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Alkaline durability of glass fibre containing SiO_2, PbO and Al_2O_3

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In the process of developing an alkali-resistant glass composition to be used as reinforcing fibres with cement, a glass in the system SiO_2–PbO–Al_2O_3–R_2O (R = an alkali metal) was adopted after some trials. The glass composition which possesses low melting point (1350° C), fair alkaline resistance (particularly in the long term) and appears to have satisfactory fibrilizing qualities, has the composition: SiO_2 = 34%, PbO = 59%, Al_2O_3 = 3%, K_2O = 3.5% and Na_2O = 0.5% (wt%). The alkaline durability of the glass fibres (coated and uncoated) was studied at pH 9, 10, 11 and 12. There was no significant difference in the amount of extraction of the constituents in the leaching solution at pH 9 and 10. At pH 11 and 12 the amount of extraction value of the constituents initially increased up to seven days and thereafter no significant increase could be detected. The thermodynamic stability of the different oxides under present investigation (SiO_2, Al_2O_3, PbO) in aqueous solutions at different pH values has been discussed with standard thermochemical data and it has been shown that alkaline durability of the glass fibres can be satisfactorily correlated with thermodynamic predictions. There is a lower value in the extraction of the constituents in the case of coated fibres, than those of uncoated fibres. An epoxy resin with a cycloaliphatic diamine improves alkaline durability.

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 material 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. Recently such a glass fibre-reinforced cement (commonly known as GRC) has been marketed commercially. This owes its origin to the development of an alkali resistant glass composition [1]. Commercial production methods for drawing continuous fibres from this glass 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 degradation of the properties of the matrix or to damage of the fibres; (d) chemical compatibility between the fibres and the cement matrix both during fabrication and in service; (e) physical compatibility between the fibre and the matrix; 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 effective exploitation of this new material.

The glass fibres to be used as 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 ZrO_2 to silicate glasses is well known to increase the chemical durability [3, 4], and Cem-FIL contains 16 to 17 wt % ZrO_2. The alkaline durability of Cem-FIL is satisfactory, but it has two main disadvantages: ZrO_2 is costly; and the addition of ZrO_2 to a silicate glass increases the melting and fibre drawing temperatures, thereby increasing the production cost. So in the present investigation attempts have been made to develop an alternate alkaline durable glass fibre.

In formulating an alkaline resistant glass, the glass

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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 be needed 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.

Initially an alkaline durable glass was developed in the $Na_2O-CaO(FeO + Fe_2O_3)-MnO-SiO_2$ system. But compositions in this system which produced homogeneous glass could not be easily fibrilized probably due to unsatisfactory viscosity – temperature relationships and very different thermal conductivity behaviour due to large concentration of ferrous iron in these glasses. Thus glasses of newer systems having comparable alkaline durability and easy fibre formation characteristics were investigated.

In the present investigation, fibre was drawn from glasses in the system: $SiO_2-PbO-Al_2O_3-R_2O$ (R = an alkali metal), developed for this purpose after extensive trials. The raw materials for the glass preparation are cheap and easily available. The fibre drawing temperature is also low compared to Cem-FIL. The fibre was coated (on-line) with polymeric materials.

The alkaline durability of both uncoated and coated fibres (of different diameter) were studied in varying conditions of pH.

2. Experimental details

The glass composition adopted after some trials is: SiO_2–34%, PbO–59%, Al_2O_3–3%, K_2O–3.5%, Na_2O–0.5% (wt %). The glass had relatively low melting point (1350° C), is fairly alkaline resistant particularly in the long run and appeared to have satisfactory fibrilizing qualities.

For melting the glass, after accurate weighing, the batch components were mixed thoroughly and then melted in a sillimanite crucible with occasional stirring in an electric furnace. The glass samples were studied with X-ray, differential thermal analysis (DTA) and electron microscopy to detect crystallization, phase separation, if any. Samples forming perfect homogeneous glasses were chemically analysed to determine their exact compositions. The fibres were drawn from glass of the above composition.

The fibres were coated on-line with a mixture of epoxy resin and bis 4-amino cyclohexyl methane. Alkaline durability of uncoated and coated glass fibres (drawn at 500 and 1000 r.p.m.) were measured at pH 9, 10, 11 and 12. During the study 5 g portions of the glass fibres were put in 500 ml buffered solutions of pH 9, 10, 11 and 12 at a temperature of 32° C for 28 days. During digestion the polythene bottles containing the fibres and the corroding solutions were shaken frequently. 20 ml portions of the leach solution were taken out after 4 h, 1, 2, 3, 7, 14, 21 and 28 days. The amount of silica, lead and potassium extracted in the solutions were estimated. No significant amount of alumina comes out in the leach solution. Potassium was estimated with a flame photometer, silica calorimetrically as silicomolybdic acid and lead with atomic absorption. The reagents used for making different buffer solutions were as follows: pH 9 to 12 solutions were prepared by adding appropriate amounts of NaOH solution (1 M) to saturated boric acid solution.

The resulting pH of the above solutions were measured by a pH meter (Systronics, Model No. 331).

3. Results and discussion

3.1. Corrosion of glass fibre in alkaline solutions

Corrosion behaviour of two types of glass fibres (of different diameter): (a) glass fibre of diameter 30 μm (uncoated and coated); and (b) glass fibre of diameter 22 μm (uncoated and coated) were studied.

The amount of SiO_2, lead and potassium extracted per gram of fibres and per cm^2 surface area of the glass fibres have been estimated as a function of time. The results are shown in Figs 1 to 12.

3.1.1. SiO_2 extraction

Figs 1 and 2 show the silica extraction of the glass fibres as a function of time at pH 11 and 12. The amount of silica extracted from the glass fibres at pH 9 and pH 10 was very low (0.9 mg g^{-1}). There was no significant difference in the amount of silica extraction at pH 9 and 10 solutions. At all pH values the amount of silica extraction initially increases up to seven days reaching a somewhat steady value and thereafter no further increase could be detected up to 28 days.

Commercially available glass fibres (e.g. A glass, E glass) are not stable in alkaline solution. The amount of silica extraction increases in the alkaline solution. Significant changes occurs from pH 9. The rate of extraction of silica at any instant is largely related to the amount of alkali ions in the glass. Alkali ions, brought into the solution as a result of ion-exchange, increase the pH of the solution. After pH 9 most of the silica which passes into the solution is due to the formation of $HSiO_3^-$ and then SiO_3^{2-}.

In the present investigation there is a change in the amount of silica extracted with time which becomes steady after about 7 days. From 7 to 28 days, there is no sharp difference in the amount of extraction. In the present glass fibre there is an association of silica with lead and alumina. Thus the association of silica with lead appears to improve the alkaline durability of the glass to an attack by alkaline solution considerably. An explanation is offered in the section on lead extraction. Due to this superior stability of glasses containing lead in the alkaline medium lead glass was considered as a replacement for zirconia in glass, which is costly and needs a higher temperature for melting.

3.1.2. Lead extraction

Figs 3 and 4 show the amount of lead extraction with time at pH 11 and 12. The amount of lead extracted per gram of glass fibre in pH 9 and 10 solution is very low. Initially the value increases, then after about 7 days a steady value is reached. In the case of pH 11 and 12, the amount of lead extraction per gram of glass fibre is more. But the amount of extraction attains a steady value after about 7 days.

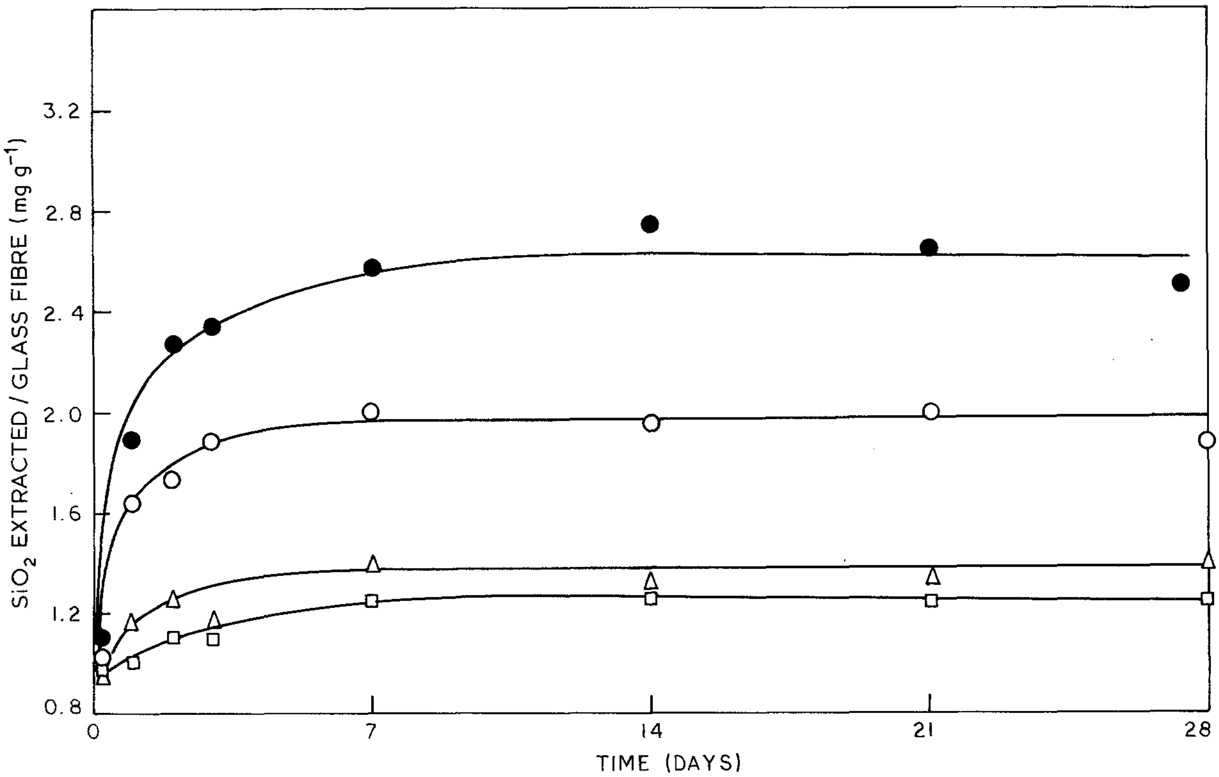

Figure 1 Extraction of SiO_2 from the glass fibre as a function of time at 32° C. (○) pH_{11} (uncoated) 500 r.p.m., (□) pH_{11} (coated) 500 r.p.m., (●) pH_{11} (uncoated) 1000 r.p.m., (△) pH_{11} (coated) 1000 r.p.m.

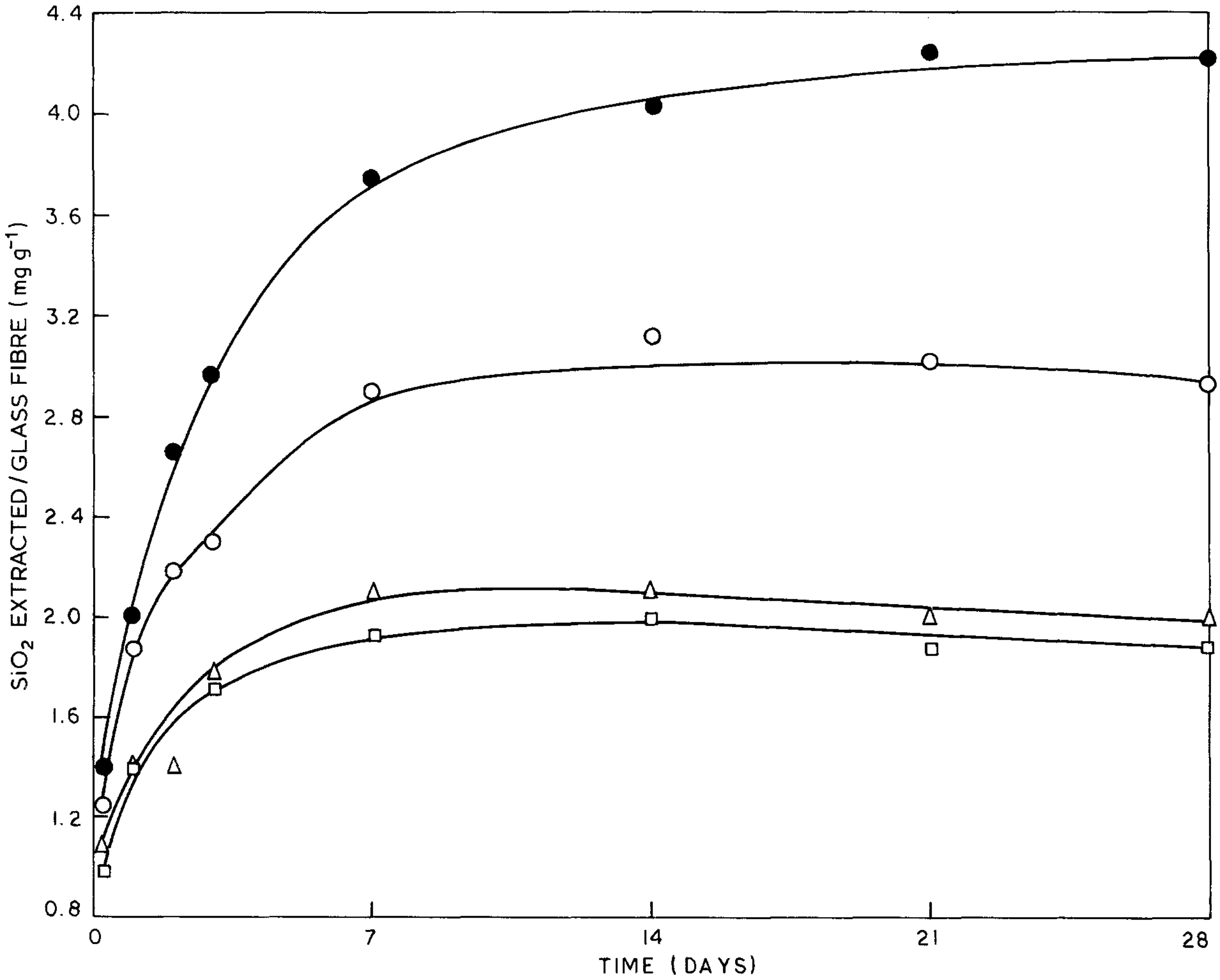

Figure 2 Extraction of SiO_2 from the glass fibre as a function of time at 32° C. (○) pH_{12} (uncoated) 500 r.p.m., (□) pH_{12} (coated) 500 r.p.m., (●) pH_{12} (uncoated) 1000 r.p.m., (△) pH_{12} (coated) 1000 r.p.m.

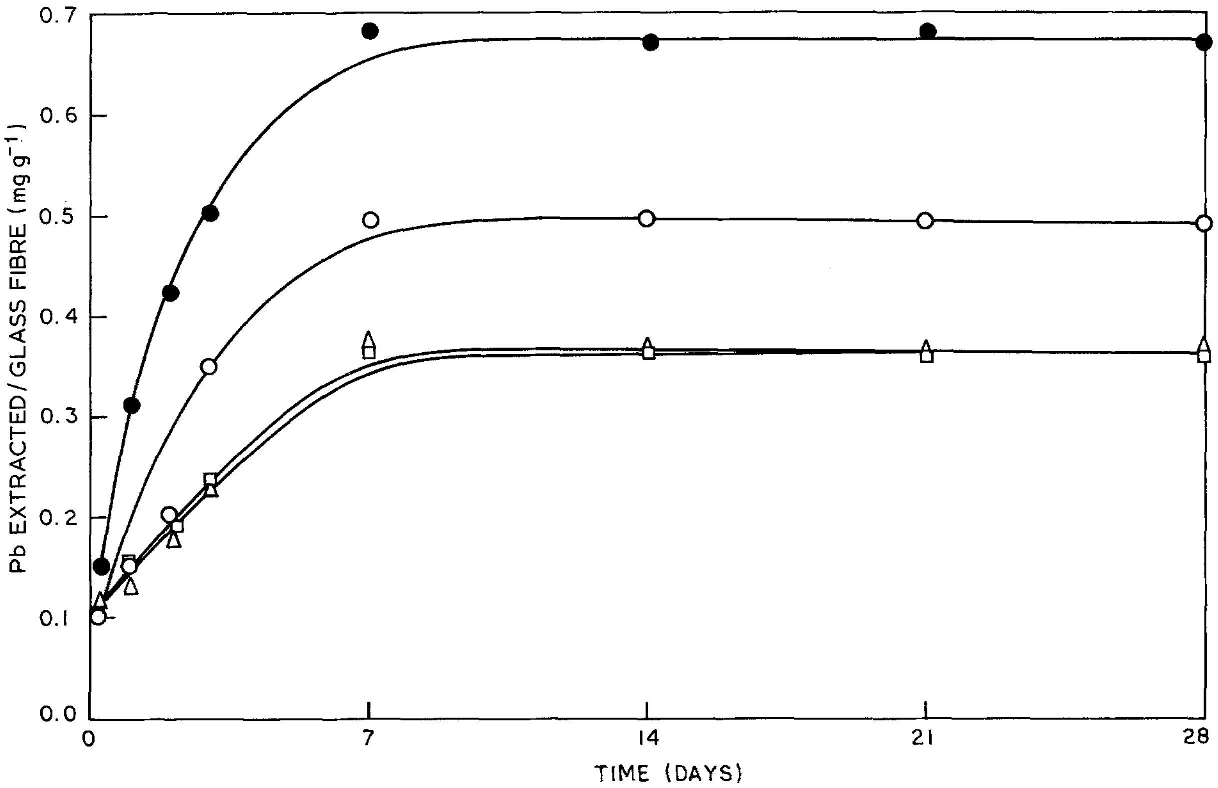

Figure 3 Extraction of lead from the glass fibre as a function of time at 32° C. (○) pH_{11} (uncoated) 500 r.p.m., (□) pH_{11} (coated) 500 r.p.m., (●) pH_{11} (uncoated) 1000 r.p.m., (△) pH_{11} (coated) 1000 r.p.m.

As PbO is an amphoteric material, a hydrated oxide film was developed at the surface in contact with aqueous solution. In the alkaline range lead forms $HPbO_2^-$ and the activity of $HPbO_2^-$ becomes greater than that of $Pb(OH)_2$ only at above pH $\geqslant 14.5$. So PbO was used in silicate glass to increase the alkaline durability. Also lead oxide containing glasses are low melting thereby reducing the production cost.

3.1.3. K_2O extraction

Figs 5 and 6 present the experimental data on the amount of alkali extracted per gram of glass fibre (uncoated and coated) in leach solutions of pH 11 and 12. The amount of alkali extraction decreases from pH 9 to 12. It is maximum in the case of pH 9 and a minimum in the case of pH 12, though a steady value is attained after a period of time in each case.

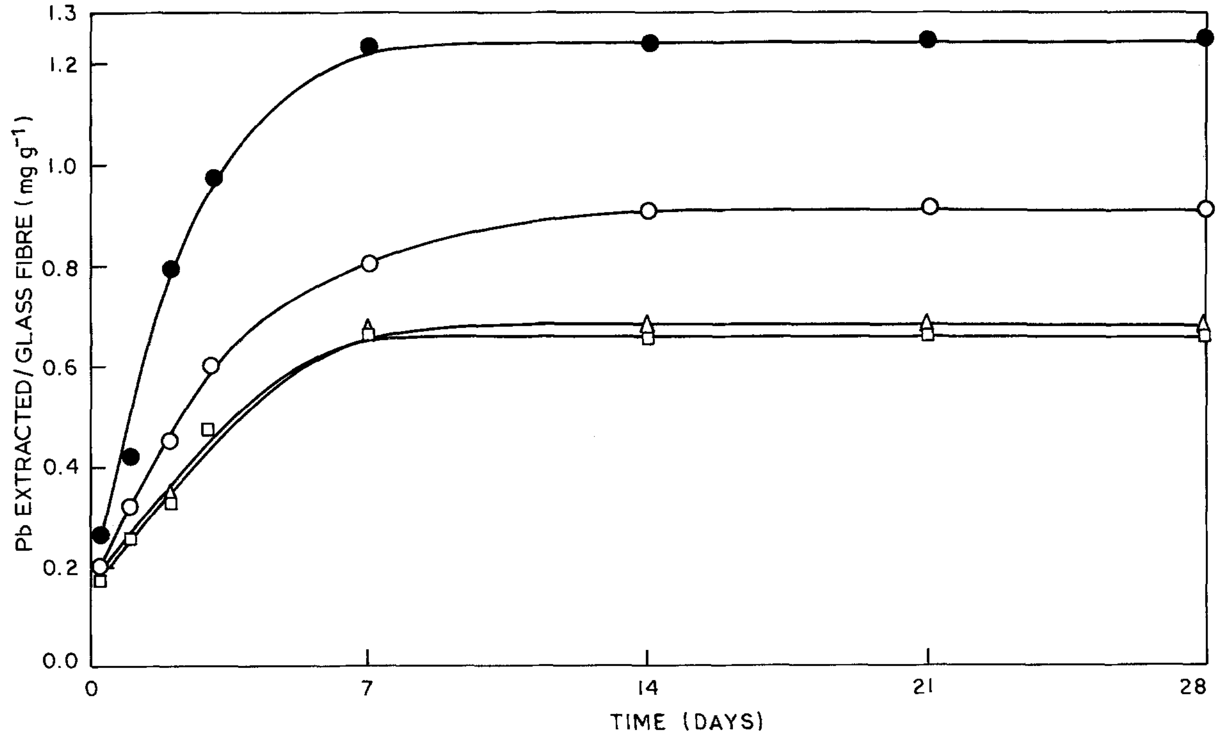

Figure 4 Extraction of lead from the glass fibre as a function of time at 32° C. (○) pH_{12} (uncoated) 500 r.p.m., (□) pH_{12} (coated) 500 r.p.m., (●) pH_{12} (uncoated) 1000 r.p.m., (△) pH_{12} (coated) 1000 r.p.m.

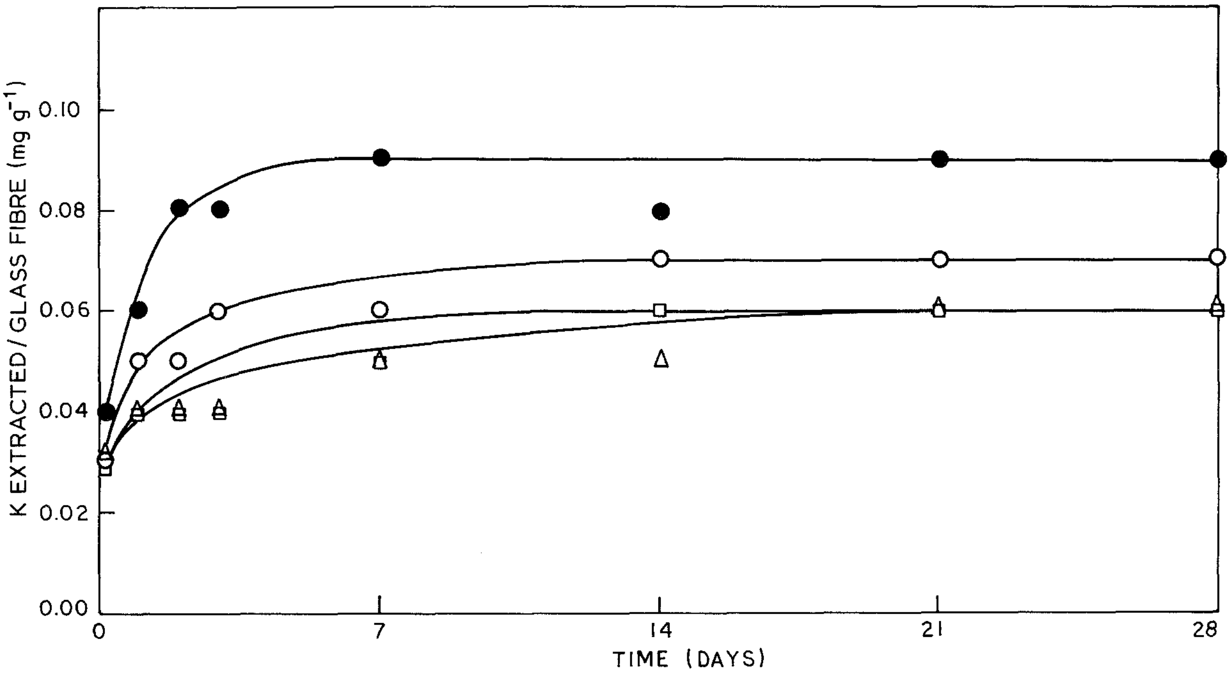

Figure 5 Extraction of potassium from the glass fibre as a function of time at 32° C. (○) pH_{11} (uncoated) 500 r.p.m., (□) pH_{11} (coated) 500 r.p.m., (●) pH_{11} (uncoated) 1000 r.p.m., (△) pH_{11} (coated) 1000 r.p.m.

The driving force for diffusion of alkali from glass into solution is the concentration gradient across the attacked layers bound by alkali concentration of unattacked glass on one side, and the alkali concentration at the interface between the attacked glass and the solution on the other. Most of the surface sites are associated with hydrogen. This accounts for higher rates of alkali extraction of low pH. Above pH 9, activity of hydrogen ions in solution becomes very low and the surface sites become increasingly associated with alkali ions. The concentration gradient is decreased and hence, the rate of alkali extraction decreases above pH 9. The small amount of alkali extracted in pH 10 solutions, corroborates this view. As pH becomes higher the amount of extraction will be lower. So in the case of pH 11 and 12 the amount of extraction is very low. The extraction of alkali from glass leaves behind a silica rich layer at the surface. PbO present in the glass stabilizes the SiO_2 rich film by filling the microvoids and forming a chemical barrier to further diffusion of alkali ions.

3.2. Thermodynamic stability and the effect of pH of the solution on the chemical durability of glass

The chemical durability of silicate glasses is critically dependent on pH and the nature of the attacking solution. In principle the thermodynamic stability of a

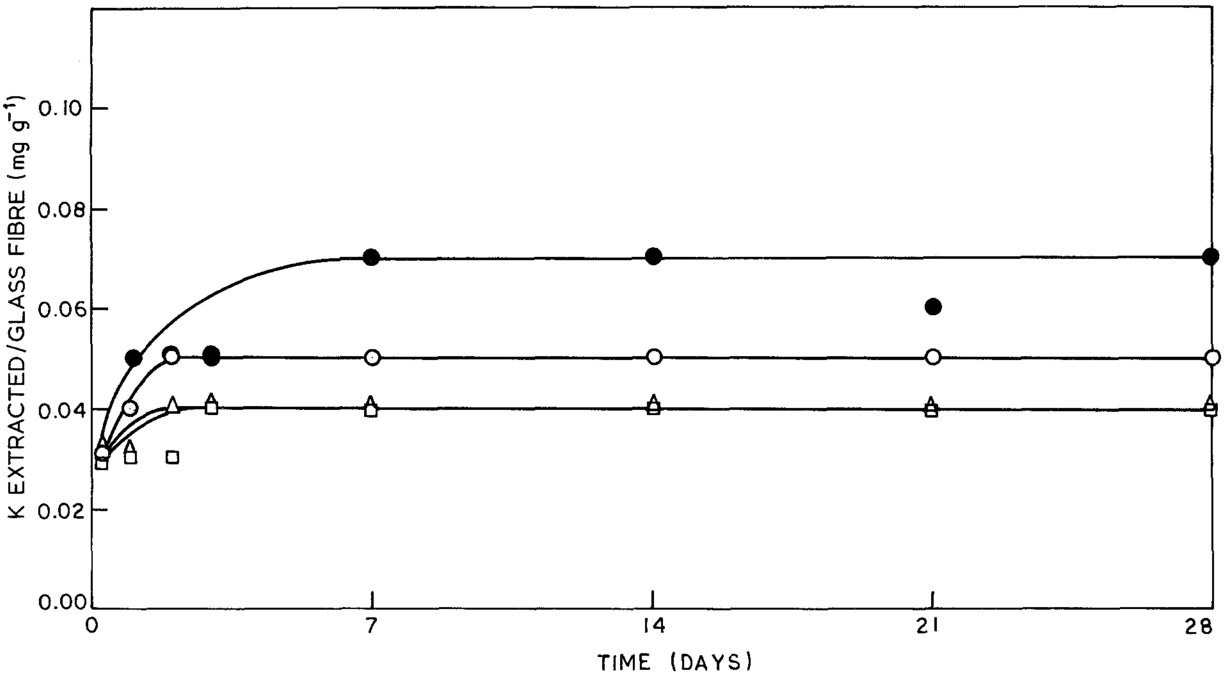

Figure 6 Extraction of potassium from the glass fibre as a function of time at 32° C. (○) pH_{12} (uncoated) 500 r.p.m., (□) pH_{12} (coated) 500 r.p.m., (●) pH_{12} (uncoated) 1000 r.p.m., (△) pH_{12} (coated) 1000 r.p.m.

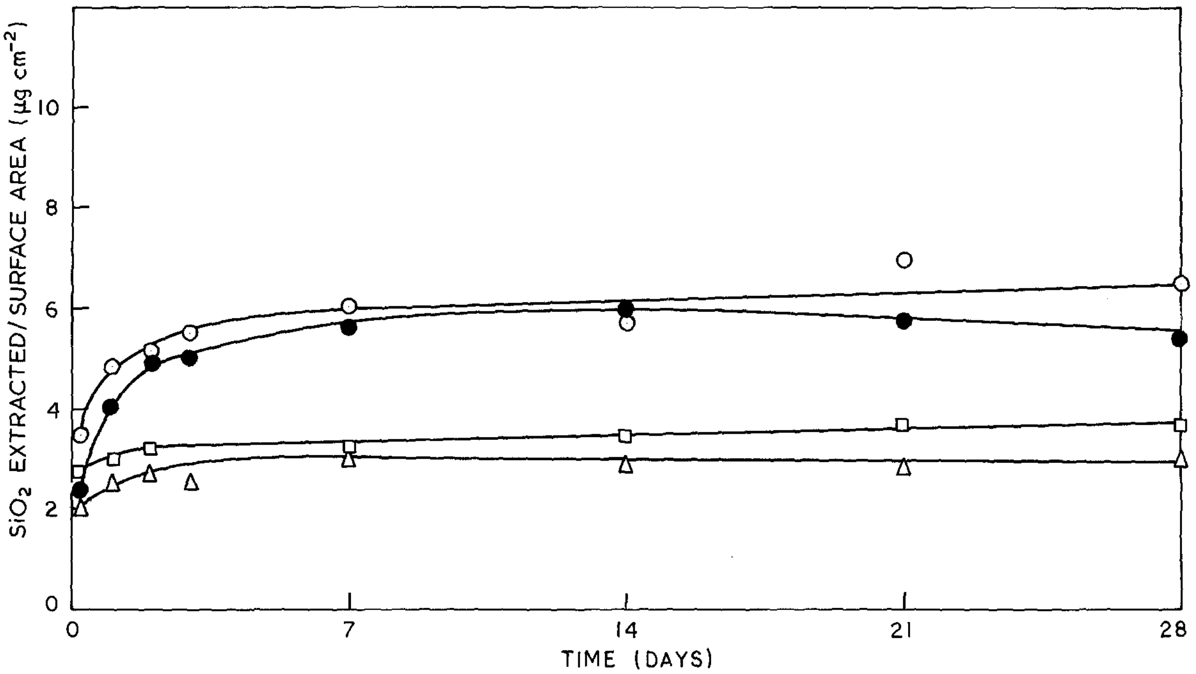

Figure 7 Extraction of SiO_2 per cm^2 surface area of glass fibre as a function of time at 32° C. (○) pH_{11} (uncoated) 500 r.p.m., (□) pH_{11} (coated) 500 r.p.m., (●) pH_{11} (uncoated) 1000 r.p.m., (△) pH_{11} (coated) 1000 r.p.m.

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 [5]. With the available thermodynamic data, one can calculate the various energy changes being associated with these processes and from these the stability of a glass at different pH can be judged. The following discussion refers to a temperature of 25° C and one atmosphere of pressure only. The various aqueous reactions of the major component oxides in the present glasses are listed in Table I. The stability diagram of the different oxides, calculated from the standard free energy (ΔG^0) data (given in Table I) are shown in Figs 13 to 15.

The very limited solubility of silica in neutral or acidic aqueous solutions (except hydrofluoric acid) is one of the main factors in determining the corrosion resistances of silicate glass [5]. From Fig. 13 it can be seen that the solubility of silica in terms of H_2SiO_3 in

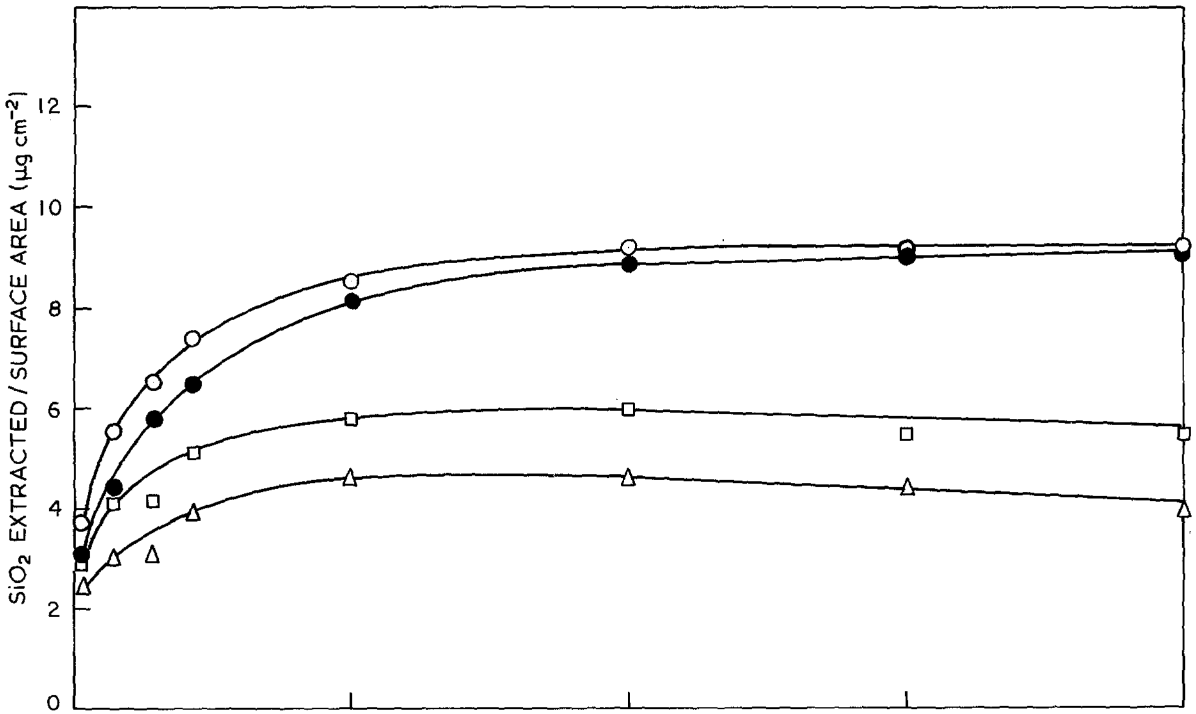

Figure 8 Extraction of SiO_2 per cm^2 surface area of glass fibre as a function of time at 32° C. (○) pH_{12} (uncoated) 500 r.p.m., (□) pH_{12} (coated) 500 r.p.m., (●) pH_{12} (uncoated) 1000 r.p.m., (△) pH_{12} (coated) 1000 r.p.m.

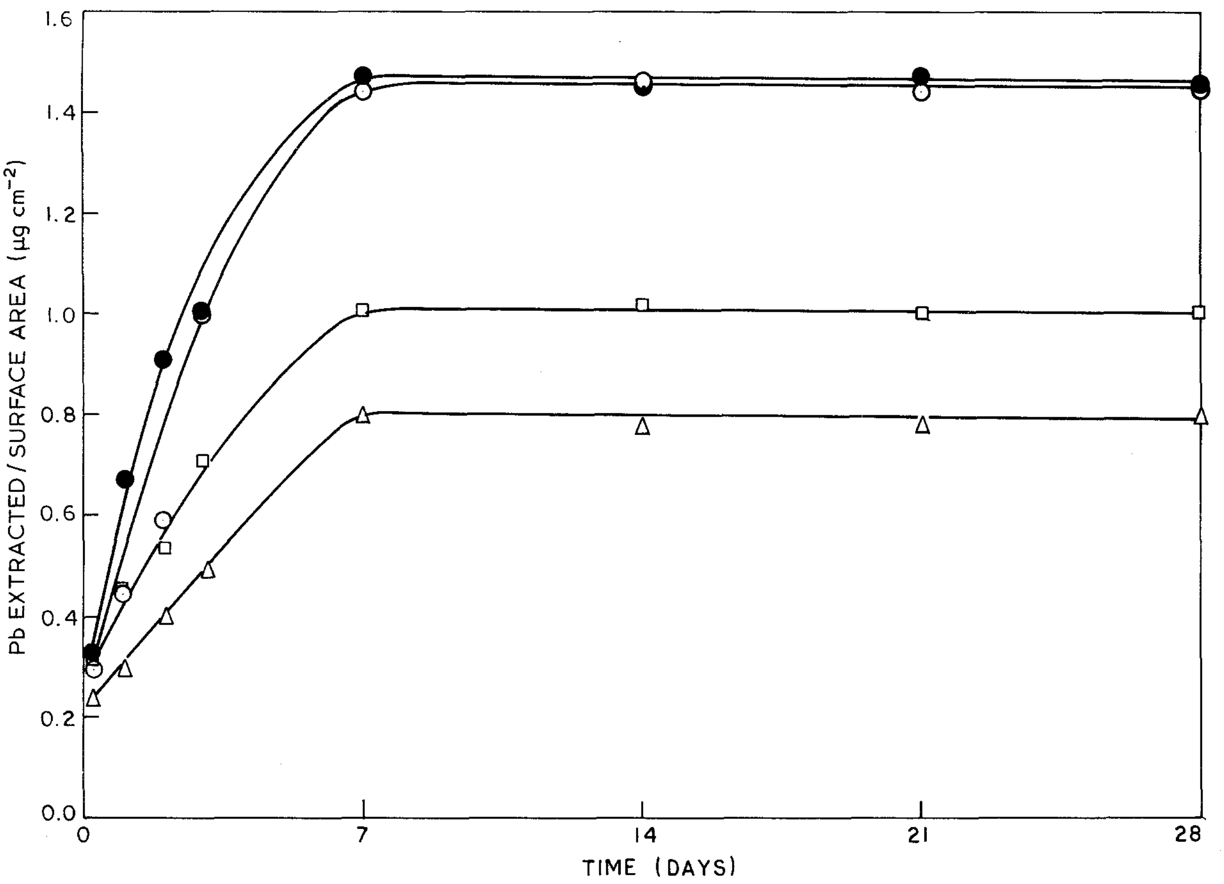

Figure 9 Extraction of lead per cm^2 surface area of glass fibre as a function of time at 32° C. (○) pH$_{11}$ (uncoated) 500 r.p.m., (□) pH$_{11}$ (coated) 500 r.p.m., (●) pH$_{11}$ (uncoated) 1000 r.p.m., (△) pH$_{11}$ (coated) 1000 r.p.m.

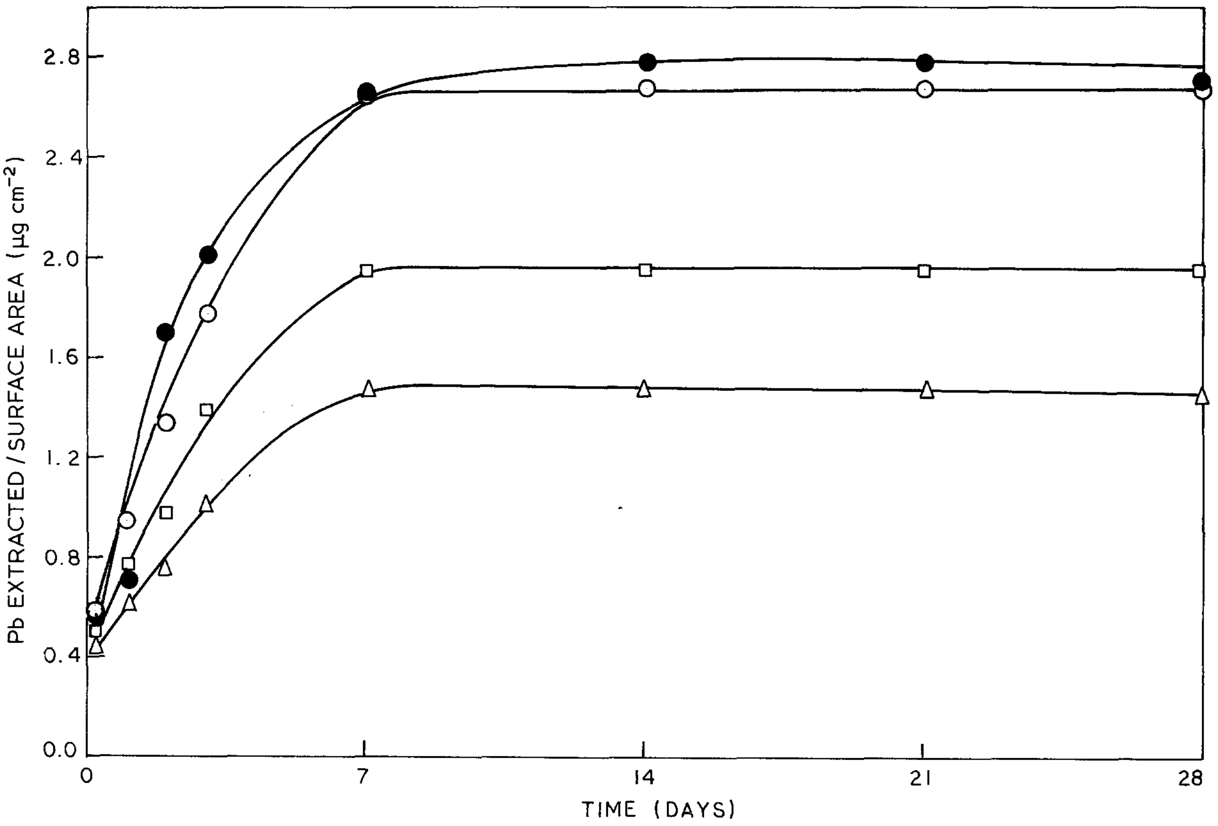

Figure 10 Extraction of lead per cm^2 surface area of glass fibre as a function of time at 32° C. (○) pH$_{12}$ (uncoated) 500 r.p.m., (□) pH$_{12}$ (coated) 500 r.p.m., (●) pH$_{12}$ (uncoated) 1000 r.p.m., (△) pH$_{12}$ (coated) 1000 r.p.m.

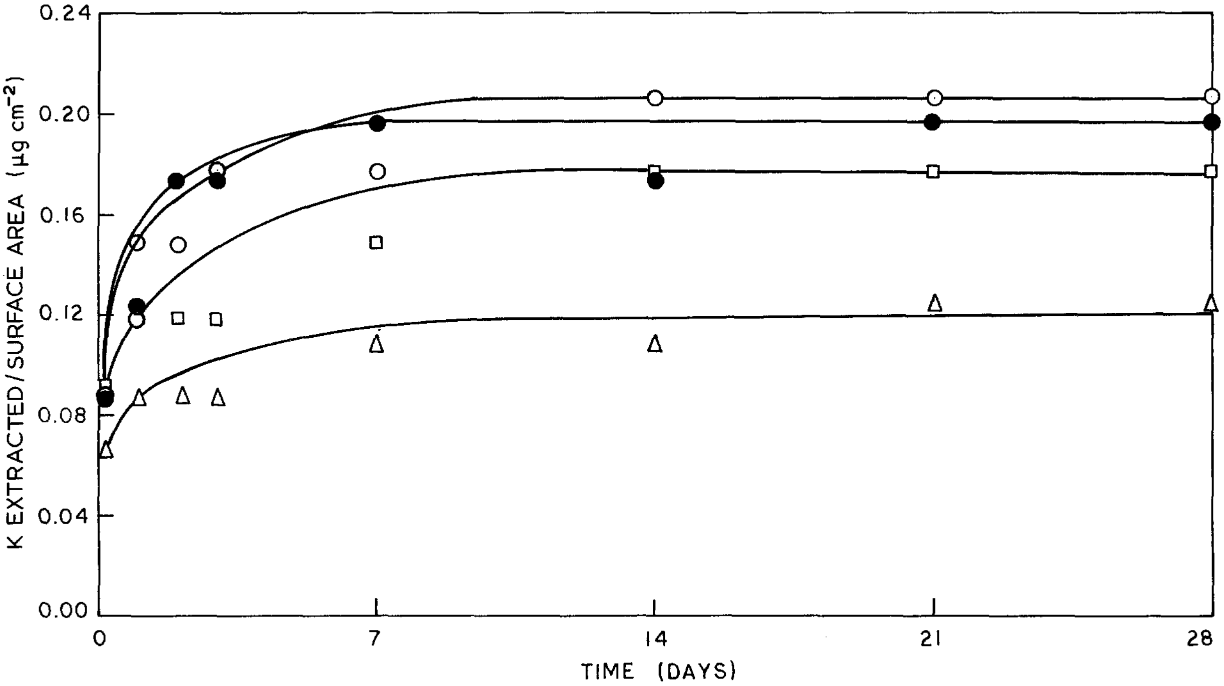

Figure 11 Extraction of potassium per cm^2 surface area of glass fibre as a function of time at 32° C. (○) pH_{11} (uncoated) 500 r.p.m., (□) pH_{11} (coated) 500 r.p.m., (●) pH_{11} (uncoated) 1000 r.p.m., (△) pH_{11} (coated) 1000 r.p.m.

the solution, is independent of 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 in Fig. 13, 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 ($pH \leqslant 10$) the minimum solubility is represented by the undissociated silica (hydrated form), this species predominates between pH = 0 to 9 (independent of pH). In the second zone (pH = 10 to 12) most of the silica which passes into solution is due to the formation of $HSiO_3^-$. In the third zone ($pH \geqslant 12$), the SiO_3^{2-} ion predominates in the solution. The total silica solubility increases exponentially with the alkalinity of the solution.

The solubility of PbO in aqueous solutions with different pH values is shown in Fig. 14. Hydration of PbO is small. In the acidic range ($pH \leqslant 6.8$) lead dissolves as Pb^{2+} and $PbOH^+$, the activity of the former being always much greater than that of $PbOH^+$. In the alkaline range lead forms $HPbO_2^-$ and the activity of $HPbO_2^-$ becomes greater than that of $Pb(OH)_2$ only above $pH \geqslant 14.5$. Thus PbO in silicate glass is expected to increase the alkaline durability.

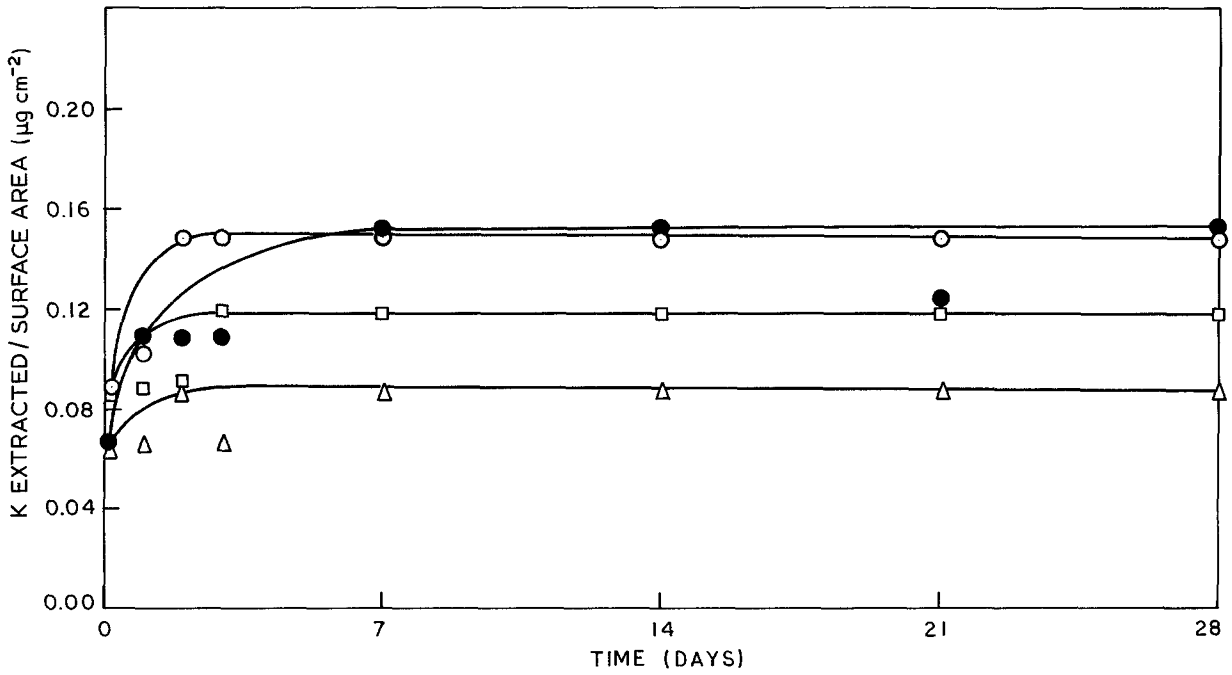

Figure 12 Extraction of potassium per cm^2 surface area of glass fibre as a function of time at 32° C. (○) pH_{12} (uncoated) 500 r.p.m., (□) pH_{12} (coated) 500 r.p.m., (●) pH_{12} (uncoated) 1000 r.p.m., (△) pH_{12} (coated) 1000 r.p.m.

TABLE I Thermochemical data for reactions of SiO_2, PbO, Al_2O_3 with water at 25° C

Reaction	ΔG^0 (kcal mol^{-1})	log K	Relationship
SiO_2 (glass) + H_2O (liq) $\rightleftharpoons$ H_2SiO_3	+5.590	−4.098	$\log^a (H_2SiO_3) = -4.098$
$H_2SiO_3 \rightleftharpoons HSiO_3^- + H^+$	+13.640	−10.000	$\log^a (HSiO_3^-) = -14.098 + pH$
$HSiO_3^- \rightleftharpoons SiO_3^{2-} + H^+$	+16.360	−11.994	$\log^a (SiO_3^{2-}) = -26.092 + 2pH$
PbO (cryst) + H_2O (liq) $\rightleftharpoons$ $Pb(OH)_2$	+1.140	−0.836	$\log^a (Pb(OH)_2) = -0.836$
$Pb(OH)_2 + H^+ \rightleftharpoons PbOH^+ + H_2O$	−7.820	+5.736	$\log^a (PbOH^+) = 4.9 - pH$
$Pb(OH)_2 + 2H^+ \rightleftharpoons Pb^{2+} + 2H_2O$	−18.590	+13.629	$\log^a (Pb^{2+}) = 12.793 - 2pH$
$Pb(OH)_2 \rightleftharpoons HPbO_2^- + H^+$	+19.600	−14.369	$\log^a (HPbO_2^-) = -15.203 + pH$
Al_2O_3 (corundum) + $3H_2O$ (liq) $\rightleftharpoons$ $2Al(OH)_3$ (cryst)	+3.04	−2.23	$\log^a Al(OH)_3$ (cryst) $= -1.115$
Al_2O_3 (corundum) + $6H^+$ (aq) $\rightleftharpoons$ $2Al^{3+}$ (aq) + $3H_2O$ (liq)	−23.30	+17.08	$\log^a Al^{3+}$ (aq) $= 8.54 - 3pH$
Al_2O_3 (corundum) + H_2O (liq) $\rightleftharpoons$ $2AlO_2^-$ (aq) + $2H^+$ (aq)	+32.06	−23.50	$\log^a AlO_2^-$ (aq) $= -11.75 + pH$

The experimental results corroborate this expectation.

Al_2O_3 is also known to improve the chemical durability of silicate glasses. The stability diagram of Al_2O_3 in aqueous solution of different pH is shown in Fig. 15. In the acid range of pH $\leqslant$ 3.2 the predominant species is Al^{3+} and is expected to be leached out from the glass surface. In the alkaline range AlO_2^- is formed and becomes significant around pH $\geqslant$ 10.7. Thus Al_2O_3 in glass is expected to slightly increase the alkaline durability of glass. In the present study small amounts of Al_2O_3 were added to the glass primarily to improve the viscosity–temperature relationship and this addition also improved the alkaline durability of the glass.

3.3. Effect of coating on fibre

In the present investigation, a suitable epoxy resin, which is alkaline resistant, was selected. For this purpose, Araldite Cy-230 (CIBA-Geigy of India Ltd) has been found suitable. It is a liquid-solvent-free epoxy resin. It has outstanding properties for industrial and technological applications. The curing agent selected was bis 4-aminocyclohexyl methane. The basicity is the same as an aromatic amine. But curing is faster than that of an aromatic amine.

The kinetics of the curing reaction of an epoxy resin based on bisphenol-A-diglycidyl ether with a cycloaliphatic diamine bis 4-aminocyclohexyl methane was studied [6]. From the study it has been observed that cycloaliphatic amine was more reactive than an analogous system, and the network is much more rigid.

The work done by Yilgor *et al.* [6] shows that on the basicity consideration, cycloaliphatic amines are much more reactive than their aromatic counterpart and still can provide a rigid epoxy network. They also have a comparatively long pot life. Therefore, one may anticipate that their importance should increase in the various industrial applications. The morphology and final properties of epoxy resins which are widely used as matrices for various composites strongly depend on the state and extent of cure of the resin.

In the above (Figs 1 to 6) it has been observed that there is a lower value in the amount of extraction of the constituents in the case of a coated fibre than those of an uncoated fibre. There was no significant difference in the amount of extraction of the coated fibre in the case of fibre of diameter 30 and 22 μm, respectively. So the above mentioned epoxy resin with a curing agent helps to reduce the extraction value of the

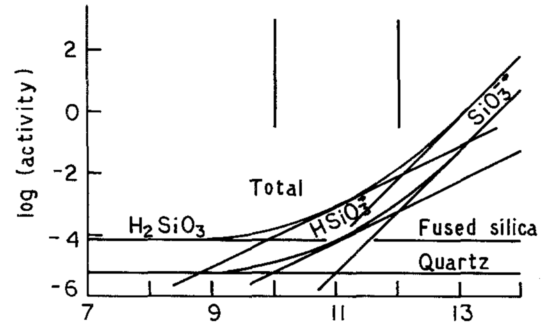

Figure 13 Stability of SiO_2 in aqueous solutions at different pH (25° C).

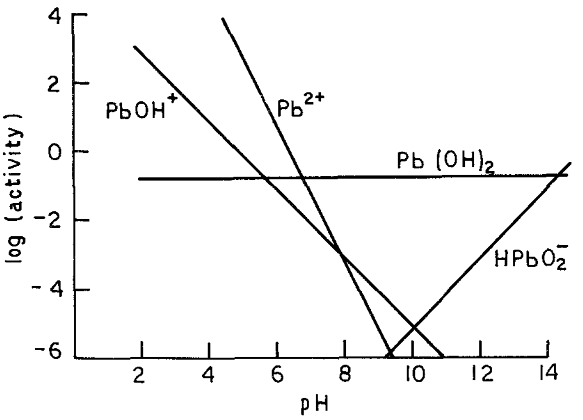

Figure 14 Stability of PbO in aqueous solutions at different pH (25° C).

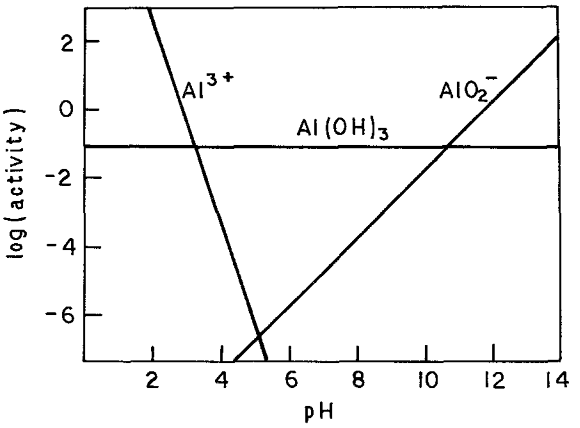

Figure 15 Stability of Al_2O_3 in aqueous solutions at different pH (25° C).

constituents in the leaching solution. Experimentally it has been established that the coating of fibres improves their chemical durability, which serves the present purpose of the investigation. The improved performances of the coated fibres in strength tests indicate effective protection of the fibres due to the coating during drawing, collection and storage.

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