Journal of the European Ceramic Society 20 (2000) 2499–2508

The chemical durability of SrO–MgO–ZrO_2–SiO_2 glasses in strongly alkaline environments

B. Karasu *, M. Cable

Department of Engineering Materials, University of Sheffield, Sheffield, UK

Received 23 July 1999; received in revised form 11 April 2000; accepted 11 May 2000

Abstract

A large region of glass formation was found in the system SrO–MgO–ZrO_2–SiO_2 and some properties have already been reported. Detailed studies have shown that glasses with only 40 wt% silica unusually durable in 1 M NaOH and also in model cement extract solutions. Glasses with higher silica contents are more easily attacked; zirconia and magnesia are the constituents giving the best durability. These results suggest that these glasses could be of interest for reinforcement of cement and concrete. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali attack; Corrosion; Durability; Glass

1. Introduction

The subject of the durability of glass, or its resistance to weathering and chemical reagents, has generally been recognised as one of the most important features in glass technology and its literature is probably greater than that of any other property of glass.[1,2]

Glass is often thought of as an 'inert' material. Most glasses have high corrosion resistance but one must take note that all glass products are chemically reactive to some degree. It is often important to know how glass alters a solution that it contacts or how the glass product is altered by the solution. The prediction of such effects, even when the conditions are well specified, is an inexact process; there are no neat formulas to account for the numerous variables. However, given a knowledge of the glass and its proposed environment, it is possible to make extremely useful comparisons and often to make good predictions.

There is no absolute or explicit measure of chemical durability and glasses are usually graded relative to one another after subjecting them to similar experimental conditions.[3]

Many studies were made during the last century of the reactions of silicate glasses with aqueous solutions, and it is more than 70 years since the first systematic studies were made of the effects of changes in glass composition on the reaction rates.

The different constituents are usually extracted from the glass at different rates resulting in the formation of a surface layer which has a composition different from that of the bulk glass. The thickness of the layer increases with time. In the case of more durable glasses such surface layer decreases the dissolution rates of glass constituents and can eventually stop leaching of glass by the attacking solution.

Although silicate glasses are generally resistant to water and acid attacks they become particularly susceptible to decomposition above pH = 9–10. This happens because strongly alkaline solutions decompose and dissolve the silicate network itself. For the current system does not contain alkali which make silicate glasses susceptible to alkali solution attack causing the total dissolution of glass eventually and since it has zirconia, as one of the major glass constituent, whose positive effect on the improvement of durability in different kind of solutions with changing pH values is a very well known fact, the glasses in this system are expected to show better durability when exposed to an alkaline environment.

---

* Corresponding author at present address. Department of Ceramics, Faculty of Engineering, Architecture, Iki Eylul Campus, Anadolu University, Eskisehir, Turkey. Tel.: +90-222-321-3550 ext, 6357; fax: +90-222-323-9501.

E-mail address: bkarasu@anadolu.edu.tr (B. Karasu).

PII: S0955-2219(00)00155-2

Therefore, a variety of glass compositions have been investigated for different lengths of time. Durability experiments involved glasses with different levels of silica, from maximum to minimum content, as well as with different ratios of the other constituents.

2. Experimental

It has recently been found that the SrO–MgO–ZrO_2–SiO_2 system has a capacity of producing glasses and either melting behaviour[4] or other technological properties[5] of these glasses were thoroughly investigated (Table 1). Here only the chemical endurance of the system will largely be introduced.

In order not to cause misunderstanding all glass compositions were coded in the form of SiO_2/ZrO_2/SrO/MgO (in wt.%) throughout the study. When other oxides such as Al_2O_3 and TiO_2 were added, glass compositions were then named with the symbol of Al+Ti at the end of their codes, such as SiO_2/ZrO_2/SrO/MgO/Al+Ti. When a glass ceramic product was prepared from a glass a GC sign was added at the end of code.

As a first step in this investigation 4 compositions with 50 wt.% silica were chosen to confirm that the compositions with 50 wt.% silica base are capable of giving clear glasses as reported by Ghanbari.[6] After producing glasses with this silica level, as a second step, SrO, MgO and ZrO_2 were kept constant at the relative proportions already used in the first 4 compositions as ZrO_2/SiO_2, SrO/SiO_2 and MgO/SiO_2 and the amount of silica was increased. Consequently, a wide range of glass compositions with silica content of 35–62% have been prepared and called the first set of glasses. At a later stage of the present study more than 50 glass compositions at different silica levels without having any ratio between their constituents were prepared and called the second set of glasses. In this study minimum and maximum limits of the glass compositions searched were: 40–62% SiO_2, 2–15% ZrO_2, 20–50% SrO, and 4–22.5% MgO.[5]

During the experimental investigations a large number of different glass compositions prepared by using laboratory grade raw materials were melted in the temperature range of 1400–1640°C with melting time ranging from 4 h 38 min to 7 h 30 min. Annealing temperatures varied from 750 to 850°C with the annealing time being from 1 to 6 h, depending on the glass compositions.

Glasses with different levels of silica varying from 40 to 60% and some glass ceramics produced were taken to determine their resistance to NaOH attack. Firstly, rectangular shaped specimens of size about 27×8×2.5 mm were prepared and their large faces polished in order to decrease the effect of surface roughness. 1 M NaOH solution was prepared, 40 g NaOH in 1 l deionized water. The specimens were weighed to ±0.0001 g accuracy and suspended in a 300 ml capacity plastic bottle containing 300 ml of solution. A water bath was heated to 75°C and set at that temperature. The plastic bottles were sealed and immersed in the bath for a certain period of time. During the experiments the alkaline solutions were not replaced. A propeller was employed in a water bath to ensure a homogeneous temperature throughout. After taking the samples out of the bath they were washed, cleaned using acetone and the glass ceramics were dried above 140°C for 15 or 20 min in an autoclave to remove the gel like phase on their surface, then weighed. The difference in weights were inspected. After each durability experiment all the solutions were chemically analysed.

Some of the glasses which proved resistant to strong alkali solutions were also tested in a model cement extract with a pH value of 12.5–13. Two identical rectangular glass samples were prepared for each different glass to be examined and polished to decrease the effect of surface roughness. For the preparation of the cement extract 250 g of Portland cement was added to 1.25 l of distilled water in each of two plastic containers. AR grade $CaSO_4.2H_2O$ was also added to the cement extract to give the equivalent of a half saturated solution (1.2 g $CaSO_4.2H_2O$/l). Those two containers were then rolled at 70 rev/min continuously for 18 days. After that the solid and liquid phases were separated by vacuum filtration in a nitrogen atmosphere. Soon after filtration glass samples were inserted into 200 ml capacity plastic bottles and well sealed under the same atmosphere and the experiment carried on for 35 days at 17°C.

3. Results

From the chemical durability point of view the best results in alkaline solutions have been given by the glasses with 40% silica content. The compositional distributions in the ternary phase diagram of these glasses on which the main and detailed studies have been made could be seen from Fig. 1.

Table 1
The results of measurements of physical properties

Densities values (g/cm^3)	2.823 (62.3/4.8/27.4/5.5)–4.074 (40/14.5/25/20.5)
Thermal expansion coefficient values ($\alpha \times 10^{-6}$/°C) (50–300°C)	4.40 (62.3/4.8/27.4/5.5)–9.65 (40/8/40/12)
Transformation temperatures (°C)	720 (45/5.1/41.4/8.5)–805 (40/14.5/32/13.5)
Softening temperatures (°C)	763 (45/5.1/41.4/8.5)–837 (40/15/35/10)

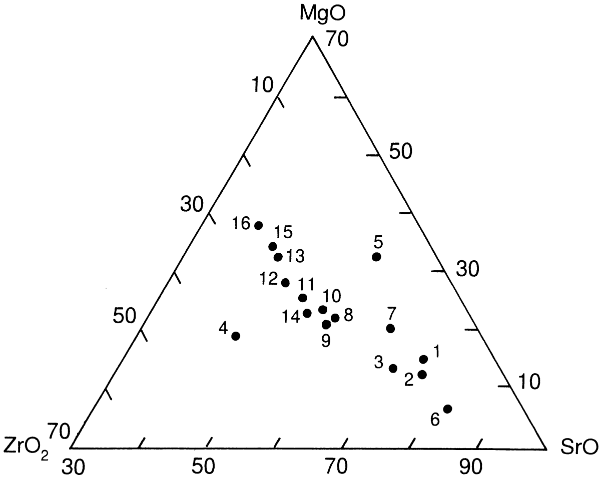


Fig. 1. Compositions (wt.%) of glasses investigated at the 40% silica level.

At the beginning of the investigations on chemical endurance of all the glasses in the system, 13 different glass compositions from first set with different level of silica content were taken for their chemical durability against NaOH attack in 1 M NaOH solutions with pH values of 14 for 33 days at 75°C. In order to compare the durability of those 13 glasses with that of commercially available microscope slides all these glasses were studied under the same conditions (Table 2).

Effect of high silica content on durability can be seen for the 55/4.2/33.9/6.9 glass (Table 2) which has given one of the highest weight loss values in the MgO–SrO–ZrO_2–SiO_2 system after being exposed to alkaline attack for 228 days (Fig. 2). After a gradual increase in weight loss values the glass reached to a point where weight loss value was stabilised as 215 mg after 221 days. In order to see if this occurred because the attacking solution reached saturation, the solution was twice replaced by a fresh solution and each time the glass again started to dissolve. Those new conditions of the 55/4.2/33.9/6.9 glass are numbered II and III and the results in terms of weight loss (in mg) are shown in Fig. 2. It has been seen that after replacing the solution the glass started dissolving again.

For most of the glasses whose durability results are given in Table 3 the column headed time for final weight loss refers to the time that a constant weight loss value was given. Therefore time values in this column do not show the total duration for exposure of these glasses. The experiments were carried out further to ensure that these constant values did not change. Glasses shown with a (∗) denotes full duration of experiment. Since they carried on dissolving continuously the experiments were stopped in that case.

Glasses with 40 wt.% silica from both the first and second set showed better durability results against alkali attack (Tables 2 and 3). Introducing ZrO_2 into the glass is much easier for those glasses as far as melting temperature is concerned. As a result, a detailed study of durability is based on this group and improved durability is also expected with higher ZrO_2 contents.

Even a small amount of alumina is well known to improve the durability of many silicate glasses. For that reason, 5 wt.% Al_2O_3 was added to some glass compositions (Table 3). Addition of 4 wt.% TiO_2 was also made to see its effect on crystallisation behaviour. Chemical durability results of these glasses in 1 M NaOH showed the positive effect of Al_2O_3 on chemical durability of the glasses in the present system (Fig. 3).

Fig. 4 shows the comparison between the 40/15/35/10 and 40/12.5/35/12.5 glasses with high level of zirconia. The 40/15/35/10 glass unexpectedly carried on dissolving without reaching a constant weight loss value after a long period of time. Since this particular glass had melting difficulties and consisted to some extent of undissolved zirconia after melting, it is expected that the zirconia content of the final glass is less than 15%. Consequently, the continuous weight loss can be counted on such fact. As a result, the study of maximum zirconia addition to this glass system was carried out at this stage of the study and finally it has been found that

Table 2.
Durability results for the first set of glasses with different silica levels in 1 M NaOH solution at 75°C for 33 days

Composition	Weight loss (mg)	Weight loss / Total surface area (μg/mm^2)	Composition	Weight loss (mg)	Weight loss / Total surface area (μg/mm^2)
Glasses with 40 wt.% silica			*Glasses with 55 wt.% silica*		
40/10/39.3/10.7	12.05	14.83	55/7.5/29.4/8.1	36.85	45.25
40/10/42.2/7.8	11.75	15.03	55/7.5/31.7/5.8	42.60	51.22
40/7.8/45.5/6.7	14.95	20.36	55/5.8/34.2/5.0	45.35	62.95
40/5.6/45.2/9.3	22.10	29.88	55/4.2/33.9/6.9	48.50	120.44
Glasses with 45 wt.% silica			*Glass with 61 wt.% silica*		
45/9.2/36.0/9.8	15.55	17.66	61.5/8.5/23.5/6.3	64.55	83.32
45/9.2/38.7/7.1	20.50	25.18	Microscope slides	227.35	236.58
45/7.1/41.8/6.1	31.85	36.07			
45/5.1/41.4/8.5	35.20	43.12			

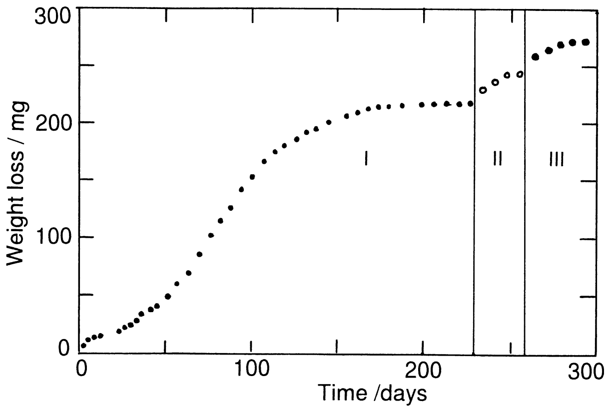


Fig. 2. Durability of 55/4.2/33.9/6.9 glass in 1 M NaOH at 75°C. The effect of twice replacing the attacking solution is shown by the vertical divisions.

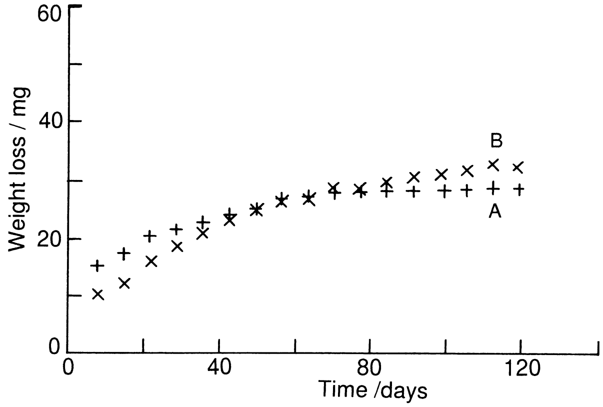


Fig. 3. Durability of 40/6/34.3/10.7/Al+Ti (A) and 40/4/34.3/12/Al+Ti (B) in 1 M NaOH at 75°C.

14.5% zirconia could easily be introduced into glass compositions with 40% silica content.

A comparison of durability behaviour for the 40/5/35/20 glass and its glass ceramic product was also made. The result is given in Fig. 5. Final weight loss value of 49.3 mg after 113 days was given by the glass whereas its glass ceramic product gave a constant weight loss value of 27.9 mg after 98 days. Such a high weight loss value of the glass ceramic may be caused by the dissolution of residual glass phase which can remain after heat treatment.

3.1. The comparison of the durability of the system with other alkali resistant glasses

Majumdar and Ryder[7] made a study on the alkali resistance of glass fibres made of the compositions coded G1 (71% SiO_2, 1% Al_2O_3, 16% ZrO_2, 11% Na_2O and 1% Li_2O) and G2 (64.5% SiO_2, 15.5% Al_2O_3, 10% CaO, 10% MgO). They indicated that alkali resistant glass fibres could reinforce Portland cement effectively and that such composites may be durable over a long period of time. Glasses having compositions in the system Na_2O–ZrO_2–SiO_2 in certain areas of the CaO–Al_2O_3–MgO–SiO_2 system have given promising results.

Larner et al.[8] studied G1, A and E-glass fibres in an ordinary Portland cement (OPC) extract at different temperatures for certain periods of time. According to their study the corrosion of zircono-silicate glass fibres, such as those made from the G1 composition, in alkaline cement extracts proceeds at a very much slower rate than either of the other two glasses studied, namely A and E-glass fibres.

Table 3
The durability results of the glasses investigated

Composition	Weight loss (mg)	Time (days)	Final weight loss (mg)	Time for final weight loss (days)
40/14/26/20	4.65	28	4.65	28
40/14.5/32/13.5	5.40	28	5.40	21
40/12.5/35/12.5	6.00	25	7.40	44
40/14.5/25/20.5	8.30	28	8.30	28
40/14/33/13	8.30	28	8.50	35
40/14/31/15	8.75	28	8.75	35
40/14/29/17	6.20	28	9.50	56
40/13.5/34/12.5	8.40	28	10.20	49
40/14.5/23/22.5	11.90	28	13.75	42
40/8/40/12	15.70	29	23.30	78
40/6/34.3/10.7/Al+Ti	21.70	29	28.90	113
40/4/35/12/Al+Ti	18.80	29	32.50	113
40/6/50/4	21.75	29	301.25	244*
40/15/35/10	8.00	25	32.60	253
40/5/35/20	26.80	29	49.30	113
40/5/35/20 (GC)	20.00	35	27.90	98
55/4.2/33.9/6.9	20.70	27	215.00	221*
Commercial glasses				
G1	2.00	28	16.80	138
G2	30.60	28	126.40	105
CR-G	17.45	28	37.10	84*

*Full duration of experiment.

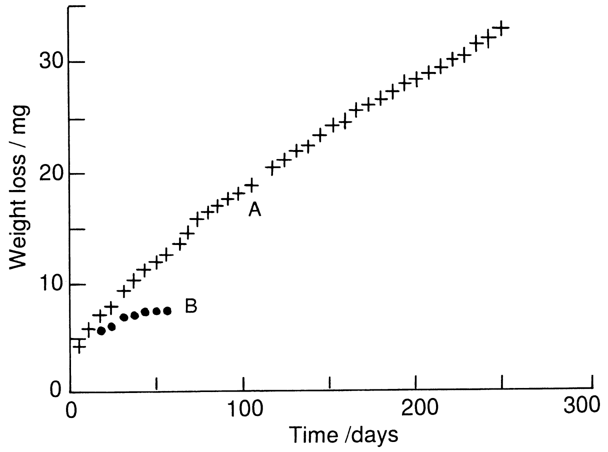


Fig. 4. Durability of 40/15/35/10 (A) and 40/12.5/35/12.5 (B) in 1 M NaOH at 75°C.

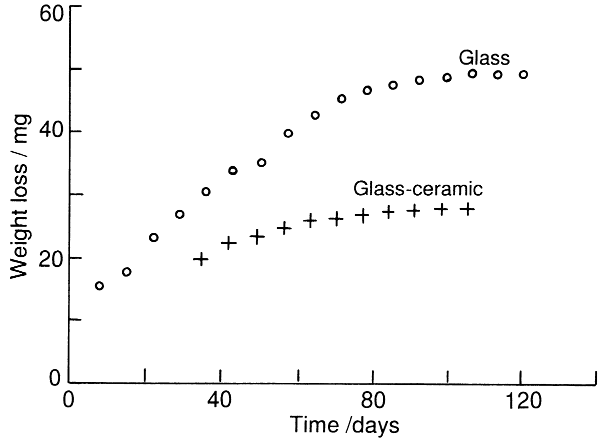


Fig. 5. Durability of 40/5/35/20, as both glass and glass-ceramic, in 1 M NaOH at 75°C.

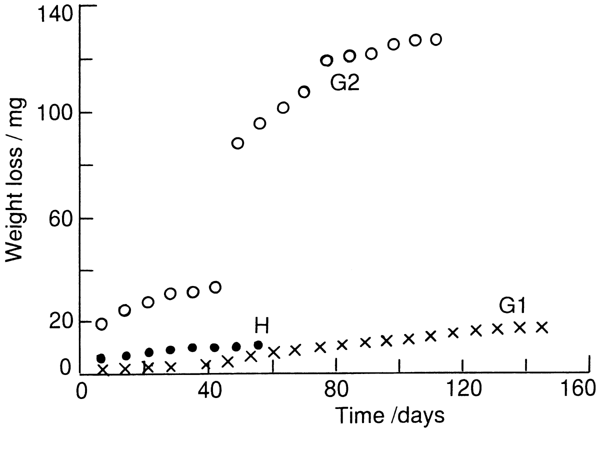


Fig. 6. Durability of glasses G1, G2 and 40/13.5/34/12.5 (H) in 1 M NaOH at 75°C.

In order to make a comparison between commercially available alkali resistant glasses G1, G2, and Corning Glass CR-G (71.3% SiO_2, 15.8% ZrO_2, 0.1% CaO, 0.1% MgO, 11.5% Na_2O, 0.8% Li_2O and 1% K_2O) and glasses in the quaternary system which showed high chemical durability in an alkali environment, these commercially available glasses have also been prepared and melted. CR-G was produced and reported as an alkali resistant glass in 1968. The 40/13.5/34/12.5 glass, which is one of the glasses with a high level of zirconia and gave a higher weight loss value when compared to the other glasses containing higher zirconia in composition, has been chosen for the comparison with G1 and G2. The results are shown in Fig. 6. The 40/13.5/34/12.5 glass has given better chemical durability results than the other two. The sudden big jump of the weight loss value for G2 was because of the loose surface layer which came off. In another experiment Corning glass (CR-G) was compared to the glasses which gave the lowest weight loss values in the quaternary system. Results showed that all the glasses with 40 wt.% silica have lower weight losses than Corning glass (Table 3). After these durability experiments it can be suggested that the glasses with high levels of magnesia and zirconia at constant silica level of 40% can be used for cement reinforcement in the form of fibres.

3.2. Experiment with cement contract

In another durability experiment G2 and the 40/13.5/34/12.5 glass were taken for an investigation in a model cement extract solution with the pH value of 12.5–13. Two identical glass samples were prepared for each different glass. Details of preparing the extract solution have been given before. According to chemical analysis results of the solution before experiment the amounts of Ca^{2+}, Na^{+} and K^{+} in the attacking solution were found to be 510, 332 and 1418 ppm respectively.

The results of this experiment in the model cement extract solution for 35 days at 17°C are as follows (Table 4).

The effect of Ca^{2+} on the dissolution of glass has also been examined. For this examination glass samples were exposed to a solution containing Ca^{2+} for 35 days at 17°C. The results are given in Table 5.

All the solutions used for chemical durability experiments throughout the study were chemically analysed as soon as the experiment was finished. Variation of constituents in attacking solution (in ppm) of the first set of glasses exposed to 1 M NaOH solution at 75°C for 33 days are given in Table 6.

When looking at the compositions of these glasses it is quite obvious that increase in both silica and strontia level with the decrease in both magnesia and zirconia level in glass compositions causes both Si and Sr to leach out into attacking solution. The other point which

Table 4

Glasses	Weight loss (mg)	Weight loss / Total surface area (μg/mm^2)
40/13.5/34/12.5	0.2	0.33
G2	0.3	0.53

should be taken into account was that the Mg level in solution was < 1 ppm. Depending on the composition, level of zirconia was either a bit above 1 ppm or below it.

3.3. *Modelling studies of chemical durability of the glasses with 40 wt.% silica in the system*

After doing multiple regression analysis of density, thermal expansion coefficient, transition and softening temperatures of all the glasses in the system,[5] the next question was, if it can be done, a regression analysis of durability results to get some insight into relative effects of MgO/SrO/ZrO_2.

As a first step, all the durability data from Table 2 were taken for Gaussian Elimination Method.[5] The equation was as follows:

$$\text{Weight loss } (\mu\text{g/mm}^2) = 137.45 - 332.8[\text{Zr}] - 44.18[\text{Sr}] - 25.39[\text{Mg}] \qquad (1)$$

$R^2 = 0.7051$.

Eq. (1) suggests that zirconia has a much larger effect than either SrO or MgO but SrO is somewhat is better than MgO. Implication was that the best durability could be given by maximum possible ZrO_2 and SrO. However, the quantity of Sr dissolved into the attacking solution was much higher than Mg which was always below 1 ppm.

Secondly, glasses mainly with 40% silica exposed to alkaline solution for 35–38 days (from Table 7) were taken for the similar calculations.

In that case the equation became:

$$\text{Weight loss } (\mu\text{g/mm}^2) = 38.11 - 95.34[\text{Zr}] + 0.953[\text{Sr}] + 7.074[\text{Mg}] \qquad (2)$$

$R^2 = 0.905$ which is quite high and this was largely due to having 9 out of 10 with the same silica content.

Table 5

Glasses	Weight loss (mg)	Weight loss Total surface area (μg/mm^2)
40/13.5/34/12.5	0.2	0.33
G1	0.2	0.38

Table 6

Glasses	Si	Sr	Zr	Mg
With 40 wt.% silica	8.29–13.80	11.70–20.05	3.25–< 1	< 1
With 45 wt.% silica	11.25–2.50	13.95–40.50	3.25–< 1	< 1
With 55 wt.% silica	32.50–47.00	36.00–52.50	< 1	< 1
With 61 wt.% silica (C4)	61.00	34.50	< 1	< 1
Microscope slides	191.00	–	–	–

Eq. (2) suggests that the highest possible ZrO_2 is the best and that high SrO/low MgO is also best, a similar result given by Eq. (1). Since some of the durability graphs clearly show that some glasses which behave similarly up to 30 days change considerably. After that calculations were made of some glasses exposed to alkali solution for at least 49–51 days (Table 8) in order to see what the related equation would suggest about the role of main glass constituents on durability. Consequently, the equation was:

$$\text{Weight loss } (\mu\text{g/mm}^2) = 59.39 - 114.3[\text{Zr}] - 0.164[\text{Sr}] - 20.4[\text{Mg}] \qquad (3)$$

$R^2 = 0.877$.

Although R^2 value was not as high as that given by Eq. (2) it is fairly high. Moreover, according to Eq. (2) all the constituents except silica result in an increase of chemical durability in the order: Sr < Mg < Zr.

This also matches the chemical analysis results of the glasses examined. Pure silica/extrapolated results for 36 and 50 days exposure are given: $38.2/36 = 1.061$/day and $59.4/50 = 1.19$/day. They are, interestingly, very similar.

3.4. *The effect of sample thickness and temperature on durability*

In order to see the effect of sample thickness on weight loss a moderately durable glass 40/8/40/12 has been chosen and two identical rectangular samples of 27.5×8×6, 4 and 2 mm size have been prepared to have more accurate results and both surface of the samples have been polished. After 5 days in 1 M NaOH solution at 75°C weight losses of the samples have been measured. The results is given in Table 9.

Polished face = 27.5×8 mm^2, total area (×2) = 440 mm^2. Ground edges = c (27.5 + 8)×2 where c is the thickness of the sample in mm. Nominal area = $71c$ mm^2.

If ground faces act exactly like polished, total area exposed to solution = $440 + 71c$ then it should be found that measured loss/$(440 + 71c)$ = constant.

The apparent weight loss values, weight loss/total area, are found as follows:

$c = 2$ 5.3 mg/582 mm^2 = 9.11×10^{-3} mg/mm^2;
$c = 4$ 5.9 mg/724 mm^2 = 8.15×10^{-3} mg/mm^2;
$c = 6$ 7.3 mg/866 mm^2 = 8.43×10^{-3} mg/mm^2.

Table 7
Durability results of some glasses exposed to alkali solution for 35 to 38 days

Composition	Time (days)	Weight loss (mg)
40/5/35/20	36	30.50
40/6/50/4	36	30.75
40/8/40/2	36	16.95
40/12.5/35/12.5	38	7.00
40/13.5/34/12.5	35	9.30
40/14/29/17	35	6.70
40/14/31/15	35	8.75
40/14/33/13	35	8.50
40/14.5/23/22.5	35	12.75
55/4.2/33.9/6.9	36	32.30

Table 8
Durability results of some glasses exposed to alkali solution for 49 to 51 days

Composition	Time (days)	Weight loss (mg)
40/5/35/20	50	35.00
40/6/50/4	50	48.05
40/8/40/2	50	20.20
40/13.5/34/12.5	49	10.20
40/14/29/17	49	8.30
40/14.5/23/22.5	49	13.75
40/15/35/10	51	12.00
55/4.2/33.9/6.9	51	48.00

The values do vary but not systematically with *c*, suggesting that ground faces do act very like polished ones. The typical glass density is about 3.5 g/ml, so a loss of 0.9 mg/cm^2 would be equivalent to a total loss of about:

$$\delta = 0.9 \times 10^{-3}\ \mathrm{g/cm^2}/3.5\ \mathrm{g/cm^3} = 2.6 \times 10^{-4}\ \mathrm{cm}$$

$$= 2.6\ \mu\mathrm{m}$$

This, therefore, suggests that, as only some constituents are removed, not the whole glass, a thickness of 5–10 m has been depleted. The effective diffusivity of constituents in glass is given by, approximately, $\sqrt{Dt} = \delta$ $(Dt/\delta^2 \sim 1)$. Taking $\delta = 2.6$ μm thus gives $D = \delta^2/t = 6.76 \times 10^{-8}/t(\mathrm{s}) = 6.76 \times 10^{-8}/4.32 \times 10^{5}$ cm^2 s^{-1} for 5 days exposure then $D = \delta^2/t \cong 1.56 \times 10^{-13}$ cm^2 s^{-1} at 75°C.

Few measurements of diffusivity have been reported near room temperature but this order of magnitude seems reasonable.

In order to see the effect of temperature on weight losses the 40/8/40/12 glass was examined. Thickness of 2.5 mm was used and same sample preparation route which was used throughout the study was followed. For this particular experiment temperature of 65, 70 and 75°C were used. The result of the experiment is tabulated in Table 10. A difference of 5°C in temperature causes an increase of about of 2.3 mg in weight losses.

4. Discussion

If one looks at the literature to see the effect of glass composition on durability it can be noticed that a number of investigations have been made in this field and the high resistance of zirconia containing glasses was reported.[1]

Larner et al.[8] who used the Portland cement extract in their study showed that the Zr concentration was much greater at the surface than in the bulk glass and Zr/Si ratio increased as a result of attack by Portland cement extract.

Makisma et al.[9] who established the characterisation of insoluble layers formed by NaOH attack on the surface of a zirconia containing silicate glass (G1) was reported the positive effect of zirconia in silicate glasses and that dissolution rate decreases with time. According to this study the formation of an insoluble reaction product layer formed an adherent film and effectively blocked the reaction. It has also been reported that the Zr concentration was greater in the insoluble reaction product layer than in the unattacked glass. The same G1 glass was used by Makisma et al.[9] and Larner et al.[8] but both the type of alkali and the experimental procedure differed.

In the present system the effect of zirconia on durability was examined. Using the glass compositions containing 40 wt.% silica the best result has been achieved with the 40/14/26/20 glass (Fig. 7). Although zirconia content increased to 14.5% decrease in MgO content (about 7%) to 13.5% may have caused to have higher weight loss value than that in the 40/14/26/20 glass. Further decrease in zirconia content to 12.5% made the 40/12.5/35/12.5 glass give a weight loss value of 7.4 mg after 44 days. When comparing these results, it will be quite obvious that at constant level of zirconia content, as 14%, decrease in magnesia content from 20 to 17% caused a higher weight loss value, 6.2 mg, after 28 days for the 40/14/29/17 glass. Further increase in both magnesia and zirconia level up to 22.5 and 14.5% respectively did not improve durability as much as expected for the 40/14.5/23/22.5 glass having a weight loss value of 13.75 mg after 42 days. Although some of these glasses with a high level of zirconia and magnesia

Table 9

Composition				
40/8/40/12				
Time (days)	Temp. (°C)	Thickness (mm)	Weight loss (mg)	Weight loss
				Total surface area (μg/mm^2)
5	75	2	5.3	9.11
5	75	4	5.9	8.15
5	75	6	7.3	8.43

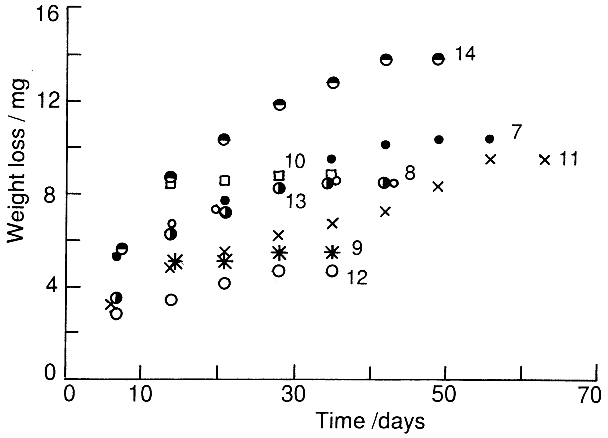


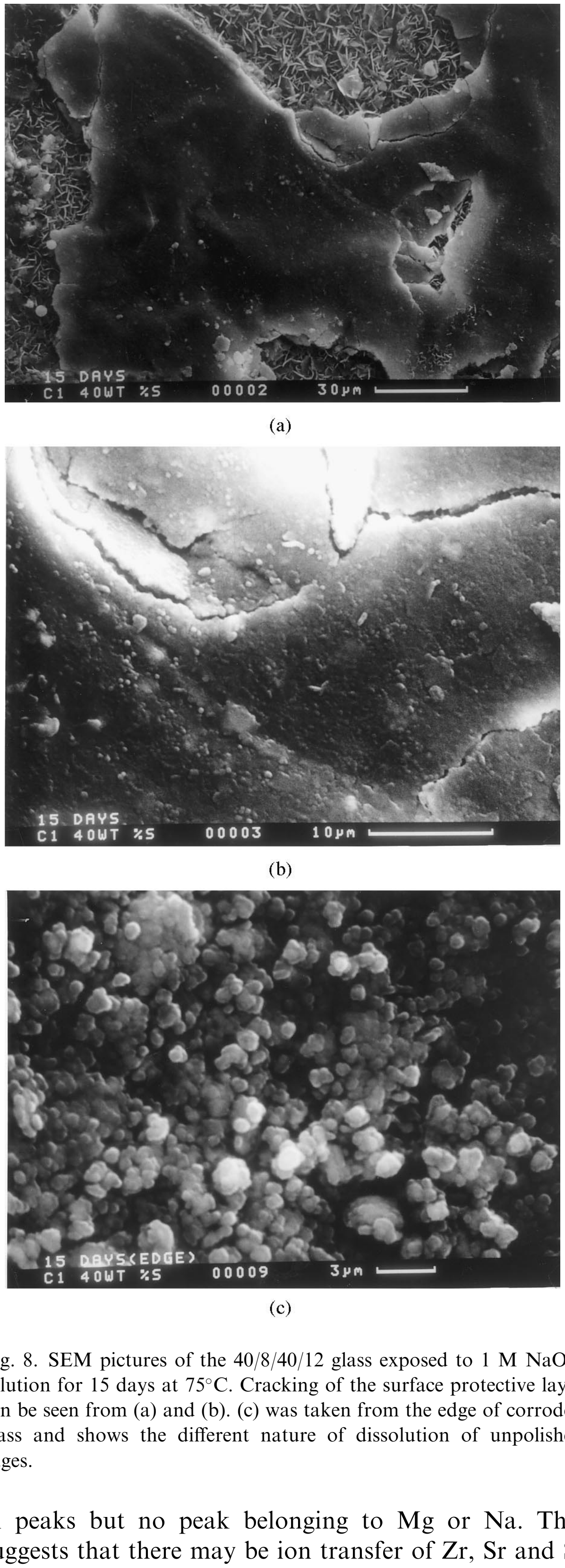
Fig. 7. Durability results for glasses in 1 M NaOH at 75°C. 7: 40/13.5/34/12.5; 8: 40/14/33/13; 9: 40/14.5/32/13.5; 10: 40/14/31/15; 11: 40/14/29/17; 12: 40/14/26/20; 13: 40/14.5/25/20.5; 14: 40/14.5/23/22.5.

seem to give high weight loss values they are superior when compared to soda–lime–silica glasses.

Paul[3] reported that MgO, SrO and BaO also improve the durability but the effects depend on such things as the temperature of the test and the radius of cation. Furthermore, when one moves up in the group of alkali earth metals Sr is expected to be better than Mg at high temperature since it has a larger radius than Mg.

In the present system it has been found that up to a certain limit (~20 wt.%) Mg has a more positive effect than Sr on durability of glass of 40 wt.%. This may suggest that a higher amount of strontia in glass composition increases the possibility of its ionic movement to the glass surface like silicon ions, after Sr–O and Si–O bonds being broken by either sodium or hydrogen ion from the aqueous solution. On the other hand, Sr with a larger radius can accommodate more oxygen than Mg, therefore, having a lower bond strength and Mg may be more strongly bonded with oxygen atoms than Sr in the glass structure.

Some of the durability samples have been investigated by X-ray diffraction, SEM and EDX after durability experiment in order to examine the surface layer occurred during exposure. The X-ray diffraction pattern given by the 40/6/50/4 glass, after 244 days in NaOH, was thoroughly examined for hydrated compounds which may possibly have formed during exposure. Only the Joint Committee for Powder Diffraction Standards (JCPDS) data of $NaHSi_2O_4(OH)_2$, sodium hydrogen silicate hydroxide, matched data given by X-ray diffraction of the glass. These crystals may be embedded in the hydrated zirconia surface layer. In order to confirm the presence of Na in the glass surface SEM and EDX analyses were also made. The presence of Na was not so clear through SEM pictures but EDX analysis showed that as well as Si and Zr peaks Na was given by the protective surface layer, whilst the glass part, which had no protective layer, on the surface has shown Zr, Sr and Si peaks but no peak belonging to Mg or Na. This suggests that there may be ion transfer of Zr, Sr and Si towards the first surface layer which is in contact with the attacking solution. From this layer, dissolution of Sr and Si may take place. At the same time it is possible to think that a hydrated zirconia protective layer forms



(a)

(b)

(c)

Fig. 8. SEM pictures of the 40/8/40/12 glass exposed to 1 M NaOH solution for 15 days at 75°C. Cracking of the surface protective layer can be seen from (a) and (b). (c) was taken from the edge of corroded glass and shows the different nature of dissolution of unpolished edges.

Table 10

Composition				
40/8/40/12				
Time (days)	Temp. (°C)	Thickness (mm)	Weight loss (mg)	Weight loss Total surface area (μg/mm^2)
5	65	2.5	3.0	5.74
5	70	2.5	5.0	9.56
5	75	2.5	7.6	14.53

and finally decreases the dissolution of Sr and Si from the surface layer where glass is in contact with the solution and also prevents further diffusion of Na into the bulk glass. Since there was no sign of Mg either on the glass surface or in the glass near to the surface, it has also been concluded that Mg must be tightly bonded by oxygen ions in the glass structure, therefore, its ionic movement towards the surface of the glass is prevented. However, the glass examined had only a small amount of MgO, 4%, therefore, it might avoid detection. The other possibility is that there may be diffusion inwards rather than towards the glass surface. The 40/8/40/12 glass sample 6 mm thick after being exposed to NaOH solution for 15 days has also been examined by SEM and EDX. Similar results to that of the 40/6/50/4 glass have been achieved. Cracks of the protective surface layer have also been observed (Fig. 8).

In the current study G1 exposed to 1 M NaOH solution has also been examined by EDX and surface product layer has given the peaks of Ca, Zr and Si. In this case the reaction products of both Ca and Zr may form on the surface and are expected to protect the glass from further dissolution.

Tomozowa et al.[10] investigated the effect of alkali earth elements in hot alkaline solutions on silica microscope slide glasses in order to examine retarded dissolution behaviour caused by a minor concentration of various ions in alkaline solution. They have seen that when a solution contained a small amount of heavy alkaline earth elements such as Ba and Sr, sharp cracks formed on the glass surface and the crack caused a drastic reduction in mechanical strength of the glass.

In the present work the attacking solution soon contains some Sr during exposure of the glasses. Sr may be causing this sort of cracking of the protective layer.

According to the weight loss versus time and square root of time diagrams of the glasses examined for their chemical durability it can be said that in the early stages of attack weight loss increases linearly as $t^{1/2}$ but at long times the rate of loss becomes almost linear, of course, the solution can sometimes become saturated and attack ceases. This can be explained as that in the early stages ($t^{1/2}$ dependence) the reaction is a diffusion controlled ion exchange involving Sr and Na and H moving in opposite directions through a siliceous surface film and the Si is likely to be more or less direct dissolution of the glass at the interface, whilst later (t dependence) the surface film has attained a constant thickness. This thickness is probably determined by a balance between the diffusion of Zr, Si and Sr ions through the film, which thickens it, and the rate of removal of Si and Sr at the film-solution interface which has the opposite effect. When further studies were made on glasses with lowest level of silica, 40%, the results of chemical analysis showed that amounts of both Si and Sr dissolved into attacking solution were far more than that of Zr and Mg which were always below 1 ppm in solution.

5. Conclusions

1. The glasses with 40 wt.% silica content in the SrO–MgO–ZrO$_2$–SiO$_2$ system have given high chemical resistance to alkaline solutions.
2. Increasing silica content in glass compositions decreases chemical durability of all glasses produced. On the other hand, as well as zirconia, up to a certain value magnesia has a positive effect on chemical durability.
3. It is believed that in the early stages, the reaction between glass and the attacking reagent is a diffusion controlled ion exchange, later the surface film attains a constant thickness. This thickness is probably determined by a balance between the diffusion of Zr, Si and Sr ions through the film, which thickens it, and the rate of removal of Si and Sr at the film–solution interface which has the opposite effect.
4. The X-ray diffraction pattern given by the hydrated compounds of the 40/6/50/4 glass possibly formed during exposure in NaOH, matched the data of sodium hydrogen silicate hydroxide, $NaHSi_2O_4(OH)_2$. These crystals may be embedded in the hydrated zirconia surface layer.
5. The SEM pictures of the hydrated compounds of the 40/6/50/4 glass have shown cracking of the protective layer. The attacking solution soon contains some of Sr during exposure of the glasses. Sr may be causing this sort of phenomenon.
6. According to multiple regression analysis made by using the chemical durability data of the glasses with 40 wt.% silica content suggested that all the constituents except silica result in increase of chemical durability in the order:
   $Sr < Mg < Zr$
7. It can be suggested that the glasses with high level of magnesia and zirconia at constant silica level of 40% can be used for cement reinforcement in the form of fibres.

Acknowledgements

The authors are grateful to The Turkish Government's Ministry of Education for the award of the grant to fund the present study.

References

1. Dimbleby, V. and Turner, W. E. S., *Glass Tech*., 1926, **10**, 304–363.
2. Newton, R. G., The durability of glass — a review. *Glass Tech*., February 1985, 26, (1).
3. Paul, A., *Chemistry of Glasses*. Chapman and Hall, London, 1982.
4. Karasu, B., Melting behaviour of the glasses in the SrO–MgO–ZrO_2–SiO_2 system, *Glass Technology*, June 1999, **40** (3), 92-96.
5. Karasu, B., Properties of glasses and glass ceramics in the MgO–SrO–ZrO_2–SiO_2 system, PhD Thesis, Sheffield University, Department of Ceramics, Glasses and Polymers, England, 1994.
6. Ghanbari, A., Phase equilibria and glass formation in the ZrO_2–MgO–SrO–SiO_2 system, PhD Thesis, Sheffield University, Department of Ceramics, Glasses and Polymers, England, 1989.
7. Majumdar, A. and Ryder T. F., Glass fibre reinforcement of cement products. *Glass Tech*., June 1968, 9, (3).
8. Larner, L. J., Speakman, K. and Majumdar, A. J., Chemical interactions between glass fibres and cement, *Journal of Non-Crystalline Solids. 20*, 43–74.
9. Makisma, A., Tsutsumi, M. and Shimohira, T., *Communication of the American Ceramic Society*. August 1983, **C-139**.
10. Tomozawa, M., Oka, Y. and Wahl, J. M., *Communication of The American Ceramic Society*. February 1981, **C-52**.