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Glass Fibres for Cement Reinforcement [and Discussion]

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Glass fibres for cement reinforcement

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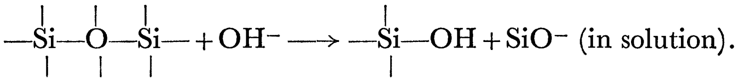
The development of glass fibre compositions having sufficient alkali resistance to provide useful reinforcement in Portland cement and, at the same time, being capable of commercial scale fibrizing, is described. Chemical tests for alkali resistance were used in an initial evaluation of glass compositions, which were then further assessed by strength retention measurements in alkaline solutions and in cement. The different types of tests gave different results in some instances and indicated the need for thorough and wide ranging assessment techniques when evaluating and proving glass fibres for cement reinforcement.

1. Introduction

The commercial potential in the building and construction industry for an inexpensive composite material based on glass fibre reinforcement of cement has been apparent for many years – at least since the early days of glass fibre reinforced plastic composites, and made evident by numerous enquiries addressed to glass fibre manufacturers throughout the 1950s asking if their high strength E-Glass fibres were suitable for the reinforcement of cement. (E-Glass is the accepted nomenclature for a world-standardized borosilicate glass fibre composition used for reinforcement of plastics.)

Unfortunately, these queries had to be answered negatively since the glasses available at that time were subject to severe corrosion and strength loss in the highly alkaline environment of hydrating Portland cement. In a simple view the silicon–oxygen–silicon network which forms the main structural and mechanical skeleton of conventional silicate glasses is broken down according to:



$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\underset{|}{\overset{|}{\mathrm{O}}}-\underset{|}{\overset{|}{\mathrm{Si}}}- + \mathrm{OH}^- \longrightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{SiO}^- \ \text{(in solution)}.$$

Other components of the glass may be leached out, reaction products may be more or less soluble and/or deposited on the glass surface and the nature of the alkali cation can have considerable effect. Thus the rate and nature of surface attack can be very variable, but it is always severe enough to have prevented serious consideration of use of E-Glass fibres in Portland cement.

During the 1950s workers in the U.S.S.R. (e.g. Biryukovitch & Biryukovitch 1961) attempted to avoid or reduce the attack on E-Glass fibres by making composites with the relatively low alkali high alumina cement (h.a.c.). These experiments do not appear to have been successful and our own more recent results indicate that E-Glass fibres are in fact heavily attacked in low alkali cements.

Even if E-Glass/h.a.c. composites had possessed adequate durability their use would have been restricted due to the limitations of high alumina cement. A. J. Majumdar and coworkers at the Building Research Establishment recognized that the real technical and commercial prize lay in a glass fibre of sufficient durability to be usable in the cheaper, much more widely used, and much more alkaline Portland cement.

The addition of zirconia to sodium silicate glass compositions was known to confer alkali resistance in the bulk glass state (see, for example, Dimbleby & Turner 1926). However, fibre behaviour might have differed from that of bulk glass and even experimental scale fibre drawing posed special problems. Majumdar & Ryder (1968), Majumdar (1970) and Larner *et al.* (1976) describe the investigation and evaluation of various alkali resistant glass fibre compositions which led to the selection of a sodium–zirconia–silicate glass, known as G20, which was capable of being produced in experimental quantities in fibre form and which had sufficient durability to function as useful reinforcement in Portland cement.

2. DEVELOPMENT OF A COMMERCIALLY ACCEPTABLE ALKALI RESISTANT GLASS

(*a*) *Requirements of production scale fibrizing*

In the production of continuous filament glass fibre reinforcement on a commercial scale several hundred individual filaments are drawn simultaneously from holes or 'tips' in the base of a platinum–rhodium alloy bushing. Breakage of one single filament rapidly leads to breakdown of the drawing operation for the whole bushing, and operating cost is closely related to uninterrupted running. The temperature of fibre drawing also has a marked effect on bushing life. Thus the requirements of continuous and economic production operation impose severe restrictions on the characteristics of the glass and hence on its chemical composition. In addition the cost and availability of raw materials, the possibility of effluent pollution and the compatability of the melt with available refractory materials must be considered.

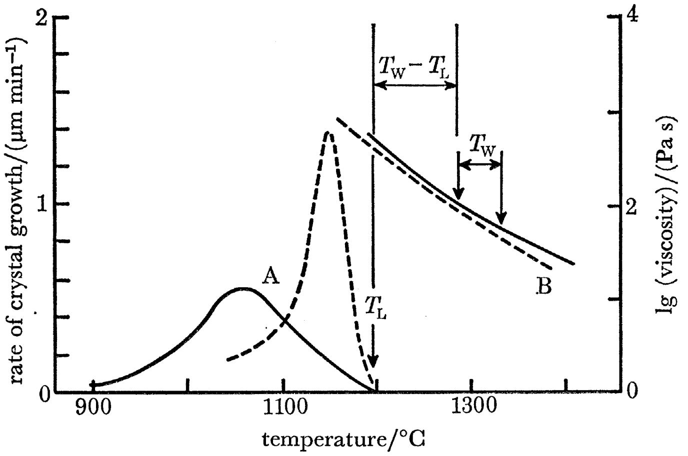


FIGURE 1. Rates of crystal growth and viscosity plotted against temperature. Dotted curves, earlier development glass; full curves, later composition. Curves A, crystal growth rates; curves B, viscosities.

A general description of the requirements for the actual fibre-drawing process has been given by Lowenstein (1973). For economic large scale fibrizing the fibres must be drawn from a glass melt having a viscosity within the narrow range of 50–100 Pa s, in practice the higher viscosity value usually is used. The temperature required to give this required fibrizing viscosity is known as the working temperature T_W. At the same time it is essential that the glass shows no tendency to devitrify or recrystallize during fibrizing. This means that the fibrizing or working temperature (T_W) must exceed the liquidus temperature of the glass (T_L) by an adequate margin: 40 °C is an absolute minimum and generally about 80 °C is preferred as indicated in figure 1.

There are no other absolute restrictions on the actual values of T_L and T_W for the glass but clearly the higher the working temperature the greater the manufacturing costs due, principally, to higher fuel costs and reduced bushing and refractory life. Homogeneous and complete melting of the raw materials is necessary to avoid breakage during fibrization and compositions of high viscosity require higher melting (as well as fibrizing) temperatures, and more prolonged melting, in order to dissolve the raw batch materials. For these reasons manufacturing costs increase quite sharply as T_W exceeds 1300 °C, and 1320 °C is in fact taken as a working maximum limit.

The G20 composition originally developed and evaluated for cement reinforcement at B.R.E. (Majumdar & Ryder 1968) had a working temperature, T_W, of about 1400 °C. Thus, when Pilkington first became involved in a joint research project with B.R.E. in 1968 the target was to further develop the glass composition to give an economically viable full scale production characteristic without in any way detracting from the durability of the G20 composition.

During the pilot stage of the subsequent glass composition development work a further detailed but importance production factor was found to affect process efficiency to a marked degree; this was the actual *rate* at which crystal growth occurred in the glass melt when it was cooled just below its liquidus temperature T_L. This is also illustrated in figure 1. An early development glass (viscosity and crystal growth curves shown dotted) proved quite unacceptable for large scale continuous filament production owing to frequent outbreaks of devitrification, and the composition was slightly modified to give reduced crystal growth rates below the liquidus temperature. The second glass ran satisfactorily although the two liquidus temperatures themselves were identical.

(*b*) *Initial glass composition selection by chemical tests*

The matching of required fibre drawing characteristics with adequate alkali resistance was clearly a complex problem requiring considerable experimental investigation. Many hundreds of potential glass compositions needed to be evaluated in a limited time scale. It was a matter of principle that the ultimate test for a new glass would be satisfactory long term performance in actual composite materials. However, accelerated tests would clearly have to be used to identify compositional trends bestowing an alkali resistance which was also balanced with acceptable forming behaviour, so that a very small number of possible compositions could be selected for pilot plant production trials and thence manufacture of glass reinforced cement (g.r.c.) composites.

There was no established and accepted test for alkali resistance. An I.S.O. 'Recommendation' was in existence for weight loss measurements on small plates of polished glass. This was not judged suitable, yet there was thought to be an advantage in having a test based on some recognized 'Standard' procedure, and eventually a British Standard test for water resistance of crushed grains was modified and adapted for use with alkali. Glass grains passing a 425 μm sieve but held by a 300 μm sieve were autoclaved at 121 °C in contact with various reagents, and the extract solutions analysed for glass components. The chosen reagents were distilled water, saturated calcium hydroxide solution, 0.1 M and 1 M sodium hydroxide solutions. It soon became apparent that little was to be learned from the calcium hydroxide test, the degree of attack being negligible for most glasses except for some leaching of alkali components which also occurred in distilled water (but see comment in § 2 (*c*) and figure 4 below). The quantities of silica extracted by the sodium hydroxide solutions came to be regarded as the most useful, as well as the most consistent, criteria for alkali resistance, particularly for four-component glasses in the Na_2O–CaO–ZrO_2–SiO_2 system.

Examples of this evaluation work are illustrated in figures 2 and 3 where the effects of substituting zirconia for silica and calcia are shown. There was a marked improvement in alkali resistance, in both 1 M and 0.1 M NaOH solutions, on adding zirconia for silica (figure 2) and a less marked but still significant effect on substituting zirconia for calcia.

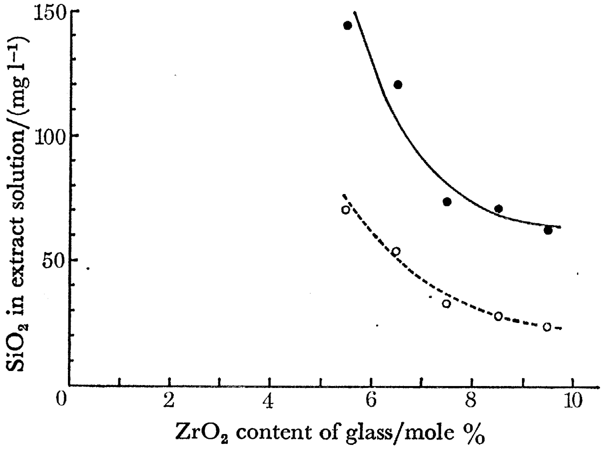


FIGURE 2

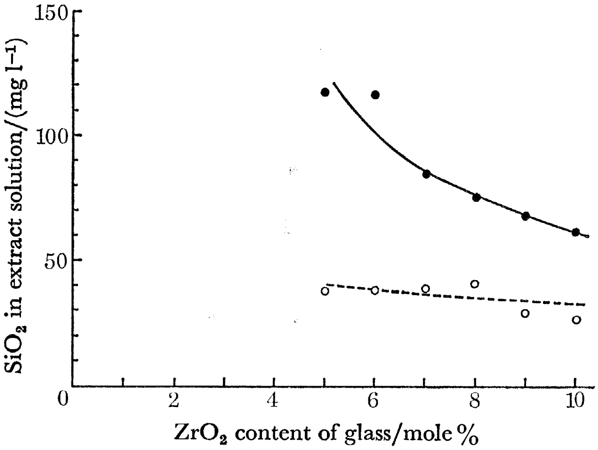


FIGURE 3

FIGURE 2. Effect of replacing SiO_2 by ZrO_2 on alkali-resistance in Na_2O–CaO–ZrO_2–SiO_2 system. Full curve, in 1 M NaOH; dotted curve, in 0.1 M NaOH. Glass series, Na_2O = 17.5 mole %, CaO = 8.0 mole %, SiO_2+ZrO_2 = 74.5 mole %.

FIGURE 3. Effect of replacing CaO by ZrO_2 on alkali resistance in Na_2O–CaO–ZrO_2–SiO_2 system. Full curve, in 1 M NaOH; dotted curve, in 0.1 M NaOH. Glass series, Na_2O = 17.0 mole %, SiO_2 = 68.0 mole %, $CaO+ZrO_2$ = 15.0 mole %.

For more complex glasses, particularly those containing Al_2O and B_2O_3, the presence of other oxides in the solution was also significant. It was rare to detect zirconia in any extract solution.

The extraction tests for alkali resistance were supported by standard gradient furnace tests to determine devitrification characteristics and standard measurements of glass viscosity to determine the suitability of the compositions to meet the fibre drawing requirements discussed in § 2 (*a*) above.

The results of this work indicated that a range of glasses existed in the Na_2O–CaO–ZrO_2–SiO_2 system which met the requirement for both alkali resistance and successful manufacture. In further experiments a number of other oxides were incorporated into the basic four component system including Li_2O, K_2O, MgO, SrO, BaO, ZnO, MnO, Fe_2O_3, B_2O_3, La_2O_3, SnO_2, TiO_2. None of these gave any outstanding improvement in glass properties, and none justified the additional complexity of a fifth component, generally more expensive than the average. Any attempt to replace significant quantities of zirconia with any of these oxides led to a marked reduction in alkali resistance.

Thus the general conclusion from the grain–extraction test work was that zirconia was the dominant oxide conferring alkali resistance, that substituting RO-type oxides (e.g. CaO, MgO) for silica generally improved durability in a zirconia containing glass, and that substituting alkali metal oxides for silica had surprisingly little effect on alkali resistance for alkali oxide concentrations between 13 and 18 mole %.

With zirconia contents in the 9–10 mole % range it was found that silica levels of about 68 mole % gave melt viscosities suitable for fibre drawing at temperatures of 1300 °C or less. From a study of liquidus temperatures in the system Na_2O–CaO–ZrO_2–SiO_2, Na_2O and CaO contents were selected so that the fibrizing requirement for $T_W - T_L$ was met, and in this way a few glass compositions were selected for pilot plant production and further evaluation.

(*c*) *Further evaluation of fibres*

In evaluating fibres for use as reinforcement tensile strength is obviously of prime importance. However, strength retention in a corrosive environment is not solely related to simple resistance to chemical attack. For instance, silicate glasses are attacked more rapidly by hydrofluoric acid than by strong alkali solutions but glass strengths may be increased or retained at a high level after prolonged exposure to HF (Proctor 1962). Also, the strength of brittle solids is known to be dependent on the shape, as well as the size, of stress raising flaws (Proctor 1966, 1971), so that strengths of glass fibres subject to alkali attack may be expected to be related to the precise nature and topography of the corrosion and to the exact conditions under which it occurs.

In the selection and assessment of the G20 fibre composition, Majumdar had confirmed the results of chemical tests by strength measurements on single fibres (Majumdar & Ryder 1968). Studies of the strengths of single fibres exposed to various alkaline solutions, using both direct tension and elastica bending test techniques, have also been used in this work and have provided valuable information. However, for reasons of economy and convenience during production, handling and incorporation, glass fibre composites are reinforced by multifilament strands rather than by discrete single filaments. The load bearing capability of these strands, rather than the actual strength of single filaments, is probably the overriding parameter in determining the strength retention of cement composites and is governed by the total retained cross section of the strand as well as by the individual filament strengths.

For these reasons it was decided to continue the evaluation of glass fibre compositions by measuring the load carrying capacity of commercial scale, multifilament strands after exposure to various hot alkali solutions. Such tests were also thought to be more reproducible and representative than tests on single filaments.

One of the possible pitfalls due to the differences between testing for chemical stability in solution by silica extraction measurements, and testing for strength retention, is illustrated in figure 4. Figure 4 (*a*) shows the amounts of silica extracted from two different zirconia containing glasses when immersed in various media. From these results alone we would have concluded that the saturated calcium hydroxide solution was little more aggressive than water and markedly less aggressive than 0.1 M NaOH (as mentioned in § 2 (*b*) above). Conversely the strand strength results given in figure 4 (*b*) clearly indicate at least as great an effect on strength in $Ca(OH)_2$ as in 0.1 M NaOH, and markedly more attack than in water.

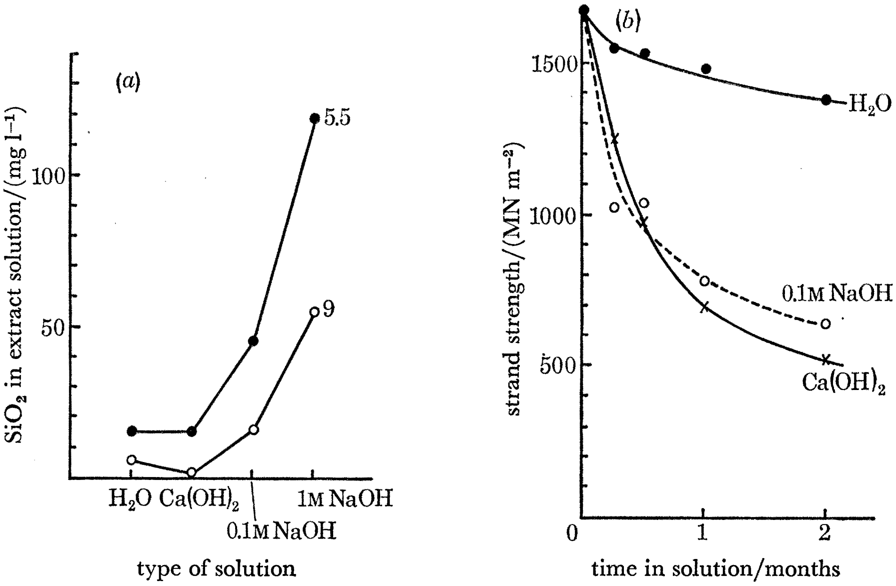


FIGURE 4. Comparison of silica extraction test and strand strength tests in water, 0.1 M NaOH, and Ca(OH)$_2$ solutions. (*a*) Silica extraction results for two glasses containing 5.5 mole %, and 9 mole %, ZrO$_2$. (*b*) Strand strength results for 9 mole % ZrO$_2$ glass in water, 0.1 M NaOH and Ca(OH)$_2$ solutions at 50 °C.

The silica extraction tests had indicated a very great difference in behaviour between high zirconia alkali resistant glasses and the borosilicate E-Glass type of composition. This was amply confirmed by the solution strength behaviour but differences between behaviour in chemical tests and in strength tests again became evident when more detailed comparisons were made between different alkali resistant glass compositions. Figure 5, giving results of strand in solution tests at 80 °C, illustrates a trend which was not apparent from the silica extraction measurements. Glass B had a higher zirconia content than A but contained

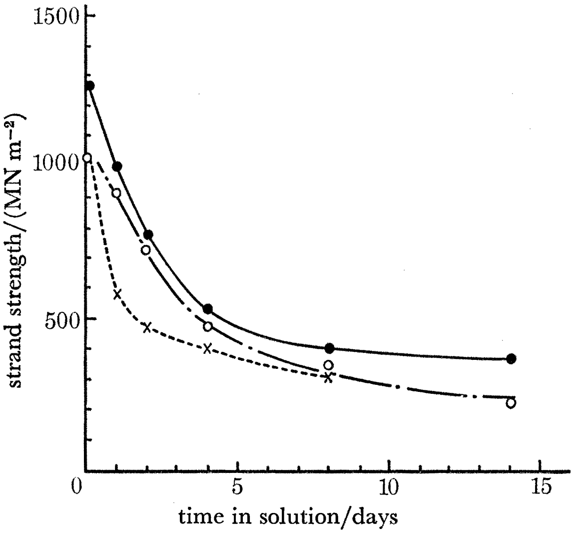


FIGURE 5. Strengths of high zirconia glasses in solution and beneath lime slurry. Full curve, glass A in solution; chain dashed curve, glass B in solution; dotted curve, glass B beneath lime slurry. Solution = 0.1 M NaOH over excess lime slurry at 80 °C. Glass A = 9.0 ZrO$_2$, 6.5 CaO, 15.5 Na$_2$O, 69.0 SiO$_2$ (mole %). Glass B = 11.3 ZrO$_2$, 20.5 Na$_2$O, 2.5 P$_2$O$_5$, 2.0 B$_2$O$_3$, 63.0 SiO$_2$ (mole %).

additions of phosphorus and boron in order to reduce the fibrizing temperature and suppress devitrification. These additions have clearly adversely affected the strength retention behaviour of composition B.

One of the difficulties of strength-in-solution tests is also illustrated in figure 5. The dotted curve shows the strength of glass B strand when placed in the bottom of the same container (and in the same solution) and in direct contact with the excess lime slurry which was used to provide a small $Ca(OH)_2$ content in the solution. The different physical conditions led to a more rapid initial fall in fibre strength and this susceptibility to differences in the precise physical as well as chemical conditions appears to be a characteristic of solution testing.

Scanning electron microscopy has also shown up marked differences in the mode of attack and the nature of reaction products in different solutions and in cement.

Solution tests are still used to provide a background understanding of the nature of alkaline attack and to compare different glass compositions, but because of difficulties and differences similar to those just discussed it became apparent that there was a need to assess glass compositions in a test which was even more directly representative of actual conditions in a real cement composite. Increasingly more and more reliance came to be placed on the results of a test, devised earlier, in which measurements were made of the strength of commercial glass strands embedded in a small block of set cement paste.

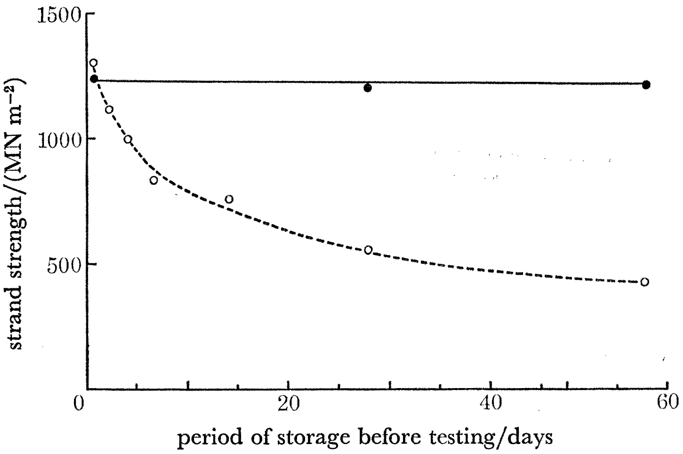


FIGURE 6

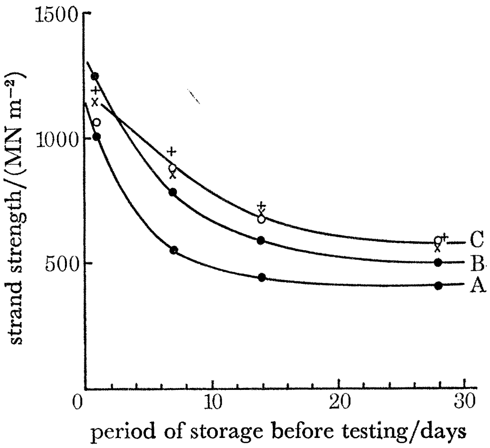


FIGURE 7

FIGURE 6. Strengths of E-Glass and A.R. glass fibres in set Portland cement, maintained wet, at 20 °C. Full curve, AR glass; dotted curve, E glass.

FIGURE 7. Strengths of different zirconia glasses in set Portland cement, maintained wet, at 50 °C. A, 5 mole % ZrO_2 glass; B, 7 mole % ZrO_2 glass; C, 3 glasses, O = 9.0, + = 9.5 and × = 10.0 mole % ZrO_2.

Conventional E-Glass fibres lose their strength extremely rapidly in a Portland cement environment at room temperature and marked losses may be measured over acceptable experimental time scales of a few days. With suitable alkali resistant fibres however strength changes take place extremely slowly (figure 6). In order to accelerate attack and obtain results in acceptable experimental times the cement blocks have been immersed in water and heated at various temperatures between normal ambient and about 100 °C. It was realized that such acceleration techniques would introduce uncertainties since they affect both the morphology of the cement (Copeland & Kantro 1968) and the nature of the glass–cement interaction.

However, temperatures of about 50–60 °C in particular seem to have provided an acceptable compromise in yielding realistic evaluation in practicable testing periods of a few months.

Measurements of strand strengths in cement showed that the *general trend* of increasing alkali resistance with increasing zirconia content in the Na_2O–CaO–ZrO_2–SiO_2 system (evident from the silica extraction tests) did in fact confer increased strength retention in an actual cement environment. As shown in figure 7 a clear trend of higher strength with higher zirconia content was observed up to about the 9 mole % level, with little or no improvement thereafter. The results of the solution tests, which showed that the introduction of P_2O_5 and B_2O_3 could negate the effect of high zirconia contents, were also confirmed by strand in cement tests.

In investigations of a slightly different nature the strand-in-cement test was used to compare the relative aggressiveness of high alumina and supersulphate cements with Portland cement. Measurements of the pH of high water cement ratio slurries of these cements were made over a period of months – while they were kept stirred and fluid. There were some variations in pH values with time but approximate average pHs are given in table 1.

TABLE 1. ALKALINITIES OF DIFFERENT CEMENTS

cement type	average pH over 6-month period
rapid hardening Portland	12.9–13
high alumina (h.a.c.)	12.2–12.4 (peak 12.6)
supersulphate (s.s.c.)	11.9–12 (peak 12.6)

The results of strength measurements on strands of Cem-FIL A.R. glass in these cements are shown in figure 8.

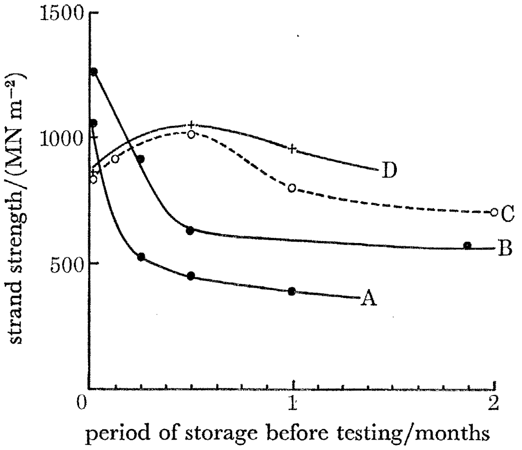


FIGURE 8. Strand strengths in h.a.c., s.s.c. and Portland cement, maintained wet, at 50 °C. A, E-Glass in supersulphate cement; B, A.R. glass in Portland cement; C, A.R. glass in high alumina cement; D, A.R. glass in supersulphate cement.

At the start of the experiment the strengths of the h.a.c. and s.s.c. specimens were lower than the Portland cement specimens owing to abrasion of the fibres by the coarser and harder cement grains. After ageing, however, the strengths of the strands in h.a.c. and s.s.c. were noticeably higher than in Portland cement – in line with the pH measurements. Also shown in figure 8 are results obtained with E-Glass strands in s.s.c. which is the least alkaline of the cements. These samples are considerably weaker than the A.R. glass in Portland cement and perhaps explain the apparent failure of the early E-Glass/h.a.c. experiments referred to in § 1 of this paper.

3. Summary and conclusions

It was realized from the outset that the final evaluation of the glass would have to be based on both its suitability in pilot scale production tests and its long term strength retention in g.r.c. composite panels exposed to real weather. However, an initial coarse screening of possible compositions was based on chemical alkali resistance tests, backed by standard glass-maker's measurements of viscosity and devitrification characteristics.

As work proceeded, more relevant tests were introduced based on the strength retention of a typical reinforcing strand of fibres in various conditions which increasingly approached those in an actual cement composite. The conditions could never be made truly representative, however, since a significant time acceleration factor was required in order to obtain results within a reasonable working period.

The guiding principle throughout the composition development work was that a suitable glass should perform well in *all* types of test and little reliance was placed on a good result in only one or two tests. With the experience of several years research we remain convinced of the validity of this principle, particularly in view of the artificial acceleration conditions which have to be used. Increasingly, however, the most closely representative test – i.e. strand strength retention in a cement block – has come to be regarded with greater and greater confidence as the most effective assessment, short of final testing in real composites. Indeed, good correlation has now been obtained between the results of strand strength measurements in cement and strength retention in composites.

It has become clear that purely chemical tests, such as silica extraction or weight loss measurements, while effective in distinguising between completely non-alkali resistant glass (such as E-Glass) and a reasonably alkali resistant material, frequently could not distinguish between different grades of alkali resistant glass with sufficient reliability to decide on their suitability for use as reinforcement in cement composites. On occasion they have even provided anomalous or incorrect information depending on the precise conditions of the test.

The extraction tests revealed that zirconia was the main alkali resistance conferring component in silicate glasses, and this was confirmed by the more direct strength tests, both in solution and in cement. However, these latter tests also revealed that the requirements for strength retention were more complex than simply having a high level of zirconia – it had to be part of a balanced and appropriate glass system. In particular, additions of phosphorus and boron oxide could reduce the effectiveness of the zirconia.

Tests with less alkaline cements such as high alumina and supersulphate cements have confirmed that an alkali resistant glass is needed with these cements in order to achieve effective fibre reinforcement and give good composite properties.

Industrial research and development is very much a team effort. The authors are indebted to many colleagues whose work and results have contributed to this paper.

The authors also acknowledge the permission of the Directors of Pilkington Brothers Limited and Mr A. S. Robinson, Director of Group Research and Development, to publish this paper.

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Discussion

A. R. Ubbelohde, F.R.S. (*Imperial College, London, S.W.* 7). When attack by chemical reagents is used to monitor resistance of a glass to alkali, does this accelerated erosion extract any of the zirconia into the solvent liquid? If not, this might give a pointer to how zirconium helps to stabilize a glass against alkali, by binding the network structure more tightly together.

B. A. Proctor. Generally we are not able to detect zirconia in extract solutions above our detection sensitivity limit of about $1/10^6$, which should be compared with silica extractions ranging from about 20 to $400/10^6$ depending on the alkali resistance of the glass and on the strength of the NaOH solution used. In rare cases we have seen zirconia levels up to $5/10^6$ and when this has happened it has usually been associated with the testing of a glass of very poor alkali resistance.

The absence of zirconia in extract solutions may not necessarily be a guide to its role in stabilizing glass compositions since we also fail to detect significant quantities of calcia in extracts from calcia containing glasses which are quite heavily attacked and give large silica extracts.

G. Manfre (*Centro Ricerche Fiat, Orbassano, Italy*). It is already well known that zirconium glass fibres are alkali resistant to enable practical and useful composite, due mainly to Pilkington's research and development. Concerning the cement as a matrix it is not known yet the reason of the alkali resistance of the zirconium fibres. Can the author give some information on this point in order to make a comparison with the steel fibre reinforced cement?

B. A. Proctor. The solubility of silica is strongly pH dependent and it is increasingly attacked above pH 9, whereas zirconia is insoluble in acids, alkalis and water generally. If it is *assumed* that the stability or solubility of a complex glass is related to the sum of the stabilities of its constituent oxides then this may be one explanation for the improved stability of zirconia glasses. Another part of the explanation may lie in the insolubility of reaction products: as the glass is attacked, silica is extracted and a layer of undissolved zirconia or zirconium silicate is left on the glass surface to serve as a diffusion barrier and reduce the rate of further attack.

The situation is almost the inverse of that with steel fibres, where the presence of the alkaline cement is needed to prevent rusting of the fibres, and cracking or exposure of fresh surfaces leads to corrosion of the reinforcement. With g.r.c. the reaction is between the glass and the cement; cracking and the exposure of fresh surfaces do not accelerate these interactions.