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Volume instability of porous solids

Part 2 *Dissolution of porous silica glass in sodium hydroxide*

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Dimensional changes of porous 96% silica glass have been determined during exposure to aqueous NaOH solution. Depending on the thickness of the specimen (1, 3, 4, or 8 mm) and the concentration of the alkali (0.1, 0.4, 0.8, 1.6, 3.2 and 6.4 M), either expansion or contraction or both were observed, the maximum being 0.7%. The features of the extension curves cannot yet be fully explained, but the results suggest that dissolution of glass leads to expansion and that surface reaction and chemisorption lead to contraction. The presence of $CaCl_2$ in the solution in 1 M concentration significantly retards dissolution and expansion.

1. Introduction

It has been shown that porous solids immersed in a solution expand significantly when involved in physical or chemical processes [1]. Specifically, adsorption of inert solute ($NaNO_3$) on porous silica glass, dissolution of porous glass in NaOH or of hydrated portland cement paste in HCl, and leaching of lime from cement paste produced fractional length changes in the order of 0.03% to 0.3%.

Dimensional changes of porous solids on adsorption of gaseous substances have been studied fairly extensively [2], and the accumulated experimental results have suggested a theory to account for the features of the extension isotherm in terms of spreading force and capillary condensation [3]. A general theory relating length change of a solid surrounded by a solution to other factors has not been devised. Yet dimensional changes of porous solid–liquid solution systems are of great technical importance quite beyond that of theoretical interest. For example, chemical reaction in concrete can, under certain conditions, occur between the constitutents of concrete (alkali–aggregate reaction) or a constituent and an external agent (sulphate attack), leading to cracking and disintegration.

In order to achieve a better understanding of the processes associated with dimensional changes of solids containing solutions in their pores, a systematic investigation has been undertaken. The present paper reports the results of a study of the dissolution of porous 96% silica glass in aqueous NaOH solution.

2. Experimental procedure

The apparatus described previously was used without modification as was the experimental procedure [1]. Porous 96% silica glass was obtained from Corning Glass Co. (Code 7930) in the form of 1, 5 and 8 mm thick sheets. The 3 mm thick and 8 mm wide specimens were cut from the 8 mm stock. To avoid contamination, the glass was fully saturated with water before cutting. Cleaning was performed with 10% H_2O_2 solution. Chemicals were of analytical purity grade.

3. Results

In several cases the experiments were carried out repeatedly to assess the degree of reproducibility. To illustrate this aspect, the results of multiple runs rather than representative curves are given.

3.1. 3 mm specimens

The time-dependent length changes of 3 mm thick, water-saturated glass specimens on exposure to aqueous NaOH solution of various concentrations are shown in Fig. 1. Dissolution in 0.4 M NaOH was repeated 12 times. The average duration of dissolution was 23 h, with a coefficient of variation

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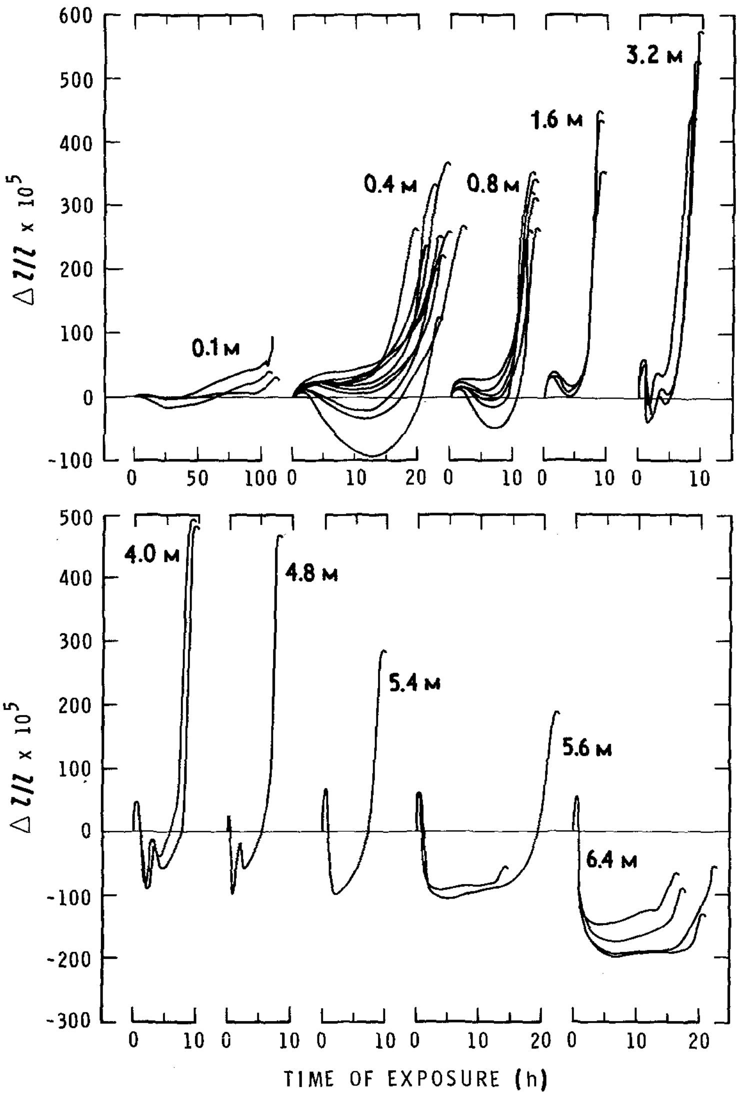

Figure 1 Length changes of 3 mm thick porous glass specimens of exposure to NaOH solutions of various concentrations.

of 8.3%. The total expansion from the original state was $263.7 \pm 62.9 \times 10^{-5} \Delta l/l$, with a coefficient of variation of 23.3%. Reproducibility in some other cases (e.g. 3 mm specimens in 0.8, 1.6, 3.2 M NaOH) appears to be better. There can be little doubt that several features of the curves in Fig. 1 can be considered typical:

1. dissolution of porous glass in NaOH is associated with significant changes in length ranging from 0.2% contraction to 0.6% expansion;
2. the ultimate expansion reaches a maximum value at 3.2 M concentration;
3. at all concentrations (except 0.1 M) an initial expansion (approx 0.04%) occurs;
4. in the second phase of the dissolution process the glass usually contracts, normally beyond the initial length. This contraction generally increases with NaOH concentration, reaching a value of 0.2% at 6.4 M concentration;
5. between 3.2 and 4.8 M concentration a transitional expansion is apparent prior to ultimate expansion.

3.2. 1 mm specimens

Length changes of 1 mm thick specimens in NaOH solutions of various concentrations are shown in Fig. 2.

1. In general, the overall expansions of specimens compared at equal molar concentrations of NaOH are larger than those of the 3 mm thick specimens.
2. At 0.1 M concentration the rate of expansion increases in the final stage of the dissolution process. The overall increase in length is 0.35%.

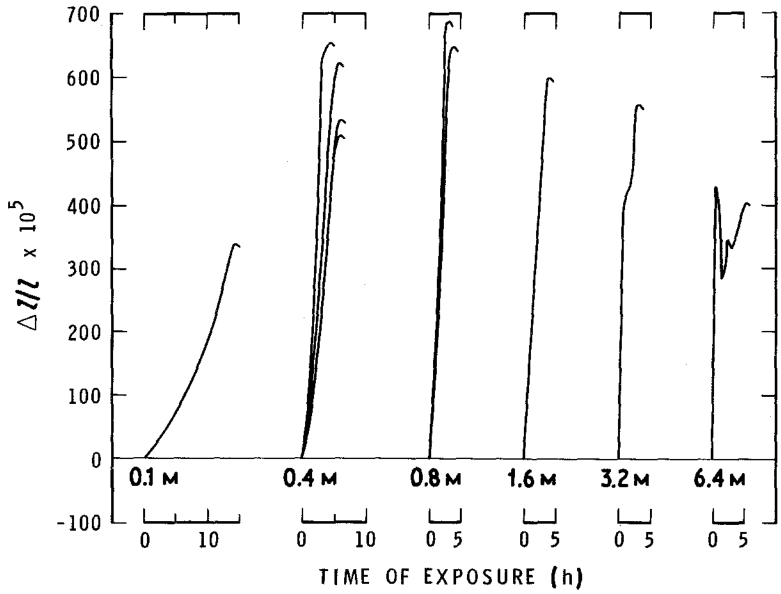

Figure 2 Length changes of 1 mm thick porous glass specimens on exposure to NaOH solutions of various concentrations.

3. At 0.4, 0.8 and 1.6 M concentrations the rate of expansion appears to be single valued almost throughout the entire process. There is no indication of contraction, which is a characteristic feature of 3 mm specimens.

4. A transient reduction of the expansion rate occurs at 3.2 M concentration.

5. At 6.4 M concentration, contraction follows a rather large initial expansion. A transient expansion similar to that for the 3 mm specimen in 3.2 M NaOH is observable.

6. Maximum overall expansion (0.7%) was found at 0.8 M concentration.

3.3. 5 mm specimens

Fig. 3 shows the extension curves obtained during dissolution of 5 mm thick specimens in NaOH solutions of various concentrations.

1. At 0.1 M concentration the expansions are larger than those for the 3 mm thick specimens. The curves show similarities with those for the 3 mm thick specimens at higher concentrations, e.g. 0.8 M.

2. Six experiments were carried out in 0.4 M NaOH. Reproducibility was rather poor, with total expansion varying between 0.05 and 0.5%. Only in one instance did contraction, which is a

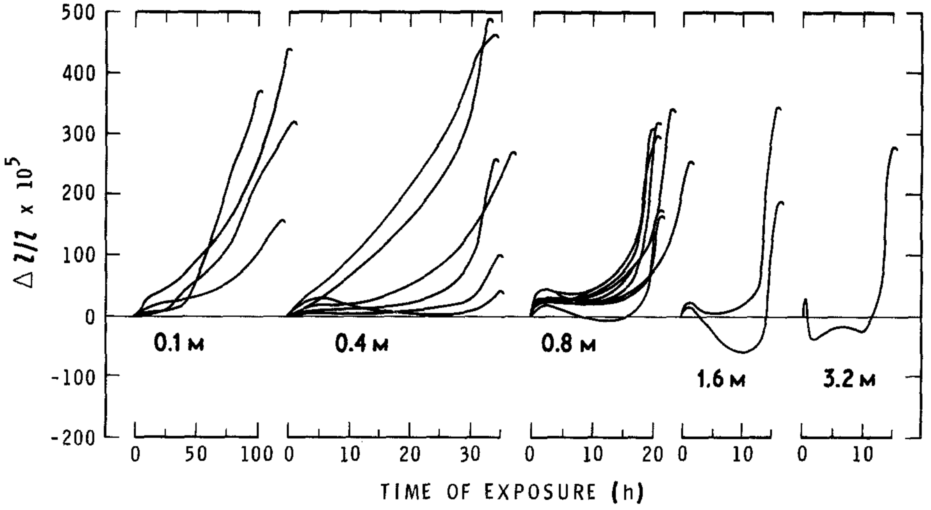

Figure 3 Length changes of 5 mm thick porous glass specimens on exposure to NaOH solutions of various concentrations.

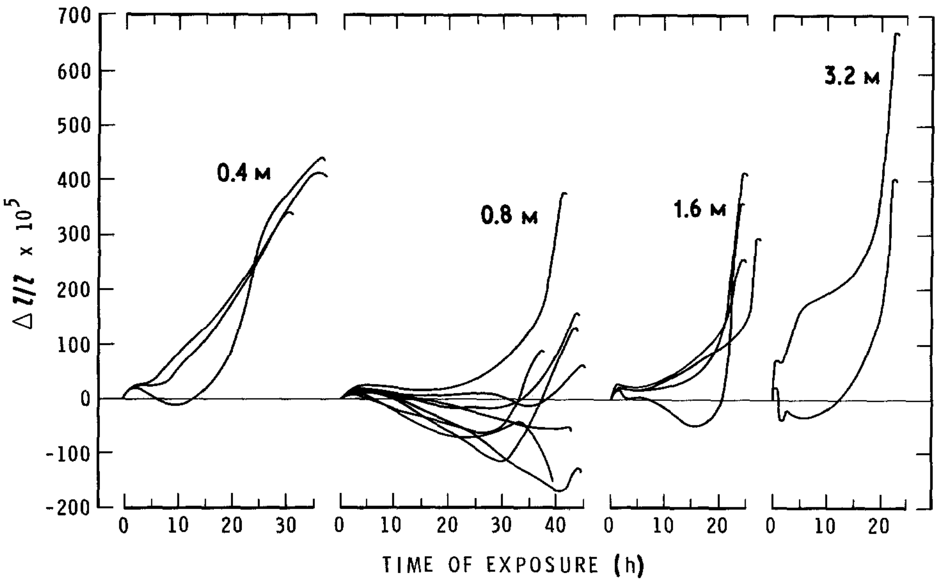

Figure 4 Length changes of 8 mm thick porous glass specimens on exposure to NaOH solutions of various concentrations.

fairly characteristic feature of 3 mm specimens at this concentration, occur.

3. Extension curves of thick specimens resemble more closely those obtained with thin specimens at lower alkali concentrations than any obtained at the same concentration. Thus, length changes of the 0.8 M NaOH 5 mm glass system are comparable to those of 0.4 M NaOH 3 mm glass. A similar relation appears to exist between 1.6 M 5 mm and 0.8 M 3 mm systems. The results for 8 mm thick specimens (Fig. 4) show trends similar to those for other samples of 3 or 5 mm thickness, but lower alkali concentrations.

4. Discussion

4.1. Dimensional changes

Although reproducibility is limited in some respects, there can be little doubt that glass undergoes significant length changes during alkali attack. Feldman and Sereda [4] observed a 0.19% expansion of porous silica glass during alkali treatment. This they interpreted as evidence of pressure in the pores. Volume changes occur also on the dissolution of silica gel particles in NaOH, as shown by Dent Glasser and Kataoka [5].

4.2. Dissolution process

The reaction between silica and sodium hydroxide produces various species of silicate, such as mono-, di- and poly-silicates, among which complex pH-sensitive equilibria exist. At pH higher than 13.5, silicic acid is present mainly in the form of the disilicate ion [6], while at lower pH values equilibrium shifts towards the formation of mononuclear species.

A 3 mm thick specimen weighing approximately 1 g represents 0.016 mol of SiO_2, and 75 ml of a 0.4 M solution of NaOH contains 0.030 mol NaOH. Thus, in the course of total dissolution of a specimen in weakly alkaline solutions the pH decreases significantly as type and quantity of silicate ion in the solution change. At the same time, (a) sodium ions surround the surface of the negatively charged glass, (b) the mass of the specimen is reduced in the dissolution process, (c) the specific surface area of the specimen decreases owing to enhanced solubility of surface irregularities with small radius of curvature, (d) an increasingly thick gel coat covers the external surface, and (e) the newly formed silicate ions diffuse into the pore-held liquid and adsorb on the glass surface.

4.3. Possible causes of expansion

Dimensional changes occurring during dissolution of porous glass have several possible causes:

1. The surface-free energy of the glass may change owing to (a) reduction of the total area by the elimination of irregularities of the surface; (b) changed composition of the surface is created in which water molecules are replaced by sodium and hydroxyl ions, and (c) adsorption of the reaction products on the interior surfaces of the solid.

2. A non-homogeneous distribution may develop

throughout the pore-held solution, a condition that leads to generation of osmotic-like pressures, if the diffusion coeeficients of the dissolved species differ greatly from each other. Because concentrations equalize in time, only transient expansion can be expected on this account. The initial expansion that immediately follows the addition of NaOH (Fig. 1) is directly proportional to NaOH concentration up to 3.2 M, a relation to be expected on the basis of the osmotic pressure mechanism. On the other hand, the magnitude of the expansion is inversely proportional to the thickness of the specimen at the same concentration level, e.g. 0.4 or 0.8 M (Figs. 1, 3 and 4). This is contrary to expectation because the specimen is exposed to larger concentration differences if the diffusion path is long.

3. The hydroxyl groups of the glass behave in alkaline solutions as weak acids [7]. The double layer outside the surface contains mainly cations adjacent to the SiO^- groups and anions in the outer regions. If the electric fields of two surfaces overlap, a repulsive force called "disjoining pressure" is created. Because of the structure of the porous network and the electric charges, disjoining pressure almost certainly is an important contributing factor to the observed dimensional instability.

4. Compression as well as tension stress may exist in the outer skin of glass. This is probably created during the manufacturing process, when the exterior layer of the glass contracts while the interior is still hot [8]. It has been noted during the production of Vycor-type glass that leaching of the phase-separated borosilicate glass is hindered by the original surface layer and that its removal eliminates the retarding effect [9]. Takamori showed [10] that birefringence in microporous glass immersed in liquids with various refractive indices is erased when specimens are soaked in 0.5 M KOH solution. In porous glass, stresses are generated also by the removal of the B_2O_3 phase that constitutes 25% of the total mass. A large new surface ($110\,m^2\,g^{-1}$) is created by leaching, accompanied by a 0.2% dimensional change [11–13].

These experimental results do not provide a basis for the identification of the cause of expansion. The effects listed under Point 1 above, are, perhaps, minor, and those under Points 2 to 4, singly or in combination, the major contributing factors.

4.4. Possible causes of shrinkage

After initial expansion, a contraction occurs that tends, in most cases, to be more pronounced with increasing alkali concentration (Figs. 1, 3 and 4). Indications of volume decrease were also obtained dilatometrically on partial dissolution of silica gel in NaOH solution [15]. This is attributed to preferential dissolution of the dense parts of the gel or to transformation of the gel into a denser form. The expansion of porous silica glass on adsorption of $NaNO_3$ from the aqueous solution was found to reach a maximum at intermediate concentrations [1], after which reduction in length occurred. It is suggested that the contraction observed during the dissolution experiments is due to adsorption of the reaction products on the undissolved glass. In support of this assumption the following observations may be cited.

Experiments were carried out with specimens of various thicknesses in 0.8 M NaOH. They showed no contraction of 1 mm specimens (Fig. 2), moderate shrinkage of 3 and 5 mm specimens (Figs. 1 and 3), and pronounced shrinkage of 8 mm specimens (Fig. 4). Because adsorption of the reaction products depends on the final silicate concentration of the solution, which is, in turn, determined by specimen thickness (at constant specimen size and solution volume), the large contraction takes place during enhanced adsorption.

Further experiments were carried out also in which the solution volume was adjusted to 600 instead of the standard 75 ml. An eightfold dilution of the silicate concentration (the specimen size remained constant) was expected to result in greatly reduced adsorption. In fact, no contraction was observed on dissolution of a 3 mm thick specimen in 0.8 M NaOH, yet in its absence the total expansion exceeded 0.5% instead of the 0.3% for the 75 ml volume (Fig. 5). Increased solution volume has a less dramatic effect at higher concentrations, in which contraction is reduced but still present. Stirring the solution decreases the extent of contraction, however, presumably because build-up of a silicate-rich zone round the specimen is minimized.

The proposed link between shrinkage and adsorption is supported also by results of experiments with 12 M solutions (Fig. 6). The 3 mm thick specimen contracted continously to a total of 1.2%, except for two intermediate periods of expansion. After 17 days the 12 M solution was replaced with one of 3.2 M concentration that

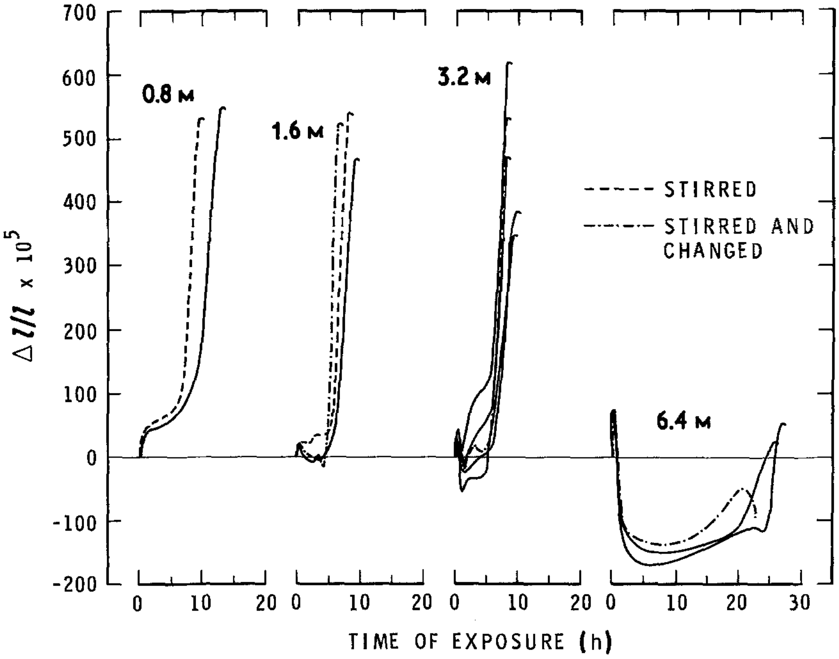

Figure 5 Length changes of 3 mm thick porous glass specimens on exposure to NaOH solutions of various concentrations and 600 ml volume stirred, or stirred and periodically replaced, as indicated.

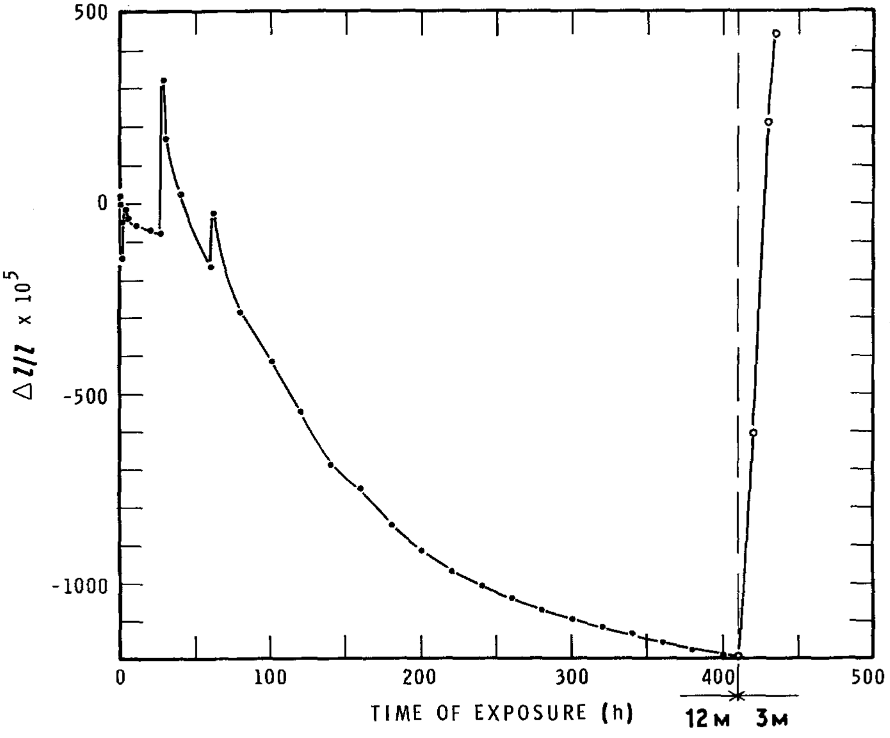

Figure 6 Length changes of 3 mm thick porous glass specimens on exposure to 12 M NaOH solution replaced after 420 h by 3.2 M NaOH solution.

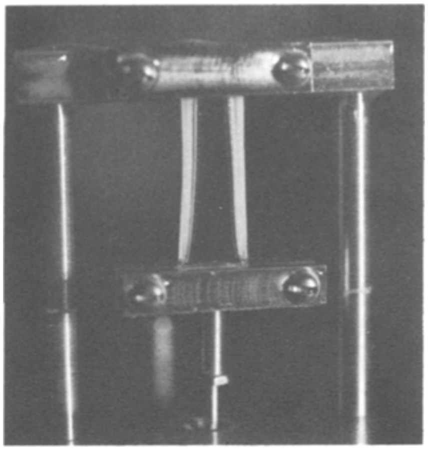

Figure 7 Residue insoluble in 3.2 M NaOH of a specimen exposed as described in Fig. 6.

brought about rapid expansion to 0.45% beyond the original length before the specimen finally collapsed. At this stage only the original surface at the edge of the specimen was left undissolved, as two posts with approximately 2 mm sides (Fig. 7).

These findings indicate that in the reaction between glass and highly concentrated NaOH the reaction products precipitate (following an initial dissolution), on the undissolved glass, protecting it from further alkali attack. The two fairly large expansions that occur in the first 60 h (Fig. 6) are due to dissolution, while subsequent contractions are due to the formation of the protective layer.

High adsorption takes place near the edges because in this area the silicates diffuse into the glass from three directions instead of from only the two faces of the specimen. The relatively deep zones of silicates at the edges are insoluble in 12 M NaOH and retard attack even in 3.2 M NaOH. Chemical attack in the less concentrated alkali solution thus proceeds through the large faces, which have a relatively thin protective zone in comparison with that at the edges.

Further support for the hypothesis of contraction–surface reaction is provided by dissolution experiments in the presence of $CaCl_2$. It is known that the addition of CaO to alkali silicate glass improves its chemical durability [14]. Oka *et al.* [15] also showed that if an NaOH solution contains calcium ions, the etching rate of 96% SiO_2 porous glass is reduced. They presented experimental evidence of calcium deposition on the surface. The retarding effect of calcium ions has also been documented [16] in the alkali attack on silica through calciumsilicahydrate formation.

When the effect of 0.01, 0.1 and 1 M $CaCl_2$ in 0.8 M NaOH on the dimensional changes of 3 mm thick specimens was investigated (Fig. 8), there were indications that the time of total dissolution is longer at lower concenttrations (Fig. 1). A dramatic difference occurs, however, when the $CaCl_2$ concentration is 1 M. Not only is the time of dissolution twice as long as in the reference calcium-free solution, but in two of the three cases the shape of the extension curve indicates shrinkage instead of overall expansion (Fig. 1).

4.5. "Saddle" effect

In 3.2 M NaOH, specimens show a transient expansion during the contraction period (Fig. 1). The "saddle" effect in the extension curve is most pronounced at 3 mm thickness; it is not present in 1 mm specimens (Fig. 2) and is not too strong in either 5 or 8 mm specimens (Figs. 3 and 4).

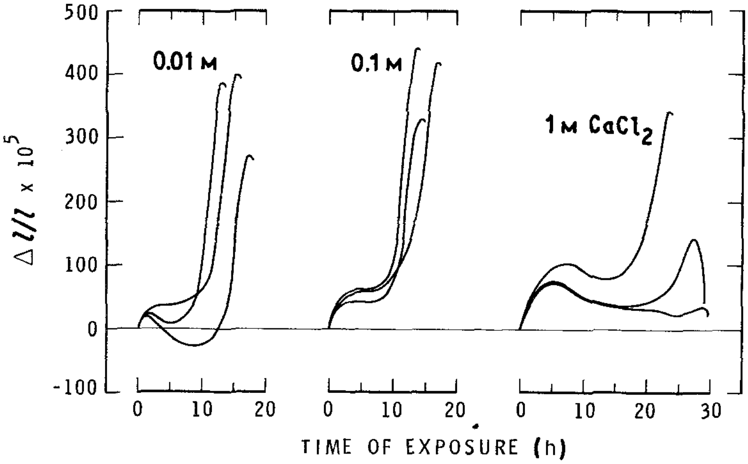

Figure 8 Length changes of 3 mm thick specimens exposed to 0.8 M NaOH containing $CaCl_2$, concentrations as indicated.

A high solution volume seems to have a definite effect on this phenomenon (Fig. 5); two of the four curves obtained with 3 mm specimens in 3.2 M solution do not show transient expansion at all. In the standard 75 cm^3 volume the saddle effect occurred at 4.0 and 4.8 M concentrations with 3 mm specimens (Fig. 1).

Saddle effect can be attributed to opposing actions: dissolution causing expansion, and adsorption causing contraction. Because the unaffected core of the glass restricts expansion of the specimen involved in the dissolution process, the largest expansions occur just before collapse, when the volume fraction of the unaffected glass is minimum or zero. On the other hand, adsorption-induced contraction depends, among other factors, on the silicate concentration of the solution (i.e. the amount of glass already dissolved), the time available for the species to diffuse to the interior of the specimen, and the size of the undissolved glass volume in which adsorption takes place. Thus, expansion is dominant in the last phase of dissolution, while adsorption and the resulting contraction increases during the course of dissolution, reaching a maximum value at an intermediate phase. It is therefore conceivable that the resultant length change can reverse sign several times in the course of the dissolution process.

5. Conclusions

1. The dimensions of porous 96% silica glass change very significantly during attack by aqueous NaOH.

2. Dissolution of the glass is associated with expansion.

3. Adsorption of the corrosion products on the undissolved glass causes contraction.

4. The presence of $CaCl_2$ at 1 M concentration in the solution mitigates the corrosive action of aqueous NaOH.

5. The shape of the extension curves is affected by specimen thickness, solution volume, and solution concentration.

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