GLASS FIBRE REINFORCED CEMENT

A. J. Majumdar, OBE, PhD

and

V. Laws, MSc

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Foreword

Glass fibre reinforced cement, grc for short, is an interesting construction material of considerable potential. The development of its potential was one of the most exciting research projects being carried out by the Building Research Establishment during my time as Director between 1979 and 1983.

To make the material, a small amount of an alkali-resistant glass fibre is incorporated in cement mortar to overcome the traditional weakness of inorganic cements, namely poor tensile strength and brittleness. In grc the length and content of the glass fibre reinforcement can be chosen to meet the strength and toughness requirements of the product. Manufacturing methods have been specially developed for producing articles of various shapes and designs, from architectural cladding panels to housing for electrical machines, and the material is playing an important part in the renovation of old buildings. Conceptually, grc is similar to asbestos cement and as the use of the latter is declining in some countries the use of grc as a substitute is increasing. This trend is likely to grow.

The first commercial alkali-resistant glass fibre, Cem-FIL, was produced in the UK by Pilkington Brothers PLC in 1971 after pioneering work on glass compositions had been carried out at the Building Research Establishment. Prior to this a considerable amount of research and development work on grc was done in the USSR in the late 1950s and early 1960s using ordinary glass fibres. But it is fair to say that the production of the AR glass fibre Cem-FIL, by the collaborative efforts of Pilkington, the National Research Development Corporation (now part of the British Technology Group) and BRE, marked the beginning of the grc industry. AR glass fibres similar to Cem-FIL have now been produced in the USA and in Japan. On a worldwide basis the grc industry is currently supplying goods and services worth several hundred million US dollars.

In the 1970s research on grc was generously supported at BRE. Work was done on fibre incorporation techniques, on different types of cement matrices (including Portland cement modified by various pozzolanic materials and polymers), on the fundamental chemistry of glass/cement interactions, and on some theoretical aspects of reinforcement of brittle matrices such as cements by glass fibres. One important aspect of this programme was to expose test boards made from different types of grc to different environments for assessment of their long-term properties. In 1979 Pilkington launched their second generation AR glass fibre Cem-FIL 2 provided with an 'inhibitive' surface coating that is considered to be much more resistant to corrosion by cements than the earlier Cem-FIL. At BRE, only a limited amount of work was undertaken on Cem-FIL 2; in the 1980s much of BRE's effort went towards accumulating results on the long-term properties of various types of the grc composites that were already under investigation.

The authors of this book have been involved in grc research at BRE from the very beginning and they have given a detailed account of research results obtained by them and their colleagues over a period spanning two decades. Results for up to ten years' storage in different environments are given for many grc composites, and in some cases longer-term results have been obtained. These results are supplemented by important contributions from other sources, notably from Pilkington. The production methods and current applications of grc are also described briefly.

The book is likely to be of interest to engineers, architects, specifiers and component manufacturers who wish to know about the development of various properties in the different types of grc over long periods of time in different environments. It will be of general interest to materials scientists in the construction field, not least because grc is an interesting example of a composite material where the components are reactive towards each other. The reader may learn how this inherent reactiveness has been counteracted to produce a material that is useful for many purposes. Above all, the book is a historical document of the development of the subject. The authors present their views about likely future developments, whilst being careful to point out the limitations of the material.

GRC has reached a stage where Standards are already in existence for several products made of it, and for test methods. Several other Standards are in preparation and I am sure that this book will be a significant contribution to that work.

Dr I. Dunstan
Director General,
British Standards Institution

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Chapter One
Alkali-Resistant Glass Fibres

1.1 Historical

As the name implies, glass fibre reinforced cement (grc) comprises two essential components, namely glass fibres and cement. Inorganic hydraulic cements used in the construction industry are highly alkaline and therefore require special alkali-resistant glass fibres for their reinforcement. The development of such fibres during the past 20 years has been responsible for the foundation and growth of a new industry, the grc industry.

The art of drawing fibres from heat-softened glass was known to glass makers of ancient Egypt but the use of strong glass fibres as reinforcements is a relatively modern idea, materialising after the almost simultaneous development in the USA in the 1930s of (a) manufacturing methods for continuous glass fibres and (b) thermosetting polyester resins. Borosilicate E-glass fibres, originally developed for making electrical insulation tape, were used to manufacture strong and tough resin composites that could be formed to shape. This heralded the dawn of the glass fibre reinforced plastics (grp) industry.

Following the success of the grp industry in the 1950s attempts were made to examine the potential of glass fibres as reinforcements for concrete. Cement and concrete are weak in tension and against impact. Conventionally the weaknesses are overcome in concrete structures by the use of steel reinforcement bars or cables. One way to use glass fibres was to make up ropes of glass rovings joined together and coated with plastics so as to make a reinforcing bar or cable directly replacing steel. E-glass fibres were used and experiments were carried out with unstressed as well as stressed reinforcement[1,2]. The modulus of the glass is rather low for the former method to be efficient, but the combination of low modulus and high tensile strength makes stressed reinforcement a promising approach. However, very little interest has been shown in this area in recent years. Another and more successful approach has been to produce grc sheets, conceptually similar to asbestos cement, which can be moulded to shape. Most of the grc products now in use are made from thin sheets.

In these products cement is rarely used alone; a proportion of sand or other fine aggregates is needed to prevent cracking due to drying shrinkage. It is also now becoming common practice to modify the cement matrix by the addition of pozzolanas, admixtures or polymers to make it more suitable for reinforcement by fibres. In grc, such a matrix based on Portland and other cements is reinforced by a relatively small amount of glass fibres.

The first systematic study on grc as a composite material was carried out in the USSR by Biryukovich and his colleagues[3,4]. Borosilicate E-glass was used in these investigations, and as these are not resistant to alkalis special low-alkali cements or cement plus polymer were selected as the matrix. The reinforcement was used in a variety of forms including woven mats, and glass contents of up to 50% by weight of the finished product were achieved. Advantages claimed were high tensile strength and a high degree of elasticity in thin sections, water tightness and good thermal, acoustic and dielectric properties. Some prototype structures such as thin shell roofs were constructed.

An English translation of the Russian work became available in 1965[4]. This more or less coincided with the publication of pioneering research by Romualdi and Batson[5] on the reinforcement of concrete by steel wires and by Krenchel[6] on several types of fibre composite including fibre reinforced cement. Much interest was being directed at that time to metal matrix composites and to grp, and the fundamental basis of the science and technology of fibre composite materials was being laid. At the Building Research Establishment (BRE) a research project was launched in 1966 to look into the prospects of reinforcing cement and concretes with fibres. One of the objects of the project was to identify fibres that could be used as replacements for asbestos.

From the very outset the BRE work concentrated on glass fibres. It was soon realised that the approach taken by Biryukovich and co-workers of using special cements in combination with E-glass fibres would have only limited application and an alkali-resistant fibre was required for the reinforcement of Portland cements. Initially attempts were made to produce continuous crystalline fibres from glass by using the glass-ceramic approach of controlled nucleation and crystallisation. Fibres produced in this way were found to have very poor tensile strength arising from surface flaws created from faster crystallisation on the surface than in the bulk. It also became clear that the high speed of continuous fibre production is not compatible with uniform volume crystallisation of the glass. Attention was then focused on finding glass fibre compositions that were inherently more alkali-resistant than, say, E-glass fibres and examining their potential for cement reinforcement.

After a careful search of the literature it was concluded that glasses in the system $Na_2O-SiO_2-ZrO_2$ studied by Dimbleby and Turner[7] might possess the required degree of alkali resistance for reinforcing Portland cements. A glass with the composition (by weight) Na_2O 11%, SiO_2 71%, ZrO_2 16%, Al_2O_3 1%, Li_2O 1% and referred to as G20 was being produced in the USA by Corning Glass Works for use in boiler gauges and laboratory ware. Fibre from this glass was produced at BRE using a single tip bushing, and its performance in a Portland cement extract solution was studied and compared with that of E-glass fibres (Fig. 1.1(a))[8]. Subsequently a batch of

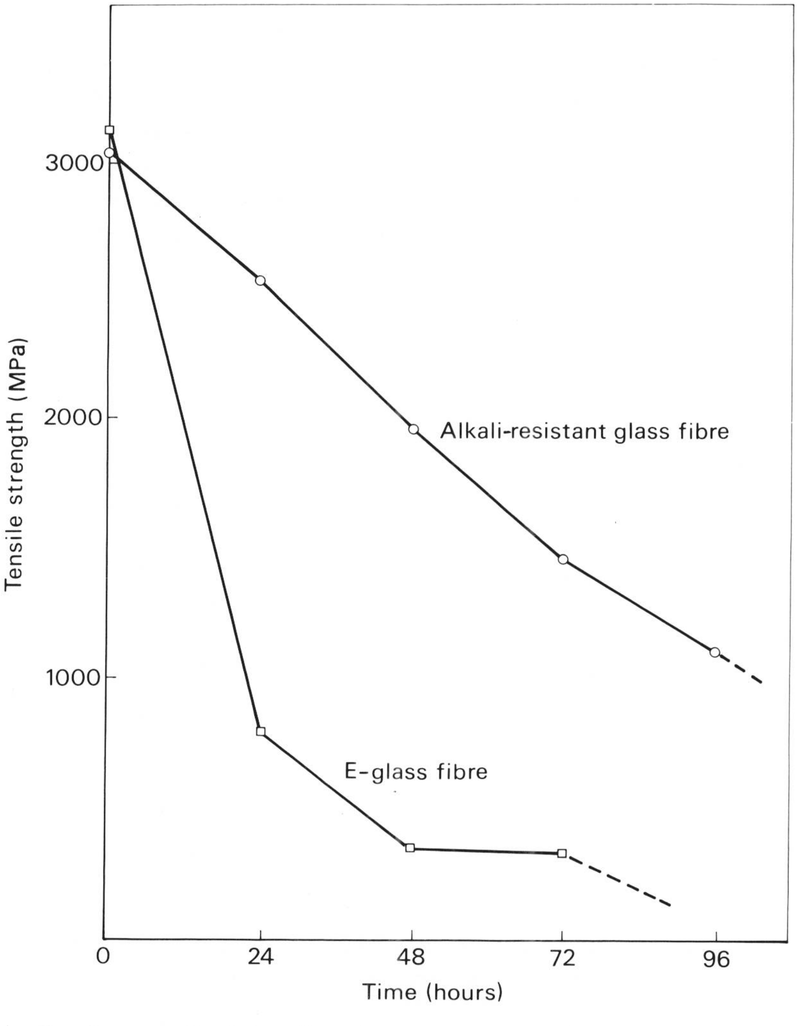


Fig. 1.1(a) Tensile strength of glass fibres in the aqueous solution phase of Portland cement at 80°C.

the G20 glass was obtained from Corning Glass Works and fiberised in the UK in the multifilament strand form. Portland cement composites made from this fibre were kept in different environments together with similar specimens made from E-glass fibres, and their strength properties were determined at various time intervals[9]. These results (Fig. 1.1(b)) clearly indicated that fibres made from glasses in the system $Na_2O-SiO_2-ZrO_2$ are more suitable for reinforcing cements than E-glass fibres. At about the same time work on zirconia containing glass fibres was also in progress in the USSR[10].

These preliminary results on the performance of an alkali-resistant (AR) glass fibre as cement reinforcement were of immediate interest to the glass industry in the UK, and one of the major glass producers in the world, Pilkington Brothers PLC, entered into a collaborative agreement with BRE and the National Research Development Corporation (now part of the British Technology Group) to develop a commercially viable AR glass fibre. Such a fibre, Trademarked Cem-FIL, was launched in 1971 by Fibreglass Limited, then a subsidiary of Pilkington. A few other AR glass fibres have been produced commercially since then. The properties of Cem-FIL fibres are compared with those of E-glass in Table 1.1.

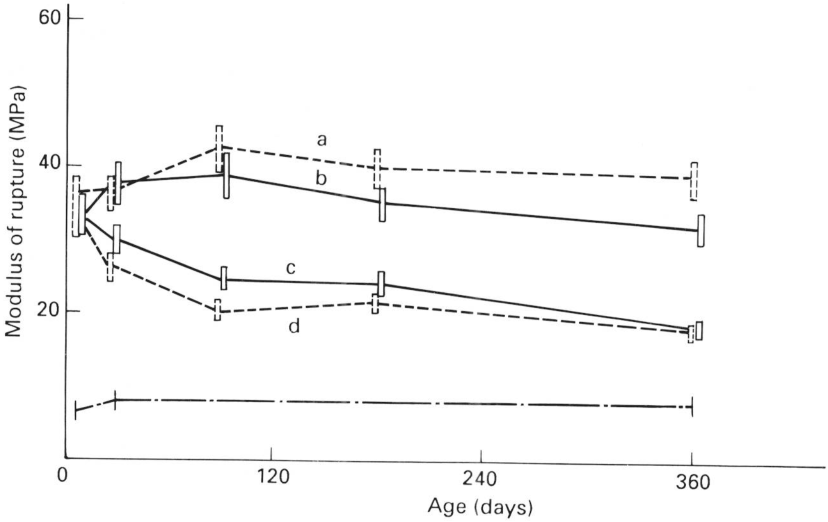


Fig. 1.1(b) Relation between modulus of rupture and age of glass fibre reinforced Portland cement composites. Fibre length 34 mm. Fibre content 4% by volume. (a) and (b) Alkali-resistant glass; (c) and (d) E-glass; ——, water cured at 18°C; ---, air (40% RH) cured at 18°C; —·—·—, average matrix strength, air and water cured.

Table 1.1 Glass fibre properties.

	E-glass[a]	AR glass[b]
Liquidus temperature (°C)	1140	1185
Fibre working temperature (°C)	1250	1283[c]
Young's modulus of fibre at 25°C (GPa)	75.5	70
Tensile strength of single fibre at 25°C (MPa)	3600	3600
Strain at failure	~2%	~2%
Tensile strength of fibre strand (MPa)	1700–2700	1450–1900
Density (Mg/m^3)	2.53	2.68
Coefficient of linear thermal expansion (per °C × 10^6)	5	7.5
Refractive index	1.550	1.561

a Lowenstein (1973)[20]
b Data from Pilkington Research and Development Laboratory
c Corresponding to 100 Pa s viscosity

With the commercial availability of Cem-FIL AR glass fibres the interest in grc as a new material of construction was immediate and its impact on the international construction scene has been sufficiently strong for an Association, named the Glass Fibre Reinforced Cement Association (GRCA) to have been formed in 1975. Through its Technical Committee the GRCA issue Codes of Practice and Guidelines for testing grc products. In safeguarding the interests of the young industry the GRCA is providing a valuable service for the producers and users of this new product.

It is worth pointing out that several applications of E-glass reinforced high-alumina cement composites were made in various countries before the advent of Cem-FIL AR glass fibres. It is believed that in many of these applications the grc material has performed adequately.

1.2 The matrix phase

In most of the applications of grc to date the proportion of glass fibres in the composite has been small – 5% by volume or less. The matrix phase is therefore very important in the development of composite properties and the durability of the material.

Various types of hydraulic cement – for example, Portland, high-alumina, supersulphated, Portland-blastfurnace slag, regulated set, etc. – are used in the construction industry, and in principle grc products can be made from any of them. However, as Portland cements are by far the most important of the inorganic cements, accounting for more than 90% of the world production of cements, nearly all grc products use this type of cement as the matrix at the present time. In recent years the use of blended cements has grown. In these a part of the Portland cement is replaced by a pozzolanic material such as pulverised fuel ash (pfa), ground granulated blastfurnace slag (ggbs) or microsilica (silica fume). The pozzolanas play an important role in combining with $Ca(OH)_2$ and other alkalis produced in cement hydration, thereby reducing the potential for corrosive alkaline attack on the glass fibres. It has also been found useful to add polymer dispersions of certain types – styrene–butadiene and acrylics are good examples – to control the flow properties of the slurry during the manufacture of grc components. By incorporating a low-density component such as perlite or pfa cenospheres, lightweight grc products have been made. Alternatively, a lightweight matrix can be produced by autoclaving lime plus silica or cement plus silica mixtures.

The properties of the matrix phase in grc are greatly influenced by the fabrication variables. The constitution and fineness of the cement powder and the amount of water used are the most important variables controlling the degree of hydration of the cement at a given time. A high water/cement (w/c) ratio produces a matrix that is very porous and therefore weak. On the other hand, if a low w/c ratio is used in grc manufacture much of the cement may remain unhydrated for a very long time when exposed to weather.

The effect of w/c and other fabrication variables on the properties of important hydraulic cements has been studied in detail and the results can be found in standard works of reference[11,12]. Since Portland cement is currently the principal binder in grc manufacture some of its important physical and engineering properties are listed in Table 1.2 as a guide. As the properties of the matrix are very dependent on w/c and curing conditions, a range of possible values is listed.

Table 1.2 Properties of hardened Portland cement paste.

Elastic modulus (GPa)	7 – 28
Compressive strength (MPa)	14 – 140
Tensile strength (MPa)	1.4 – 7
Modulus of rupture (MPa)	2.8 – 14
Tensile failure strain	0.02 – 0.06%
Poisson ratio	0.23 – 0.30
Thermal expansion (per °C × 10^6)	12 – 20
Volume change on drying	0.2 – 0.3% (negative)
Density (Mg/m^3)	1.7 – 2.2

The property of the matrix phase that is of utmost importance in grc is its alkalinity. It is not easy to obtain a realistic measure of this property at various stages in the life of the product, as the hydration of cement is a progressive process that can continue for many years. The presence of external components such as pozzolanas or polymers makes the attainment of equilibrium in hydration reactions even more difficult. The alkalinity of the matrix must refer to the composition of the pore solution that can be obtained by forcing out the solution from hardened cement pastes by the application of pressure. The technique, first used by Longuet *et al.*[13] is proving very useful and a considerable body of research results now exists on the compositions of pore solutions present in Portland and blended cement pastes and mortars. Nixon and Page[14] have recently reviewed the current state-of-the-art in this field with particular reference to alkali–aggregate reactions, and the following observations are taken from that review.

The alkalinity of the pore solution in cement pastes as measured by the hydroxyl ion concentration depends primarily on the amounts of the alkali metal oxides present in the cement. This is shown in Fig. 1.2 for 28 day old pastes studied by various investigators. There is not much information yet on the compositions of pore solutions in pastes that are several years old but Longuet *et al.*[13] found that the hydroxyl, sodium and potassium ion concentrations increased to a maximum between 7 and 28 days and then remained constant or decreased slightly. The calcium concentration fell to less than the detection limit in a few months. For Portland and other similar cements $Ca(OH)_2$ is a major product of hydration reactions. The lowest alkalinity of such a matrix would therefore correspond to that of a saturated $Ca(OH)_2$ solution, and this is shown in Fig. 1.2.

Pozzolanic additions such as microsilica (silica fume), metakaolin and pulverised fuel ash (pfa) to Portland cements are playing an increasingly important role in the grc industry, and the potential of glassy slags either in granulated or pelletised form is also being explored. Of these, microsilica additions have the largest effect in reducing the hydroxyl ion concentration in the cement pore solutions, the degree of reduction depending on the amount of microsilica added. The experimental results of Page and Vennesland[15] are shown in Fig. 1.3. Nixon and Page[14] conclude that pf ashes need a minimum of 28 days to have a significant effect on the pore solution chemistry and they reduce the hydroxyl ion concentrations more effectively in high-alkali cement pastes by means of pozzolanic reactions. In contrast, the available evidence suggests that granulated blastfurnace slags operate more as a diluent. Some typical values of the reduction of OH^- ion concentrations in the pore solutions in blended cement pastes are given in Table 1.3 from the work of Page and co-workers[16].

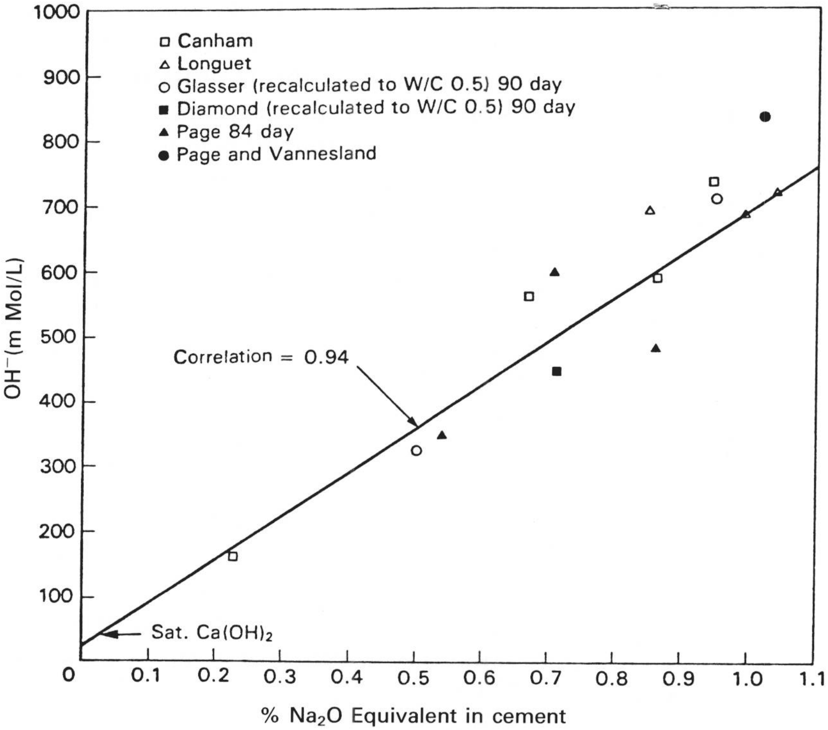


Fig. 1.2 Hydroxyl ion concentrations in pore solution of pastes with 0.5 w/c, 28 day results except where otherwise stated; approx. 20°C storage (Reference 14).

Table 1.3 Hydroxyl ion concentration in cement paste pore solution.

% Na_2O equivalent: Cement	% Na_2O equivalent: Addition	wt% addition	$\frac{\text{water}}{\text{solids}}$ ratio	Storage time (days)	OH^- ion concentration (m mol/ℓ)
0.67	—	—	0.45	28 365	604.0 661.7
0.67	pfa 3.37	40	0.45	28 365	331.1 319.6
0.67	slag 0.97	40	0.45	28 365	466.4 505.8
0.67	slag 0.97	60	0.45	28 365	341.1 358.9

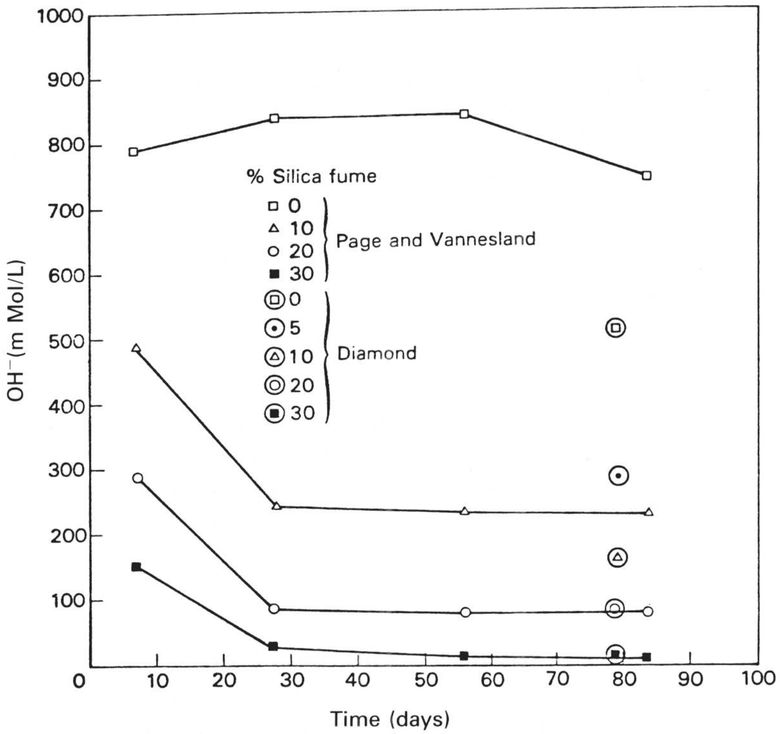


Fig. 1.3 Change in hydroxyl ion concentration with time and proportion of silica fume (Reference 15).

Alternative but less relevant methods of assessing cement alkalinity consist of suspending the ground cement paste in a known quantity of water or making a cement slurry with a very high w/c and keeping it stirred for a long period of time. The analysis of the solution phase gives some idea of the alkalinity of the matrix. The results from one series of experiments are shown in Table 1.4[17].

One recent innovation in the grc industry has been the use of a special type of cement in Japan and China. The cement manufactured by Chichibu Cement Company in Japan consists mainly of calcium silicates, $3CaO.SiO_2$ and $2CaO.SiO_2$, calcium aluminosulphate $3CaO.3Al_2O_3.CaSO_4$, calcium sulphate $CaSO_4$ and water quenched blastfurnace slag[18]. On hydration, the major products are calcium silicate hydrates (C−S−H) and ettringite $3CaO.Al_2O_3.3CaSO_4.32H_2O$. Very little, if any, calcium hydroxide is pre-

Table 1.4 Composition of the aqueous phase in contact with various cements.

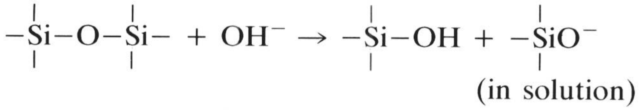
g/litre	Portland cement	60% Portland cement + 40% pfa	60% Portland cement + 40% pozzolana*	High-alumina cement
Ca^{2+}	0.71	0.53	0.51	0.16
Na^+	0.24	0.33	0.28	0.06
K^+	0.57	0.56	0.54	0.30
Alkalinity as $(OH)^-$	1.04	0.95	0.87	0.67
pH	12.07	12.65	12.60	12.05

* Italian pozzolana from Naples.

sent in the hydrated cement and the OH^- ion concentration is low. Similar cements are now made in China for use in the grc industry. The pH value of the pore liquid in the low-alkalinity sulphoaluminate cement paste is around 10.5[19]. A sulphoaluminate cement has been in production in the UK also for a number of years.

1.3 Alkali-resistant glass fibres

Inorganic silicate glasses are inherently reactive towards alkalis; the silicon–oxygen–silicon network which forms the main structural skeleton of silicate glasses is attacked by the hydroxyl ions:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{OH}^- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}^-$$

(in solution)

The addition of ZrO_2, which is present in all commercially available AR glass fibre compositions, reduces the rate of the silicate network breakdown in a substantial way but does not eliminate it altogether. Hence AR glass fibres are not immune to alkali attack from cements. Attempts to improve the alkali resistance of glass fibres are still continuing and it is instructive to discuss some of the factors that are important in the development of a new fibre.

1.3.1 Fiberising considerations

Continuous glass fibres are produced by the rapid mechanical attenuation of a stream of molten glass exuding under gravity through small orifices or tips located in the base of a rectangular electrically heated vessel made of platinum alloy and called a 'bushing'. A bushing is provided with a large