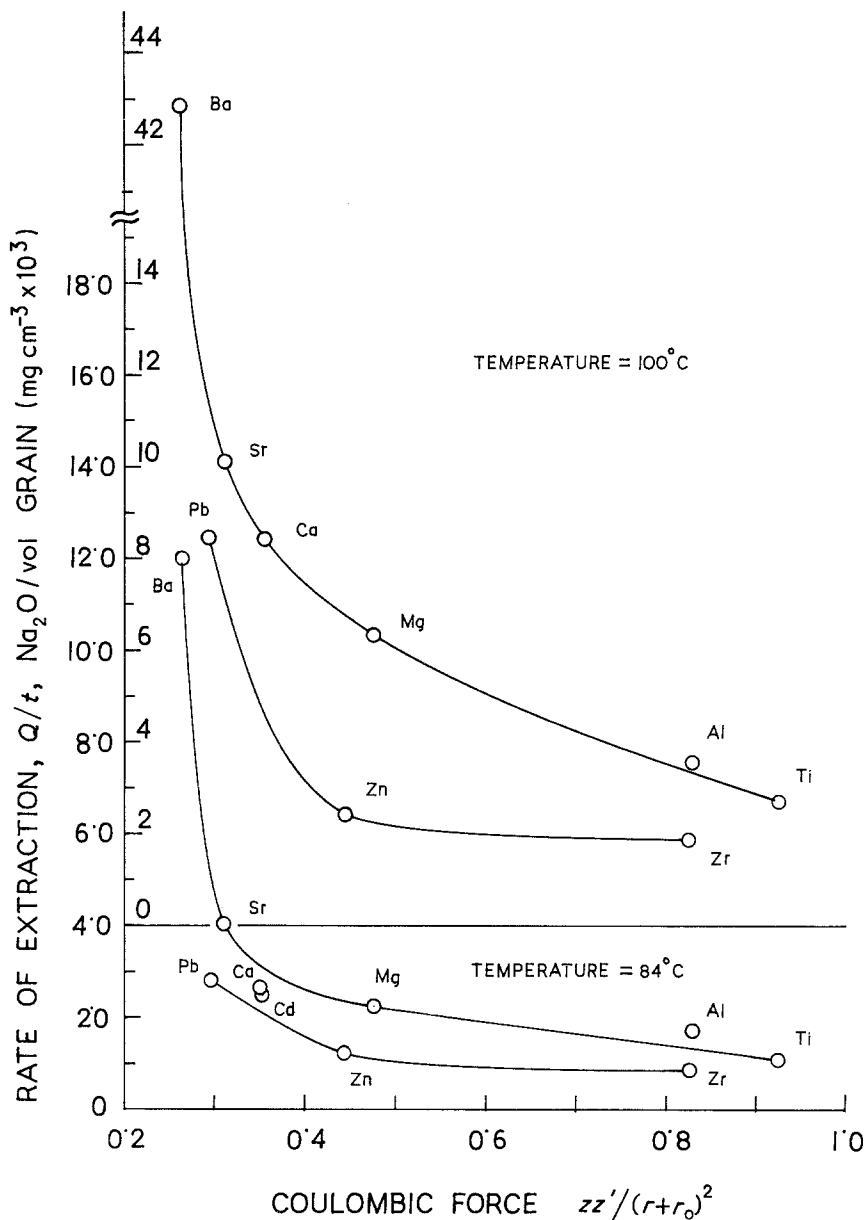
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Figure 3 Effect of coulombic force on rate of extraction, Q/t, of Na_2O per cm^3 grain in $15Na_2O \cdot 5RO \cdot 80SiO_2$ glasses.

the dominant role. During reaction of water with glasses in the present investigation, it is assumed that both an ion-exchange mechanism and network dissolution play a part.

Charles [26] represented the mechanism of reaction between water and glass by the following three chemical reactions:

(1) H^+ from the water penetrates the glass network, replacing an alkali ion which is released into solution, producing an OH^- ion and a non-bridging oxygen bond attached to an H^+ ion (NSH);

(2) reaction with OH^- ions destroys the $\geqslant Si-O-Si \leqslant$ bond to form a non-bridging $\geqslant Si-O$ bond (NS); and

(3) the NS bond interacts with an H_2O molecule, forming another NSH bond and an OH^- ion, which is free to repeat reaction 2.

In ternary silicate glasses an increase in coupling interactions between $\geqslant Si-O-Si \leqslant$ and NS bonds influenced by the presence of the divalent cations, has been reported [27]. The stronger structural coupling retards the dealkalization of the glass. The divalent cations have been reported [27] to
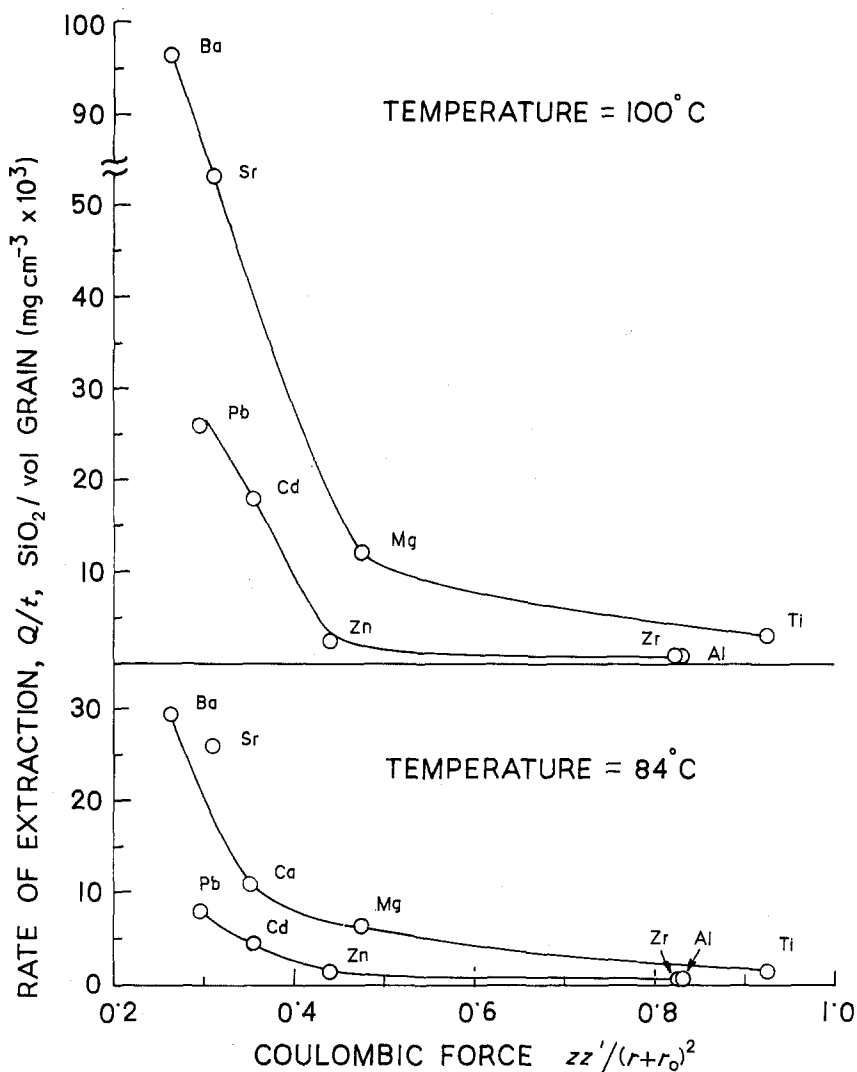
Figure 4 Effect of coulombic force on rate of extraction, Q/t, of SiO_2 per cm^3 grain in $15\,Na_2O \cdot 5RO \cdot 80SiO_2$ glasses.

stabilize the SiO_2-rich surface film by filling the microvoids, satisfying the bonds, and forming a chemical barrier to sodium diffusion. The chemical bond between divalent cations and non-bridging oxygens changes depending on the nature and size of divalent cations. As the coulombic force between divalent cations and non-bridging oxygens increases, bond strength is expected to increase resulting in a greater chemical barrier to sodium diffusion.

The quantities of Na_2O and SiO_2 extracted per cubic centimetre glass grains were plotted against the coulombic forces and results are shown in Fig. 2. It is observed from Fig. 2 that the quantities of Na_2O and SiO_2 extracted per cubic centimetre glass grains decrease as the bond strength between the divalent cations and non-bridging oxygen increases for each series of glasses.

To confirm the above findings, the data given by Das and Douglas [8] were recalculated. Utilizing the values of quantities of Na_2O and SiO_2 extracted per gram grain per unit time for the second mechanism in which breakdown of the glass network is predominant, the theoretically calculated densities [28], and the quantities of Na_2O and SiO_2 extracted per cubic centimetre glass grains per unit time were calculated. Results plotted against coulombic forces and presented in Figs. 3 and 4 also confirm that the chemical durability of glasses increases with increasing bond strength between the divalent cations and the non-bridging oxygens. It may be pointed out that Das [29] had earlier plotted Q/t per gram glass grain per unit time against field strengths of the various cations but this did not give a correct picture of the relative effect of

TABLE II Effect of coulombic force between cations and non-bridging oxygen ions on the rate of extraction Q/t of Na_2O and SiO_2 per cm^3 glass grains (based on the results of Das and Douglas [8]) for the second mechanism

Group	Stabilizing ions	Density (calc) ($g\,cm^{-3}$)	Co-ordination no. of cation	Coulombic force (Pauling's radius)	Na_2O (10^4 mg) extracted at		SiO_2 (10^{-4} mg) extracted at	
					$100°\,C$	$84°\,C$	$100°\,C$	$84°\,C$
I	Mg^{2+}	2.365	6	0.476	63.86	22.47	122.99	66.23
	Ca^{2+}	2.412	8	0.350	–	26.53	–	108.50
II	Sr^{2+}	2.537	8	0.313	101.47	40.59	532.71	261.28
	Ba^{2+}	2.680	8	0.265	428.83	120.61	964.87	294.82
	Zn^{2+}	2.450	4	0.440	24.50	12.74	24.50	12.25
	Cd^{2+}	2.567	4	0.356	84.70	25.67	177.09	46.20
	Pb^{2+}	2.811	4	0.294	84.34	28.11	258.65	78.72
III	Al^{3+}	2.393	4, 6	0.830	35.89	17.47	10.53	5.74
IV	Ti^{4+}	2.513	6	0.925	27.65	10.81	31.16	13.57
	Zr^{4+}	2.579	6, 8	0.826	19.60	8.77	8.51	5.93

various cations as the surface area exposed per gram varied with the density of the glasses.

For divalent cations having the same coulombic force, the bond strength would be greater for those ions having lower co-ordination numbers [30, 31]. The glasses having divalent cations of lower co-ordination numbers should be more resistant to the breakdown of the network than glasses having divalent cations of higher co-ordination number (Tables I and II). The polarizability of oxygen ions decreases with increasing bond strength or coulombic force between the modifying cations and non-bridging oxygens. The results given in Tables I and II show that the chemical durability decreases with increasing polarizability of non-bridging oxygen ions in glasses.

Thus not only the coulombic force between the divalent cations and non-bridging oxygens but also the co-ordination number of the divalent cations play an important role in the chemical durability of glasses.

The results on Al^{3+}, Ti^{4+} and Zr^{4+} ions show that the above generalization is true for trivalent and tetravalent ions also.

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