

# Properties of high-alumina cement reinforced with alkali resistant glass fibres

A. J. MAJUMDAR, B. SINGH, M. A. ALI

*Building Research Establishment, Building Research Station, Garston, Watford, UK*

The changes in the mechanical properties of cement composites made from high-alumina cement and Cem-FIL AR-glass fibres kept in three different environments up to 10 years are described. While the flexural and impact properties of the composite remained largely unaffected with time in a relatively dry atmosphere, in wet conditions a reduction in strength takes place. In natural weather the 10 year modulus of rupture and impact strength values are  $22.8 \text{ MN m}^{-2}$  and  $6.7 \text{ KJ m}^{-2}$ , respectively, corresponding to the 28 day values of  $41.2 \text{ MN m}^{-2}$  and  $22.8 \text{ KJ m}^{-2}$ . These values are significantly better than the corresponding results obtained with Portland cement composites made from Cem-FIL fibres. High-alumina cement composites reinforced by E-glass fibre lose a very large proportion of their flexural and impact strength under wet conditions. The strength reduction with time observed for glass fibre reinforced high-alumina cement composites can be related to two sources: (a) the reduction in the strength of the glass fibre due to chemical corrosion and (b) "conversion" of the matrix. The latter has greater influence on those composite properties that are matrix controlled such as the Young's modulus whereas any significant reduction in fibre tensile strength is reflected in a corresponding loss in composite tensile and bending strength. Matrix conversion may also influence the fibre-matrix bond.

## 1. Introduction

The use of high-alumina cement (HAC) is severely proscribed in the UK since the collapse of a number of buildings a few years ago was assessed as being the result of the loss of strength of HAC concrete with time due to conversion of one hydrate phase to another [1, 2]. HAC is well-known for its rapid hardening and it is less alkaline than Portland cement. Taking advantage of these properties E-glass fibre reinforced HAC had been used in the past [3]. A detailed study of such a composite was first made by Biryukovich and co-workers [4]. In a later paper Grimer and Ali [5] pointed out that the strength of the composites made from HAC and E-glass was reduced substantially with time when kept in a continuously wet condition. Subsequent contributions on this subject have come from Chan and Patterson [6] and Allen [7].

With the development of alkali-resistant glass fibres [8, 9] for cement reinforcement in the late sixties a programme of work was undertaken to

evaluate the performance of these fibres in different types of cement including HAC. Ten-year results on the properties of HAC composites reinforced with AR-glass fibres kept in various environments have recently become available. These are published here for theoretical interest and are compared with the results of the other studies mentioned above.

## 2. Materials and fabrication

The high-alumina cement used in this study was Ciment Fondu. Two batches were used and these were supplied by the same UK manufacturer. The properties of the cements are given in Tables IA and B.

The AR-glass fibre used was the first prototype of the Cem-FIL fibre developed by Fibreglass (UK) Ltd, a subsidiary of Pilkington Brothers. Both AR and E-glass fibres were supplied in the form of continuous rovings. In the case of the AR-fibre each strand consisted of 204 filaments having

TABLE IA Physical properties of cements

Cement code number	Setting time		Specific surface (cm <sup>2</sup> g <sup>-1</sup> )	Density (g cm <sup>-3</sup> )	Compressive strength (MN m <sup>-2</sup> ) 1:3 cement mortar			
	Initial	Final			1 day	3 days	7 days	28 days
	685	4 h-25 min			5 h-0.5 min	3010	-	66.4
759	3 h-45 min	5 h-0 min	3355	3.23	66.6	72.0	77.8	84.3

diameters in the range 13 to 15  $\mu\text{m}$  whereas E-glass filaments were 11 to 13  $\mu\text{m}$  in diameter and 136 fibres formed a strand. Both types of glass fibres had a polyvinyl acetate based "size" on them.

In fabricating glass reinforced cement (grc) composite boards the spray-suction method developed at BRE [10] was employed. In this method, cement slurry having a high water/cement ratio and glass fibre rovings chopped *in situ* to the desired lengths are sprayed simultaneously onto a paper covered, perforated metal face of a suction mould. Spraying is continued until a thickness of approximately 10 mm is attained. The top surface is then levelled off and the excess water extracted by the application of suction to leave a final water/cement ratio of  $\sim 0.35$ . Immediately after this the sheet is demoulded.

The glass contents of the grc boards were calculated from the weights of the glass fibre consumed in fabrication and the weights of the boards measured soon after demoulding. The glass content is expressed as a percentage by weight of the freshly prepared board. Nominally a 5 wt% glass addition was aimed at.

### 3. Experimental procedure

#### 3.1. Curing conditions

Immediately after the grc boards were demoulded onto a rigid plywood board, they were cut into 150 mm  $\times$  1 m strips with a knife, covered with polythene sheets and stored under laboratory conditions for 7 days. Sometime during this storage, when the boards had hardened sufficiently, they were sawn into small 150 mm  $\times$  50 mm specimens and numbered. After 7 days storage in the moist environment, the numbered specimens were randomly selected and were placed under different

curing conditions. In the case of the board made with the AR-fibre, a portion of the board measuring 1 m  $\times$  1 m was left uncut and this was placed in a 90% humidity room for storage subsequent to the initial 7 day moist curing. Two composite boards incorporating AR-fibres ( $\sim 5$  wt%) were also prepared where the HAC matrix was modified by the addition of pulverized fuel ash (pfa) and butadiene styrene dispersions, respectively. Boards made from E-glass fibres were placed in water 28 days after they were manufactured.

In general, three storage conditions were used: under water at 18 to 20 $^{\circ}$  C, in air of 40% r.h. at 18 to 20 $^{\circ}$  C and natural weathering. Specimens subjected to natural weathering were kept in a horizontal position well above the ground on a wooden frame placed on the exposure site at Garston. Also, a few 1 m  $\times$  1 m sheets were exposed to weather as vertical wall and inclined roof panels on the same site.

Some composite specimens made from HAC and AR-glass fibres were also exposed to temperatures slightly higher than the ambient. For dry storage, specimens were placed in an oven maintained at 35 $^{\circ}$  C. For storage under water, specimens were placed in glass jars partially filled with water and the jars were kept in different ovens maintained at 25, 35 and 50 $^{\circ}$  C. For the curing at 60 $^{\circ}$  C the water filled glass jars containing the specimens were stored in a water tank maintained at this temperature.

#### 3.2. Testing

For each type of grc stored under the environmental conditions mentioned above, tests were carried out to determine the flexural strength, the tensile strength and the resistance to impact. The

TABLE IB Chemical properties of cements

Cement code number	Percentage by weight															
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe (metal)	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	CO <sub>2</sub>	C	H <sub>2</sub> O	SO <sub>3</sub>
685	4.30	32.28	10.98	5.28	0.18	1.90	0.09	0.11	37.84	0.41	0.09	0.16	0.14	0.03	0.29	-
759	3.89	38.76	12.56	3.06	-	2.02	0.035	0.12	37.95	0.54	0.07	0.12	-	-	-	0.14

flexural properties in four-point bend and the tensile strength were determined using an Instron testing machine whereas for measuring the impact strength of the material an Izod-type instrument having a capacity of 12 J was employed. The details of the testing procedures have already been described [11]. It will be appreciated that the measured strength values of materials such as grc are dependent on the strain rate used. Some idea of the magnitude of this effect can be obtained from the following figures. A change in the cross-head speed on the Instron from 20 to 2.0 to 0.2 mm min<sup>-1</sup> gave flexural strength values (for nominally identical grc specimens) of 34.8, 30.4 and 29.6 MN m<sup>-2</sup>, respectively. Throughout the present study, strength measurements have been carried out using a cross-head speed of 2.0 mm min<sup>-1</sup>.

The stress-strain behaviour of grc composites under tension was recorded using the Instron machine and having an extensometer of 50 mm gauge length attached to 50 mm × 150 mm specimens. The specimens were strained at 2 mm min<sup>-1</sup> and the output from the extensometer was fed to the x-y plotter via a pre-amplifier unit. The Young's modulus values were derived from the resulting plots. As in the case of bend tests, the limit of proportionality (LOP) values were taken from points in the stress-strain graphs that marked the deviation from linearity.

### 3.3. Bond strength

The strength of the interfacial bond between the cementitious matrix and the glass fibre strand was computed from the results of pull-out tests carried out in accordance with the procedure used in this laboratory previously [12]. For this calculation, it was necessary to assume a fixed geometry, that of

a type 0.9 mm wide and 0.06 mm thick, for the glass fibre strand. The fibre embedment lengths chosen in the present study were 4 and 6 mm and the water/cement ratio was 0.35. After casting, the specimens were placed in a damp environment for 24 h, then demoulded and kept in air for six more days at 18°C and 90% r.h. Following this, one set of specimens was placed in water at 18°C and tested after 3 months.

### 3.4. Characterization of phases

Some work was also done on the identification of cement hydrate phases present in several composite specimens. In particular, the specimens cured at higher than ambient temperatures and those tested after 10 years were examined by X-ray diffraction procedures employing a Guinier focussing camera.

## 4. Results

The results of the present investigation are presented in Figs 1 to 5. The experimental strength values represent an average of at least six measurements in most cases and the variability in the results has been expressed as 90% confidence limits calculated in accordance with the standard procedure. These limits are shown as bars at each experimental point in the graphs. Where single points are shown in the figures, they represent an average of two determinations. In the absence of any knowledge of the theoretical nature of these graphs the bars have not been joined to give durability plots. Nevertheless the trends are apparent in most cases.

Figs 1 to 4 are self-explanatory and will not be described here. In Fig. 5 average stress-strain plots of several HAC/grc specimens subjected to a direct tensile test are shown. The specimens were kept

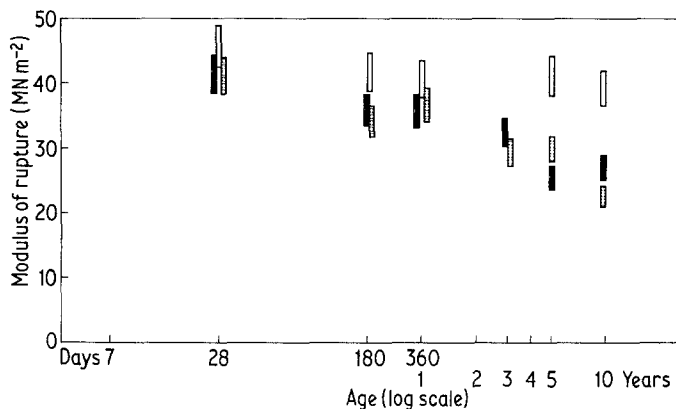


Figure 1 Modulus of rupture of grc made from HAC and AR-glass fibres. In air at 20°C, 40% r.h. □, in water at 20°C ■ and under natural weathering ▨.

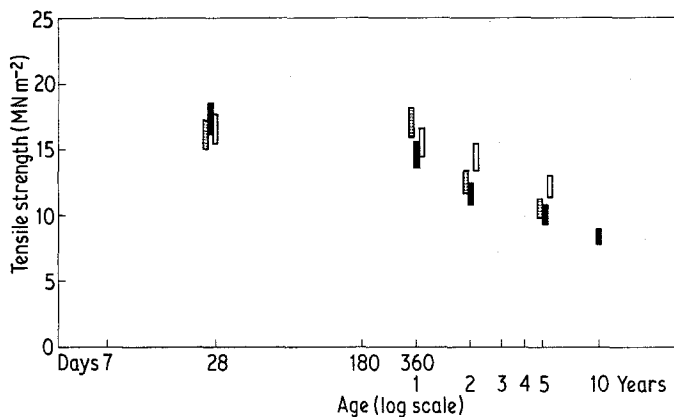


Figure 2 Tensile strength of grc made from HAC and AR-glass fibres stored in air 40% r.h. □, water at 20° C ■ and under natural weathering ◻.

immersed in water for specified periods of time before testing.

The grc board made from high-alumina cement and AR-glass fibre and stored in air of 90% r.h. gave the following results after 18 months. For specimens selected from areas that include the cut edges the modulus of rupture (MOR) and impact strength values were  $43.4 \text{ MN m}^{-2}$  and  $23.5 \text{ KJ m}^{-2}$ , respectively, with coefficients of variation of 4.7 and 21.5%. When the specimens were selected from the central portion of the board the MOR and impact strength values were  $44.4 \text{ MN m}^{-2}$  and  $23.0 \text{ KJ m}^{-2}$ , respectively, with coefficients of variation of 9.4 and 13.2%. The MOR values are slightly better than those of water stored specimens (Fig. 1) of similar age but at 10 years this difference was no longer present.

The strength values of cement composites reinforced with AR-glass fibres and cured at higher than ambient temperatures are given in Table II. It will be noted that at 35° C, specimens were kept both in air and under water prior to testing. The strength properties of the composites made from HAC modified by pulverized fuel ash (pfa) and a

polymer dispersion are compared in Table III with those of the grc material prepared from the cement alone.

In Table IV the tensile properties of HAC reinforced by E-glass and AR-glass fibres, respectively, are compared. The specimen coupons were cured for 51 months in the case of E-glass and 55 months for AR-glass. Unfortunately the E-glass reinforced material was not exposed to natural weather. The strength results obtained with specimens cut from the 1 m x 1 m AR-glass/HAC vertical wall and inclined roof panels after 5 years of weathering at Garston were very similar to the values listed in Tables III and IV for AR-glass fibre reinforced HAC. Only the impact strength of the larger sheets was found to be somewhat better at  $17 \text{ KJ m}^{-2}$  than the corresponding coupon values ( $15 \text{ KJ m}^{-2}$ ).

As in the previous work [12] the scatter in the bond strength results was large. For the AR-glass fibre strands, the average of five determinations at each age gave bond strength values of 2.5 to  $3 \text{ MN m}^{-2}$  at 7 days and 3 to  $4 \text{ MN m}^{-2}$  after 90 days in water. Using a different technique Maries

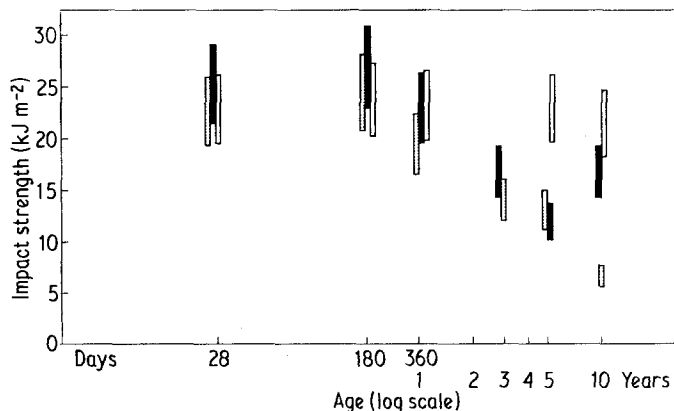


Figure 3 Impact strength of grc made from HAC and AR-glass fibres stored in air 40% r.h. □, water at 20° C ■ and under natural weathering ◻.

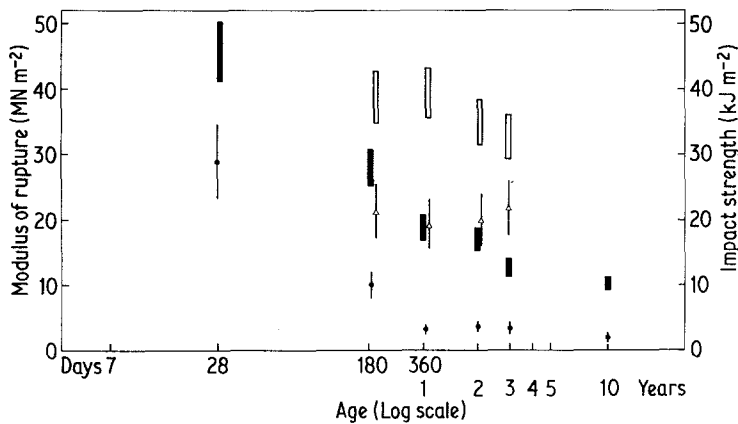


Figure 4 Modulus of rupture and impact strength of grc made from HAC and E-glass fibres, MOR air stored  $\square$ , MOR water stored  $\blacksquare$ , impact strength, air stored  $\triangle$  and impact strength water stored  $\blacktriangle$ .

and Tseung [13] reported a value of  $\sim 2 \text{ MN m}^{-2}$  for E-glass fibres in HAC.

## 5. Discussion

### 5.1. Strength durability

The results presented in Figs 1, 3 and 4 and Table IV show quite clearly that for HAC composites stored under water, the AR-glass fibre provides a more durable reinforcement than E-glass fibres. In assessing durability it has been assumed that the retention of the mechanical strength of the composite material over a period of time provides a suitable measure. For water stored samples the present results on the E-glass fibre reinforced material shown in Fig. 4 tend to confirm the previous findings of Grimer and Ali [5]. The results obtained with samples kept in dry indoor conditions (40% r.h., 20°C) are considerably better (from the durability point of view) for both E-glass and AR-glass reinforced composites. In both cases no major reduction in either flexural or impact strength has been observed (Table IV, Figs 1, 3 and 4), but the performance

of the AR-glass fibre has been better. Also it should be pointed out that the stiffness of the composite containing E-glass and cured for 51 months in a relatively dry environment was found to be unusually low, about a third of that obtained with AR-glass. The reason for this is not clear.

The present results obtained with boards made from HAC and E-glass fibres are somewhat different from the data given by Grimer and Ali [5] in two respects. Firstly, the initial strengths of the boards of the present study are appreciably higher than those in the previous study and secondly it appears that in air storage the earlier boards had an inferior durability. Grimer and Ali [5] used a fibre from a source different from that of the present study and there are minor differences in the two fibres regarding the diameter of individual filaments, the number of filaments per strand, the coating applied on the fibre etc. The relative humidities of air storage and the duration of initial curing are also different for the two studies. Grimer and Ali used 60% r.h. whereas in the present study air of 40% r.h. has been used. Whether these factors can account for the differences in the results obtained with composites made from E-glass fibres remain open to question.

Unfortunately, the results of the present study cannot be compared directly to those of Chan and Patterson [6]. The fibre content used by these authors was two and a half times that of the present work and therefore the progressive loss in strength (if any) would be expected to commence at a date much later than that observed here, since the strength durability of grc is a function of the glass content of the composite [5]. In the present study, the most severe condition of exposure which has been tried for the composite specimens over a long period is that of continuous immersion

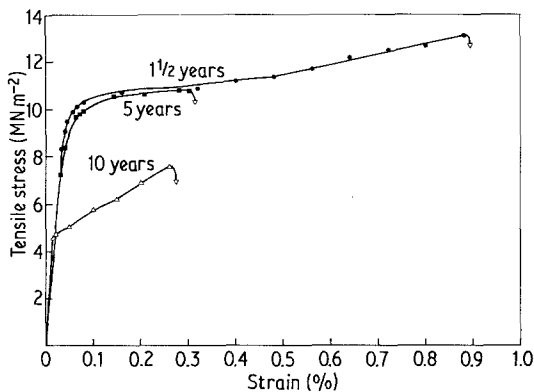


Figure 5 Stress-strain diagram of grc made from HAC and AR-glass fibres, water stored samples.

TABLE II Strength of grc made from HAC containing 4.7 wt% AR-glass fibres at various temperatures

Property	Temperature (°C)	Curing condition	Strength (days)*					
			7	15	28	90	180	360
MOR (MN m <sup>-2</sup> )	18	Under water	35	33	35	32	30	26
	25	Under water	—	—	34	30	29	25
	35	Under water	—	32	34	29	25	25
	50	Under water	—	29	28	24	20	—
	60	Under water	—	26	27	21	—	—
	35	In air	—	40	39	36	33	28
LOP in bending (MN m <sup>-2</sup> )	18	Under water	14	14	15	16	16	15
	25	Under water	—	—	16	16	15	15
	35	Under water	—	16	14	15	14	13
	50	Under water	—	14	14	11	11	—
	60	Under water	—	12	12	11	—	—
	35	In air	—	12	11	11	9	8
Impact strength (KJ m <sup>-2</sup> )	18	Under water	48	41	38	37	35	21
	25	Under water	—	—	42	36	20	17
	35	Under water	—	38	42	31	21	19
	50	Under water	—	26	19	14	14	—
	60	Under water	—	19	18	16	—	—
	35	In air	—	39	46	36	32	33

\*Includes 7 days initial curing (see Section 3.1).

in water. A very marked deterioration in the properties of HAC composites made from E-glass fibres has been observed in this environment (Fig. 4). Such a curing condition was not included in the testing programme of Chan and Patterson. From the results given in this report, no loss in the strength of the composites prepared by Chan and Patterson would be expected during a curing regime of 18 months in air.

The results obtained with specimens cut from the board made from AR-glass fibre and stored in air of 90% r.h. at ambient temperature indicate that under these conditions the mechanical proper-

ties of the board are reasonably uniform over the entire area of the board and that the storage of small specimens (standard 50 mm × 150 mm) in air of high humidity does not induce a more accelerated form of corrosion due to the presence of cut edges. The slightly higher strength values obtained after 18 months at the higher humidity relative to the 40% r.h. normally used for air storage (see Fig. 1) may be due to a larger proportion of the cement hydrating at the higher humidity. As expected longer exposures to 90% r.h. has brought grc strength to that obtained with specimens immersed in water.

TABLE III Properties of grc composites made from AR-glass fibres and HAC with some matrix modifications

Matrix	Property	Age and storage conditions								
		28 days			1 year			5 years		
		Air	Water	Weather	Air	Water	Weather	Air	Water	Weather
HAC	MOR (MN m <sup>-2</sup> )	46	41	41	41	36	37	41	26	30
	LOP (MN m <sup>-2</sup> )	16	14	13	14	16	15	13	16	13
	IS (KJ m <sup>-2</sup> )	23	25	23	23	23	19	23	12	13
HAC + 40% pfa (pfa from Castle Donnington)	MOR (MN m <sup>-2</sup> )	—	23	29	25	19	25	—	21	26
	LOP (MN m <sup>-2</sup> )	—	—	—	—	—	—	—	9	9
	IS (KJ m <sup>-2</sup> )	—	15	21	23	12	20	—	17	20
HAC + Revinex (Revinex-5% solids of the weight of OPC)	MOR (MN m <sup>-2</sup> )	27	—	—	31	34	32	31	26	32
	LOP (MN m <sup>-2</sup> )	—	—	—	—	—	—	11	21	17
	IS (KJ m <sup>-2</sup> )	55	—	—	45	49	60	51	14	31

TABLE IV Long-term tensile properties of HAC composites

Composite description	Age	Property		Storage condition		
				Air 40% r.h.	Water at 20° C	Weathering
E-glass reinforced HAC Fibre content 6.0 wt % and fibre length 43 mm	51 months	LOP	(MN m <sup>-2</sup> )	—	4.2	—
		UTS	(MN m <sup>-2</sup> )	13.7	4.2	—
		Strain at LOP	(μ-strain)	—	200	—
		Strain at failure	(μ-strain)	12 000	200	—
		Young's modulus	(GN m <sup>-2</sup> )	—	21.0	—
AR-glass reinforced HAC Fibre content 4.8 wt % and fibre length 34 mm	55 months	LOP	(MN m <sup>-2</sup> )	—	6.9	5.2
		UTS	(MN m <sup>-2</sup> )	12.3	10.1	10.6
		Strain at LOP	(μ-strain)	100	260	176
		Strain at failure	(μ-strain)	10 800	3000	8900
		Young's modulus	(GN m <sup>-2</sup> )	26.7	27.1	29.4
AR-glass reinforced HAC Fibre content 4.8 wt % and fibre length 34 mm	10 years	LOP	(MN m <sup>-2</sup> )	—	4.1	—
		UTS	(MN m <sup>-2</sup> )	—	8.0	—
		Strain at LOP	(μ-strain)	—	136	—
		Strain at failure	(μ-strain)	—	2200	—
		Young's modulus	(GN m <sup>-2</sup> )	—	30.1	—

Results obtained with samples weathered outside show (Figs 1 and 3) that the strength of HAC reinforced with AR-glass fibres is reduced significantly with age and at 10 years the values are poorer than those of composites kept continuously under water. Weathered samples had, of course, undergone major fluctuations in temperature over the 10 year period. It is known that when placed in an alkaline matrix the strength of AR-glass fibres is significantly reduced at elevated temperatures say, 50° C [14]. For HAC even a much lower increase in temperature over the ambient is considered to have a pronounced effect on its strength. Freeze-thaw tests (BS4036: 1966) carried out on 2 year old samples, however, showed only 10% reduction in strength after 25 cycles between - 20° C and + 20° C.

## 5.2. Effect of cement hydration

Some idea of the effect of a rise in temperature on the properties of HAC composites can be obtained from the data given in Table II. In the presence of water, the strength durability of the material is seen to be very adversely affected by a rise in the temperature of the sample. Even when stored in the laboratory air at 35° C ( a temperature likely to be reached on the surface of the specimen in the South-East of England in the summer), there is a significant loss in strength with age, which is

more pronounced than at ambient temperatures (Figs 1 and 3).

The loss in strength of HAC composites subject to temperature fluctuations cannot be discussed without pointing out the pronounced effects that high alumina cement pastes are known to exhibit when temperature and some other fabrication variables are altered. The details of the hydration processes can be found in the work of Robson [15]. It is only necessary to mention here that mature high alumina cement pastes consist principally of a mixture of calcium aluminate hydrates, alumina gel and/or gibbsite and sometimes an amorphous material containing iron. Contrasted to Portland cements, very little free Ca(OH)<sub>2</sub> is present. The temperature sensitivity of the strength of HAC paste derives principally from the effect that a change in the curing temperature has on the stability of various calcium aluminate hydrates.

It is accepted by most researchers that the loss in strength of HAC at temperatures slightly higher than the ambient is related to the "conversion" of other calcium aluminate hydrates to the cubic C<sub>3</sub>AH<sub>6</sub>.<sup>\*</sup> Midgley [16, 17] has carried out extensive investigations on the effects of temperature and water/cement ratios on this conversion and tried to relate these with the loss in strength suffered by HAC pastes. In their study on the hydration of CA prepared as a paste having a

\*Cement chemistry nomenclature: C = CaO, A = Al<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O. It will be understood that some Fe will be present in place of Al in the hydrates.

water/solid ratio of 0.15, Ramachandran and Feldman [18] arrived at conclusions which are, in some respects, different from those of Midgley but even in this study the fall in strength of the paste at 20°C was thought to be mainly due to the conversion of CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub> to alumina gel and C<sub>3</sub>AH<sub>6</sub>. The effect of conversion on the strength of HAC concrete has been dealt with in a comprehensive manner by Neville [2].

Calcium aluminate hydrate phases identified in the present study by X-ray diffraction in samples whose curing schedules are listed in Table II were those expected from previous studies [16, 19]. When the specimens were kept under water at 25°C, both CAH<sub>10</sub> and C<sub>3</sub>AH<sub>6</sub>, in addition to a small amount of C<sub>2</sub>AH<sub>8</sub>, were present in the 28 day and 1 year samples. At 35°C and for the aqueous environment, only a trace amount of CAH<sub>10</sub> was detected after 180 days and C<sub>3</sub>AH<sub>6</sub> was the dominant calcium aluminate hydrate at this stage. At 1 year the CAH<sub>10</sub> phase could not be detected. In specimens stored in air at 35°C, a small amount of CAH<sub>10</sub> was detected even after 1 year, although C<sub>3</sub>AH<sub>6</sub> was again the dominant aluminate hydrate. At 50 and 60°C, CAH<sub>10</sub> had disappeared by 28 days when the samples were kept submerged under water. Gibbsite was detected by X-rays in nearly all the samples.

For samples stored at 18 to 20°C in air of 40% r.h. X-ray examination revealed the presence of CAH<sub>10</sub> as the predominant calcium aluminate hydrate after 1 year. Its amount had increased substantially at the end of the third year and small amounts of C<sub>3</sub>AH<sub>6</sub> and C<sub>2</sub>AH<sub>8</sub> were also present at this stage of hydration. After 10 years CAH<sub>10</sub> was still present in significant quantities, the amounts of C<sub>3</sub>AH<sub>6</sub> were not very great and gibbsite was present in the final hydration products. A large proportion of the cement remained unhydrated at the end of 10 years. Considering the fact that the water/cement (w/c) ratio used in the fabrication of the composite board was 0.35 this is to be expected [2].

The storage of the grc specimens under water at 18 to 20°C produced some C<sub>3</sub>AH<sub>6</sub> as early as 28 days and this phase coexisted with CAH<sub>10</sub> for 3 years or more. The C<sub>2</sub>AH<sub>8</sub> phase disappeared by this time. At 4 years C<sub>3</sub>AH<sub>6</sub> became the predominant calcium aluminate hydrate phase with little CAH<sub>10</sub> and CA still remaining. The position remained the same up to 10 years but now gibbsite was a major hydration product. The phase assem-

blage in the 10 year old sample kept at 90% r.h., 18 to 20°C, was very similar to that of the corresponding water stored sample. In naturally weathered specimens both CAH<sub>10</sub> and C<sub>3</sub>AH<sub>6</sub> phases were detected by X-rays after 6 months and C<sub>3</sub>AH<sub>6</sub> was by far the most abundant phase in 3, 4 and 10 year samples. At 10 years gibbsite was present as a major constituent but the cement was not fully hydrated. It appears that the "conversion" to the C<sub>3</sub>AH<sub>6</sub> phase had taken place faster under natural weathering conditions than in water at 18 to 20°C.

A quantitative assessment of the effect of the degree of conversion of the high alumina cement on the strength properties of HAC composites has not been attempted in this study. However, the experimental results, for instance those presented in Figs 1 and 3, show a distinct trend. In water stored and weathered composite specimens the proportion of the C<sub>3</sub>AH<sub>6</sub> phase was found to be much greater than those in the specimens kept in air. In all cases the strengths of these composites were lower than those obtained with the air-stored samples. It must be remembered that the naturally weathered samples must have experienced temperatures much higher than 18 to 20°C for extended periods of time during their 10 year life. The poorer strengths of weathered coupons *vis à vis* those of the water stored samples could perhaps be ascribed to the temperature effects on the strength of the glass fibre as well as on the "conversion" of the cement. The "conversion" reaction leading to the formation of C<sub>3</sub>AH<sub>6</sub> is often accompanied by a marked increase in porosity [17] which is likely to produce a much weaker matrix for the fibres to reinforce. In glass fibre cement, the matrix is not considered to be a very important direct contributor to the ultimate flexural or tensile strength of the composite because of its very small failure strain. But its integrity is important and furthermore a progressive increase in the porosity of the matrix can have a pronounced effect on the composite properties by interfering with the stability of the interface between the fibre and the cement.

Strength losses measured for glass reinforced HAC can thus be due to two effects, namely, the conversion of the cement and corrosion of the glass fibre. The effect of conversion on composite strength is most pronounced in the regime of the stress-strain curve defining elastic deformation of the material. Since fibre volume fractions used in this study were rather small, the stress in



the composite at the elastic limit is virtually the same as that of the unreinforced cement. The load–deflection plots from which the four-point bend test results of Table II were computed indicate that in fully converted HAC composites reinforced with AR-glass fibres this stress level can be significantly lower than that of the unconverted material. In the opinion of the authors this reduction could be as high as 40 to 50%. The strength at failure, on the other hand, is largely controlled by the stresses which the fibres can support. The effect of the conversion phenomenon, on the basis of the very rough calculations which can be attempted at present, is unlikely to reduce the failure strength of the composite by more than 15 to 20%.

The relative performance of the alkali-resistant and E-glass fibres in a matrix of high alumina cement can be qualitatively understood from the chemistry of hydration of this type of cement. When the HAC/grc composites are stored under water over a long period of time, the pH of the solution phase present in the pore space is likely to be in the alkaline range but its value is not known. Experiments have shown that if samples from grc boards made from HAC stored under the various conditions of exposure discussed previously over a period of 10 years are ground up to pass a BS 200 mesh sieve and 16.7 g of this fine powder are then dispersed in a litre of distilled water, the equilibrium pH of the resulting suspension lies in the range 11.7 to 11.8. The corresponding pH values for ordinary Portland cement are probably in excess of 12.5. Since it is the  $\text{OH}^-$  ion concentration in the matrix that is believed to be responsible for the corrosion of the glass fibre, it is to be expected that both the alkali-resistant glass and E-glass will perform better, as far as the durability of the composite is concerned, in a matrix of high alumina cement than in ordinary Portland cement. But it is doubtful if the removal of the organic coating from the surface of E-glass fibre as carried out by Chan and Patterson [6] had any positive influence in increasing the resistance of such a glass against attack by  $\text{OH}^-$  ions. However, their claim that such a treatment produces a more stable composite needs to be verified.

The effect of adding a polymer dispersion of the type butadiene styrene on the properties of grc made from HAC is most noticeable in the case of the impact resistance of the composite (see Table III). Both in dry air and natural weathering

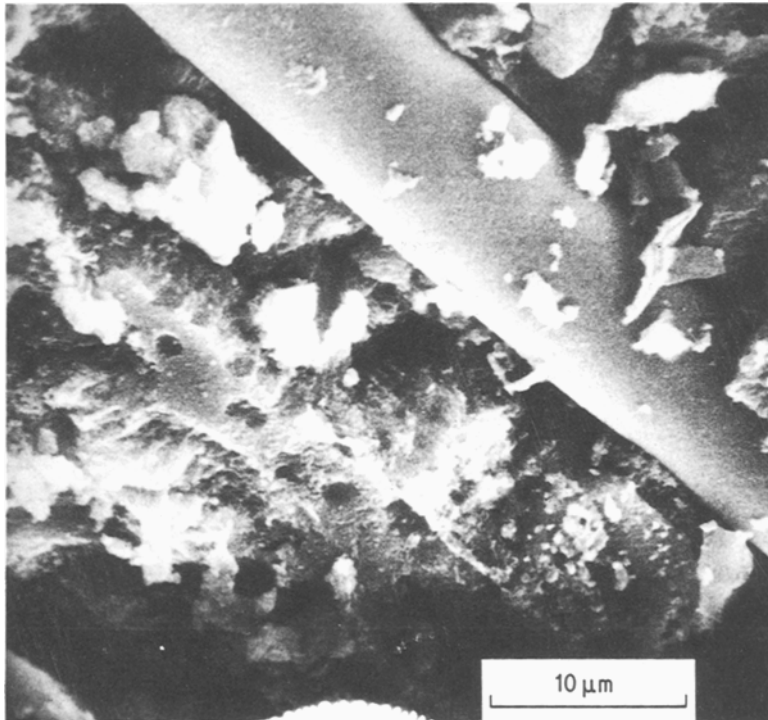
conditions the long-term improvements ascribable to the polymer are substantial but in a continuously wet environment the properties of the material are not very different from those of the plain cement composite. The addition of pfa also has a beneficial effect on the impact resistance of HAC/grc kept under wet conditions but the LOP values are lower. In this case the absence of large amounts of  $\text{Ca}^{2+}$  in the matrix does not allow pozzolanic pfa to produce enough CSH hydrates to densify the matrix, and thus embrittle the composite.

### 5.3. Stress–strain behaviour of the composite

For both E-glass and AR-glass reinforced HAC, the tensile stress–strain plots show the now familiar pseudo-ductility when the composites are kept in relatively dry air. Under wet conditions the failure strains are much reduced with time. In the case of HAC composites made from E-glass the failure strain was only  $200\mu$ -strain after 51 months whereas for the AR-glass fibre reinforced material the corresponding value was about  $3000\mu$ -strain (Table IV). After 10 years failure strain values regress slightly more but in the case of Cem–FIL/HAC composites (Fig. 5) the results are quite encouraging and confirm the better impact resistance of such composites *vis à vis* ordinary Portland cement (OPC) composites reinforced with the same glass fibre [20]. The fracture surface of such a composite (Fig. 6) does not show any obvious signs of corrosion on the glass fibre.

The stress–strain values recorded for the tension face when composite specimens of Cem–FIL/HAC cured under different conditions over a period of 55 months were tested in bending reflect the same effect of storage as observed with samples tested in direct tension. The strains at failure were 16 000, 11 000 and  $5000\mu$ -strains for air, weathering and water storage conditions, respectively. The modulus and the stress at the elastic limit are highest when the samples were kept under water and lowest when they were left in air, natural weathering giving an intermediate result. These differences can be related, in a qualitative way, to the degree of hydration attained by the matrix under these three conditions.

The failure strains recorded on the compression face showed the same environmental effects observed above. For air storage the value obtained is similar to that of the neat cement paste.



*Figure 6* Fracture surface of a grc composite made from HAC and kept under water for 10 years.

## 6. Conclusions

This study is concerned only with the properties of glass reinforced composite materials using high-alumina cement. The conclusions relate, therefore, to that issue, not to current recommendations on the use of high-alumina cement in construction.

(1) When the alkali-resistant Cem-FIL glass fibres are used in reinforcing high alumina cements, the composite material retains substantial proportions of its tensile, flexural and impact strength after 10 years in both air and water storage.

(2) When commercially available E-glass fibres are used in reinforcing high alumina cement, the composite material loses a substantial proportion of its initial strength in 1 year if stored under water. Storage in dry air gives better results.

(3) The tensile stress-strain plots of the grc composite material show that for high-alumina cements reinforced with both the alkali resistant and E-glass fibres, the failure strains of the samples depend on the conditions and time of storage. For air stored samples, composites made with both glasses exhibit high strains at failure indicating a quasi-plastic behaviour beyond the elastic limit. In water storage, over a period of 10 years the failure strain is reduced by 75% in the case of the alkali-

resistant glass. It becomes similar to that of the unreinforced matrix in the case of E-glass after 1 year.

(4) The mode of fracture of grc composites stored under various conditions can be qualitatively related to the corrosion of the glass fibre, the strength of the interfacial bond and its effect on the fibre pull-out and fracture when the material is broken.

(5) The reinforcement of HAC with glass does nothing to arrest the mechanisms by which the strength properties of HAC are dependent upon temperature, humidity and water to cement ratio which control the rate of conversion.

(6) The impact resistance of HAC/grc is improved if the cement matrix is modified by additions of pulverized fuel ash or certain types of polymer dispersions.

## Acknowledgements

The work described has been carried out as part of the research programme of the Building Research Establishment of the Department of the Environment and this paper is published by permission of the Director. The authors are grateful to Pilkington Brothers Limited for the supply of AR-glass fibres.

## References

1. S. S. BATE, "Report on the Failures of Roof Beams at Sir John Cass' Foundation and Red Coat Church of England Secondary School, Stepney", Building Research Establishment, Watford, CP58, June 1974, p. 18.
2. A. M. NEVILLE, "High Alumina Cement Concrete", (The Construction Press, Lancaster, 1975) p. 201.
3. Fibre-Reinforced Cement Composites, Technical Report 51.067 (Concrete Society, London, 1973) p. 77.
4. K. L. BIRYUKOVICH, YU. L. BIRYUKOVICH and D. L. BIRYUKOVICH, "Glass-Fibre Reinforced Cement (Budivelnik, Kiev, 1964) Civil Engineering Research Association Translation No. 12, 1965.
5. F. J. GRIMER and M. A. ALI, *Mag. Concr. Res.* **21** (1969) 23.
6. H. C. CHAN and W. A. PATTERSON, *J. Mater. Sci.* **6** (1971) 342.
7. H. G. ALLEN, *J. Composite Mater.* **5** (1971) 194.
8. A. J. MAJUMDAR and J. F. RYDER, *Glass Technology* **3** (1968) 78.
9. A. J. MAJUMDAR, British Patent 1243973 (1971).
10. B. R. STEELE, Prospects of Fibre Reinforced Construction Materials, Conference Proceedings of International Building Exhibition, London, 1971, Building Research Establishment, Watford, CP 17/72.
11. B. SINGH, P. L. WALTON and M. S. STUCKE, RILEM Symposium Proceedings, Sheffield, April, 1978, edited by R. N. Swamy (Construction Press, Lancaster, 1978) p. 377.
12. R. C. DE VEKEY and A. J. MAJUMDAR, *Mag. Concr. Res.* **20** (1968) 229.
13. A. MARIES and A. C. C. TSEUNG, International Conference Proceedings of Structure, Solid Mechanics and Engineering Division, Southampton University (John Wiley, New York, 1971) p. 1123.
14. B. A. PROCTOR and B. YALE, *Phil. Trans. Roy. Soc. London A294* (1980) 427.
15. T. D. ROBSON, High Alumina Cements and Concrete (Contractors Limited, London, 1962).
16. H. G. MIDGLEY, *Trans. Brit. Ceram. Soc.* **66** (1967) 161.
17. H. G. MIDGLEY and K. PETTIFER, *ibid.* **71** (1972) 55.
18. V. S. RAMCHANDRAN and R. F. FELDMAN, *Cement and Concr. Res.* **3** (1973) 729.
19. S. CHATTERJI and A. J. MAJUMDAR, *Ind. Concr. J.* **40** (1966) 245.
20. Building Research Establishment, Properties of GRC: Ten year results, BRE, Watford, Information Paper IP36/79.

Received 18 February and accepted 23 March 1981.