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A STUDY OF
GLASS FIBRE REINFORCED
HIGH ALUMINA CEMENT COMPOSITES

A Thesis submitted for the degree of

Doctor of Philosophy

in The City University, London

by Alan Maries, M.A.

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supervision of Dr. A.C.C. Tseung,
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ABSTRACT

Introductory chapters review the state of the art in glass fibre reinforced cement (GRC) composites: the use of high alumina cement as a matrix is probably the most practical way of ensuring component compatibility in a GRC system.

Calculation of the theoretical tensile strength for different failure modes shows that there is considerable scope for improvement of the physical properties of GRC composites. On the other hand, analogous calculations applied to the various mechanisms available for absorbing energy in fracture produce far higher impact strengths than actually observed. The value of these calculations must not, however, be over-rated as they are based on second-hand data, but they emphasise the need for a more detailed study of the glass fibre / cement interface.

An analytical method was developed for the rapid determination of Al^{3+} , Fe^{3+} , Ca^{2+} , OH^- and pH in hydrating cement pastes which showed that both alkalinity and Ca^{2+} concentration were lower in high alumina than in portland cement. This should limit the gradual deterioration of the composite caused by direct chemical attack (weakening the fibres) and by disruptive internal crystal growth, but the relative importances of these two mechanisms still need to be resolved.

Preliminary single fibre pull-out experiments to determine interfacial bond strength indicated the need for tighter control over experimental variables. An apparatus was constructed for pulling glass fibres from the melt, thereby ensuring some control over their surface condition, and greater reliability was imparted to the pull-out system by the use of an Instron tensile tester. But despite allowance for the non-uniform distribution of interfacial stress, it was still impossible to get any better than qualitative results.

It was concluded that in GRC systems the interfacial stress would be better measured by a delamination type of test.

CHAPTER ONE: FIBRE REINFORCED COMPOSITES

1.1 INTRODUCTION

The current interest in glass fibre reinforced cement (GRC) composites arises from three principal sources. Firstly, they are unusual among fibre composites in that the moduli of fibres and matrix are very similar in magnitude. Secondly, they bear a close resemblance to glass fibre reinforced plastic (GRP) composites, except that the matrix has certain advantages over resin in physical properties and cost in many structural applications. Thirdly, they offer one of the most promising of many methods of improving the strength and toughness of a very widely used constructional material - concrete.

1.2 FIBRE COMPOSITE SYSTEMS

1.2.1 Strength and Toughness

Calculations from atomic force-displacement relations suggest that the ideal tensile strength σ^* of a solid should be roughly one tenth of its Young's modulus E (Cottrell 1964).

i.e. critical strain $\alpha^* = \sigma^*/E \approx 0.1$.

In practice, however, most bulk solids fail at much lower stresses either because they are brittle and contain cracks or other stress concentrators, or because they are ductile and contain glissile dislocations. Thus for bulk glass $\alpha^* \approx 0.001$, and common metals and alloys yield plastically at $\alpha^* \approx 0.001$ and break at $\alpha^* \approx 0.01$.

It is possible to make single crystals where $\alpha > 0.02$, and near-ideal strengths can be obtained by drawing a solid into fibres: for drawn high-C steel wire $\alpha \approx 0.02$, and for glass fibres $\alpha \approx 0.35$. Although on a microscopic level these materials may be considered strong, they are extremely sensitive to flaws and are useless on their own for most practical purposes.

On a macroscopic engineering scale toughness is also important, and in general is roughly proportional to σ^* multiplied by u , the "fracture displacement". Solids in which attempts are made to raise both σ^* and σ^*u to as high a value as possible may be separated into two broad classes. Traditionally, engineering alloys exploit high values of σ^* , combined with very large values of u obtained from the glissile dislocations of ductile metals. Fibre reinforced composites are a more recent development: bundles of strong fibres and whiskers are incorporated in a protective matrix (where the failure of a single fibre is not necessarily catastrophic), whose low value of u is effectively increased by the high value of α^* of the reinforcement and possibly by some interfacial movement as well. Such fibres may also act as crack arresters.

1.2.2 General considerations: properties of fibres and matrices

Fibre composites in which chain-like molecules are bound together in an amorphous matrix are some of Nature's oldest attempts at producing strong solids: wood and muscle

ligaments are good examples. Man's imitations are comparatively recent but nevertheless extremely diverse: Tables 1.1 and 1.2 show some of the most significant average physical properties of currently available fibres and matrices.

fibre

Since the purpose of most/composites is to combine a high linear or planar tensile strength with lightness and stiffness, fibres most suitable as reinforcement will possess high values of σ and E and be preferably of low density in order to optimise the specific strength σ/ρ and stiffness parameter E/ρ^2 . Most of the fibres listed in Table 1.1 are satisfactory in these respects except for tungsten (because of high density) and the plastics (because of low stiffness). A high value of fibre breaking strain is also desirable but not vital under certain conditions of matrix-fibre stress transfer: the high values for plastics fibres may be useful in imparting toughness to composites. Of course other factors such as cost, availability and special properties like refractoriness or plasticity may also be important, some of them (e.g. compatibility) depending on the matrix material.

Suitable matrices will in general have low values of E and G (shear modulus) to enable the reinforcement to carry most of the load, combined with a reasonable value of fracture strain to enable this stress transfer to take place. In reinforced metals plastic deformation of the matrix is possible and in reinforced plastics elastic deformation, but ceramics do not possess these possibilities to any pronounced degree,

Physical properties of fibres

Fibre	U.T.S. σ_f^* (GNm ⁻²)	Elastic modulus E_f (GNm ⁻²)	Strain at failure α^* (%)	Specific gravity ρ_f	Specific strength σ/ρ (GNm ⁻²)	Specific modulus E/ρ (GNm ⁻²)	References
E-glass	3.6	76	4	2.5	1.4	30	Loewenstein (1967)
Fused silica	5.9	69	6	2.5	2.4	28	Morley (1964), Proctor (1967)
Asbestos (chrysotile)	3.0	165	1	2.6	1.2	65	Hodgson (1965)
Graphite (RAE carbon fibre)	2.0	410	0.5	2.0	1.0	200	Watt (1970)
β -SiC	20	590	3	3.2	6.3	185	Noone & Roberts (1967)
Boron	3.1	410	1	2.6	1.2	160	Morley (1966)
Tungsten	3.8	420	1	19.3	0.2	22	Cottrell (1964)
Alumina	15	540	3	4.0	3.8	135	Cottrell (1964)
Nylon	0.5	3.5	15	1.1	0.5	3.2	Cottrell (1964)
Polythene	0.25	1.0	25	0.92	0.3	1.1	Fibreglass (1963)
Steel	0.76	210	0.4	7.8	0.1	26	Shah (1969)

Table 1.1

Physical properties of matrices

Matrix	U.T.S. σ_m^* (MNm ⁻²)	Elastic modulus E_m (GNm ⁻²)	Poisson's ratio ν	Shear modulus G_m (GNm ⁻²)	Specific gravity ρ_m	Fracture strain α^u (%)	References
Polyester resin	40	2	0.5	1.3	1.3	1	Lever & Rhys (1962), Greszczuk (1969)
H.D. polythene	30	1	0.5	0.3*	1.0	3	Lever & Rhys (1962)
Aluminium alloy	500	70	0.3	26	2.7	1	Cottrell (1964)
Copper	550	170	0.3	48	8.9	0.4	Cottrell (1964)
Alumina	350	380	0.1	180	4.0	0.1	Budnikov & Kharitonov (1966), Bowen (1968)
Hydraulic cements	5	40	0.15	17*	2.1	0.01	Lea & Desch (1956), Robson (1962)
Gypsum	5	40	0.2	17*	1.7	0.07	Ali & Grimer (1969)

* calculated from $G = \frac{E}{2(1+\nu)}$

Table 1.2

and improvement of strength by reinforcement with fibres is consequently more difficult to achieve than in other matrices (Bowen 1969).

1.2.3 Practical Fibre Composites

Table 1.3 compares some significant properties of established structural materials with those of some currently manufactured fibre reinforced composites: high temperature composites such as silica fibre reinforced aluminium have not been included.

With the exception of impact strength (which is a "structure-sensitive property") the table gives average values of "structure-insensitive properties" (Biggs 1962) of typical materials of each class. Although these are not directly relevant in a comparison of meaningful engineering properties they do serve as an order-of-magnitude guide. Thus the specific strength column shows that steel is not as outstanding on a strength/weight basis (for instance in applications where weight is very much at a premium) as measurements of its yield stress would indicate. But probably the most interesting conclusion to be drawn from Table 1.3 is the general advantage that fibre reinforced materials (including wood) have over others in the weight/stiffness parameter, which compares the weight of beams giving equal deflections under the same loads.

Engineering properties of materials

-2-

Material	Specific gravity ρ	Stress at failure σ^* (MNm^{-2})	Elastic modulus E (GNm^{-2})	Fracture energy F (kJm^{-2})	Specific strength σ/ρ (MNm^{-2})	Weight/stiffness parameter $\rho/E^{1/2}$ (GNm^{-2}) ^{-1/2}	References
Steel	7.8	300	210	50	38	1.3	Fibreglass (1963), McLean (1969)
Aluminium alloy	2.7	200	70	10	74	0.65	Fibreglass (1963), Cottrell (1964)
Concrete	2.4	4	36	0.02	1.7	0.73	Malhotra (1967), McLean (1969)
Wood (pine)	0.5	80	12	10	160	0.22	Gibson (1969), McLean (1969)
H.D. polythene	1.0	100	1.0	1	100	1.0	Fibreglass (1963)
Asbestos-cement ($V_f=10\%$)	1.8	14	30	2.5	8	0.58	Krenchel (1964), Ali & Grimer (1969)
GRP random * mat ($V_f=20\%$)	1.5	100	9	10	67	0.72	Fibreglass (1963), Krenchel (1964)
GRC random * mat ($V_f=8\%$)	1.8	20	30	23	11	0.58	Majumdar & Ryder (1968)
CRP * ($V_f=40\%$) unidirectional	1.5	600	150	40	400	0.28	Phillips (1968), Harris et al. (1971)
Silica fibre / Al ($V_f=50\%$)	2.6	900	70	-	350	0.63	Sutton & Chorné (1965)
GRG * ($V_f=8\%$)	1.8	12	30	50	6.7	0.58	Ali & Grimer (1969)

* see Appendix 1

Table 1.3

The economics of these materials has not been considered in view of the complexity of relating cost to engineering requirements (Alexander 1967): the danger of over-simplified calculations for only one parameter such as stiffness (Scanlan 1968) has been pointed out by Jones (1970). However, as far as fibre reinforced materials are concerned, forming costs are likely to be similar to one another, and the relative expense of providing a material to fulfil a particular structural purpose are likely to be governed mainly by basic materials costs and by such properties as specific strength or weight/stiffness parameter.

1.3 GLASS FIBRE REINFORCED PLASTIC (GRP) COMPOSITES

Both historically and economically glass fibre reinforced plastics, generally known as "Fibreglass", are by far the most important class of fibre composites produced to date, and thus have been the most extensively investigated. An excellent review article by Loewenstein (1967) surveys most of the vast field of literature and technology of GRP's, but our main concern is with those aspects which are likely to be relevant to a study of GRC composites.

Polyester and epoxy resins are the two main types of matrix used in GRP composites, although p.v.c., furane and polypropylene have been employed in certain applications demanding particular resistance to chemical corrosion. They are both thermosetting resins and have broadly similar physical

properties, but differences in shrinkage and water sensitivity during curing may shift the emphasis on the frictional/chemical nature of the fibre-matrix bond (see Chapter 5).

Two different formulations of glass fibre are in common use: 'A'glass, a specially selected high alkali glass (10-15% as Na_2O), is used for applications less demanding than those for which 'E'glass is selected. 'E'glass contains less than 1% alkali (see Table 3.1), and has excellent electrical properties and moisture resistance: it is also used in all cases where higher strength or optical clarity is required. High Young's modulus or high strength compositions may be used in special cases.

The physical properties of GRP laminates depend very much on glass content, whose maximum value is governed by the arrangement of the reinforcement. These maximum values are given in general terms in Table 1.4.

The geometry of reinforcement and shape of the finished product usually decide which of the many production methods is to be used. Since these are so similar to GRC methods (discussed in Section 2.2) there is no need for further elaboration here other than to point out that GRC curing procedures may be much more flexible.

Much of the literature on GRP composite properties, both practical and theoretical, is applicable to GRC composites,

Experimental upper limits to fibre content

Type of reinforcement	Fibre content (%)			
	GRP		GRC	
	V_f	W_f	V_f	W_f
Unidirectional (rovings)	80	90	20	28
Bidirectional (woven cloth)	50	70	15	19
Random (chopped mat)	30	50	9	13
References	Fibreglass (1963)		Biryukovitch (1964), Allen (1969), Grimer & Ali (1969)	

Table 1.4

bearing in mind the differences in nature of the matrices (Monfore 1968). Much work has been done to relate experimental strength observations to mixture laws for composite strength and modulus, and equations for stress distribution (on a microscopic level) and work of fracture (see Chapter 4). In particular, the nature of the fibre-resin bond (see Chapter 5) has been studied more in GRP systems than in others.

1.4 COMPOSITES WITH A CEMENTITIOUS MATRIX

1.4.1 Asbestos-cement

Despite the extensive use of asbestos fibre/Portland cement laminates for over 70 years as a cheap constructional material with excellent insulating and fire-retardant properties, comparatively little basic research seems to have been carried out on this composite system.

The state of the art 30 years ago is well summarised in a review by Hayden (1942), who mentions the absorptive capacity for cement possessed by asbestos fibre. More recent work in this field by Chatterji and Rawat (1963) suggests that in addition to physisorption, chemisorption to a degree depending on the Fermi levels of adsorbent and adsorbate may also occur. Furthermore, although nearly all reactions between cement and asbestos are topotactic and occur to only a small extent under normal autoclaving conditions (Ball & Taylor 1963), the presence of asbestos in Portland cement has been

found to accelerate markedly the hydration rate of some components (Kalousek et al.1966).

A recent monograph on fibrous silicates by Hodgson (1965) gives a detailed account of the properties and uses of asbestos fibres, but the only reference to their use in composite materials is a mention of measurements of bond-strengths with polyester resins and Portland cements (Bennet 1964). The fibre-cement interface has also been investigated petrographically by Smirnov (1962) and by Bailey (1963).

1.4.2 GRP Reinforced Cement or Concrete

The success of GRP composites in the building industry has always been tempered by the cost of the matrix, and first attempts to produce a cheaper composite were made by using resin-bonded glass fibre ("fibreglass") tendons as a substitute for steel wires in reinforced concrete.

A considerable amount of research in the U.S.S.R. (Gvosdev et al. 1960), U.S.A. (Princeton 1959) and U.K. (Somes 1963) showed that the principal advantage of fibreglass reinforcement lay in its relative immunity to corrosion (Agbim 1964, Tsyapkina 1961), but that it gave very little superiority over steel wires on account of its brittleness and poor keying into the cement. Indeed, it was really suitable only for prestressed concrete (Rubinsky 1954), when it was necessary

to provide the correct stress at tensioning and good anchorage, at the same time avoiding surface damage during casting (Somes 1963).

Investigations into the optimum geometry and disposition of the reinforcing material favoured a microstructural arrangement of the tendons which was difficult to realise in practice (Biryukovitch 1959, Agbim 1964), and despite its low density twice the weight of fibreglass was needed in some applications to give reinforcement equivalent to that of steel wires (Kajfasz 1960). This, coupled with increased cost of GRP tendons, has resulted in a general decline of interest in this type of reinforcement.

1.4.3 Fibre Toughened Concrete

The non-linearity of the stress-strain relationship for concrete has been investigated by Shah (1969), who observed the microcracking of concrete under stress by using a staining technique. He found that above about 50% of the ultimate stress, first bond cracks and then matrix cracks began to increase significantly, giving concrete its plastic characteristics. Thus the fracture toughness of concrete is greater than either of its components because the relatively weak bond between paste and aggregate causes a gradual growth of stable microcracks in lieu of a rapid propagation of unstable cracks. He concluded that the addition of a small volume of

randomly orientated steel fibres (diameter 0.25 mm) should improve this composite action, and experimental work proved the following points:

(i) Increasing the volume fraction of fibres to 1½% increased both strength and fracture toughness: but whereas flexural strength was only doubled, fracture toughness was increased twenty-fold (In fact a simple "law of mixtures" calculation (see Chapter 4) shows a theoretical increase of flexural strength of 40% at the most: thus the fibres are acting to stop catastrophic cracking).

(ii) Annealing the fibres (increasing their elongation at fracture ten-fold, but reducing their strength) increases fracture toughness but leaves flexural strength unaltered. I.e. ductile fibres promote a much more efficient use of materials than brittle ones.

(iii) Reducing the strength of bond between particles and matrix increases the non-linearity (i.e. plasticity) of concrete. This idea was not carried over to the fibre reinforcement investigations but presumably could be used to increase toughness even further.

(iv) Conventional steel bar reinforcement, provided it was advantageously positioned, gave three times as much flexural strength as fibres with the same volume fraction, but lower fracture toughness.

It would therefore seem that one potential use of steel fibres is in conjunction with conventional reinforcement in order to increase toughness.

Romualdi (1965) has studied the mechanism of crack propagation in concrete in terms of stored elastic energy, and he derived an equation relating the fracture toughness of concrete to the work of pull-out of reinforcing fibres (see Chapter 4). He showed that the fibres play a dual role in increasing strength and toughness at high loads: they not only provide a crack-arrest mechanism but also stop the cracks which have overcome the restraint of the wires from propagating rapidly by absorbing energy in the fibre/cement interface.

It is important to recognise the difference between this type of reinforcement (to a low volume fraction in a brittle matrix) where it enables the load-carrying matrix to perform at a higher stress level (cf. GRC composites) and that in GRP composites, where the high volume fraction of fibres is the major load-carrying component in a tough but low-strength matrix. Monfore (1968), in a general review of fibre reinforcement of Portland cement and concrete has also pointed out that although cements are an order of magnitude stiffer than plastics, their low strength makes their elongation at fracture two orders of magnitude lower.

Flajsman et al. (1970) have found that polymer impregnation improves the effectiveness of steel fibre reinforcement, possibly because it results in superior interfacial bonding. Both they and Williamson (1965) have compared steel reinforcement with nylon and found it to be more efficient: nylon is incapable of adding to the strength of concrete on account of its very low elastic modulus (see Table 1.1). Nevertheless, in an investigation of several types of reinforcement, Goldfein

(1965) concluded that nylon was the most suitable from the point of view of flexural and impact strengths. Zonsfeld & Salmons (1968), however, have argued that from a cost/manufacturing point of view fibrillated chopped polypropylene film is a much more practicable proposition, and their patented material is on the market as "Carricrete".

1.4.4 Reinforcement of hydraulic cements by glass fibres

In the search for a man-made substitute for asbestos fibre, which suffers from the unreliability in supply common to naturally occurring materials as well as shortness (its length rarely exceeds 10 mm), the E-glass type of fibre used to reinforce plastics was an obvious initial choice. (The use of E-glass as the standard for GRP composites is fortuitous: originally it was developed as a low-cost glass with ^{high} electrical resistance and ^{low} softening point from which fibres could easily be drawn for insulating purposes.) However, fibre of this composition is attacked by the alkali released during the hydration of portland cement, causing weakening of GRC composites over long periods. There are four basic ways of overcoming this problem:

(i) Using alkali-resistant glass fibres. Certain $\text{Na}_2\text{O-SiO}_2\text{-ZrO}_2$ and $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ glasses (see Table 3.1) have been developed at the Building Research Station which are claimed (Majumdar 1970, 1971) to be alkali-resistant to the extent that portland cement composites containing these glasses

as fibrous reinforcement do not lose strength with time (Majumdar & Ryder 1968, de Vekey 1969). These fibres probably achieve their resistance by being initially attacked by the alkali to form an insoluble protective layer of Zr or Mg hydroxide. They are more difficult and costly to produce than E-glass fibres, however, and an alternative procedure might be to alter the physicochemical structure of just the surface of the glass. Of the many methods available for this (Sugarman 1967), surface diffusion of suitable ions, atoms or molecules seems to be the most promising (Symmers et al. 1962).

(ii) Applying a protective coating to the glass surface.

Biryukovitch (1961) has suggested divinyl acetate as a suitable hydrophobic protection for glass fibres, but this would be expected to provide only temporary protection against alkali. Similarly, Owens-Corning have claimed (1957) that prior wetting of the fibre with an aqueous solution of a polyvalent metal salt such as AlCl_3 and a non-metallic base such as ammonia increases the bonding relation between fibre and cement by forming a water-insoluble layer on the glass surface (cf. inhibition of the alkali-aggregate reaction with insoluble salts: see Section 6.2.).

(iii) Neutralising the alkalinity of the cement. Another

Owens-Corning patent (1964) describes how inorganic binders which attain a pH of over 10.5 on hydration may be prevented from attacking the glass by combining the harmful

Na^+ , K^+ or Ca^{2+} cations with a cation exchanger such as zeolitic clay or a sulphonated polyvinyl-aryl compound. Straight neutralising agents may also be used, although Rice (1970) has found that the addition of 3% by weight of waterglass to the cement slurry does not significantly affect the strength behaviour with age. Fluosilicates (MgSiF_6 , for instance) should not only neutralise the alkali in the cement pastes but may also strengthen the glass fibre by an etching action (Proctor 1962).

(iv) Using "non-alkaline" cements. There are many hydraulic cements which liberate less alkali than Portland cements, although nearly all of them are at least slightly alkaline. From the cost angle gypsum is an ideal binder, and in applications where its water-sensitivity is not a draw-back it has been successfully reinforced by glass fibres (U.S. Gypsum Co. 1958, Owens-Corning 1962, Ali & Grimer 1969). Such "GRG" composites possess an unusually high impact strength: 50 kJm^{-2} can be attained at maximum glass loading (Majumdar & Ryder 1968). Magnesium oxycements (Owens-Corning 1951) and aluminium phosphate (Plant et al. 1961, Chase & Copeland 1966) have been proposed as suitable composite binders for aerospace applications, where their low modulus and density, high strength and temperature resistance all offset their relatively high cost.

The most obvious and readily available alternative to Portland cement as a matrix suitable for glass fibre reinforce-

ment is undoubtedly high alumina cement (HAC), which is the only known hydraulic cement situated in a less alkaline region of the C-A-S-H phase system (see Table 3.2). Consequently E-glass fibre reinforced HAC has been extensively investigated, and the following chapter presents a review of the literature pertaining to it.

CHAPTER TWO: GLASS FIBRE REINFORCED HIGH ALUMINA CEMENT

COMPOSITES

2.1 DEVELOPMENT OF RESEARCH & MANUFACTURING INTERESTS

2.1.1 In the U.S.S.R.

The first attempts at glass fibre reinforcement were made by Burov (1945), who found that the replacement of steel bars in concrete by glass rovings was ineffective without prestressing because of isolated concentrations of relatively low elastic modulus. Prestressing could be applied only if fibreglass tendons were used, but the presence of the plastic caused considerable creep and loss of prestress with time, as well as being uneconomical and fire-hazardous. An obvious solution was to disperse the stress by using layers of glass mat or cloth, and high alumina cement was selected as a binder after research had shown Portland cement to be incompatible with the high strength low-alkali glass fibre reinforcement - roughly similar to E-glass (Budnikov & Goryainov 1955; Budnikov, Pashchenko & Serbin 1966).

Details of the investigation of physico-mechanical properties of E-glass / HAC composites may be found in publications by Y.L. and K.L. Biryukovitch (1961, 1963), but by far the most complete documentation is their monograph published in Russian in 1964 and subsequently translated by C.E.R.A. (Biryuk-

ovitch 1964). This indicates that the current manufacture in the U.S.S.R. of these laminates for general structural engineering purposes is proceeding on a large scale.

2.1.2 In the U.K.

Workers at the Building Research Station have carried out comparative feasibility studies on various fibre/matrix systems including E-glass/HAC, and for commercial reasons decided to adopt the first solution to the problem of glass-cement compatibility (see Section 1.4.4) and have developed an alkali-resistant glass fibre for reinforcing Portland cement (Majumdar & Ryder 1968, Grimer & Ali 1969, de Vekey & Majumdar 1968). "Non-alkaline" matrices have also been investigated, and although E-glass fibre/gypsum composites are being produced with excellent impact strength and fire resistance (Ali & Grimer 1969), E-glass/HAC composites were tested only for purposes of comparison.

Elkalite Ltd. have done little basic research themselves, but are now manufacturing a range of E-glass/HAC products for building and other applications (Peters 1970). A series of research projects carried out on these composites at the Queen's University of Belfast has studied the effects on the mechanical strength of ageing (Fulton 1969, Patterson 1970), weathering (Cousins 1970, Chan & Patterson 1970), and silane size on the fibres (Cousins 1970). A programme has been started at Southampton University to look into aspects of the Russian

research (Biryukovitch 1964) which require further investigation (Allen 1970). The approach is from an engineering point of view, and several interesting suggestions for strength improvement have been made.

2.1.3 Elsewhere

In a classic Danish work on the fibre reinforcement of both resins and cements, Krenchel (1964) describes extensive investigation into the theoretical and practical aspects of GRC composites. Most of his work was carried out on E-glass /portland cement systems with no reference to compatibility problems, but post-pressure and prestressing during curing were included in the test programmes. Plasticisers were added and pull-out measurements were made in steel wire/Portland cement systems.

The literature contains no reference to research in the U.S.A., apart from a mention of the use of glass fibre to increase the tensile strength of terrazzo (Neville 1964).

2.2 FABRICATION METHODS FOR DIFFERENT TYPES OF REINFORCEMENT

2.2.1 General

Methods of production are numerous, depending on the

type of glass fibre reinforcement used. In general the techniques are similar to those employed in GRP production, but the nature of wet cement slurry allows advantageous variations (Birjukovitch 1964, Fibreglass 1964, Allen 1970).

2.2.2 Rovings

Glass fibre is manufactured in the form of fine filaments, several hundred of which are bundled together (untwisted) to form a strand, Roving consists of several strands loosely gathered together and wound continuously onto a "cheese".

In the filament winding method of production, the roving is unwound from the cheese and passed through a bath of cement paste slurry to be wound onto a rotating mould or mandrel. Helically reinforced pipes, tanks and pressure vessels may be made in this way, but with a suitable shaped mould it is also possible to make flat sheets with continuous reinforcement aligned in selected directions. Chief advantages of this method are: exceptionally high strength in specified orientations, continuous flowline methods and use of the cheapest (unprocessed) type of fibre.

Products which are small and variable in cross-section such as window-frames are best made by continuous moulding: rovings previously impregnated with the required amount of paste may be compacted into specially shaped moulds.

2.2.3 Mats (woven or unwoven)

Strands may be twisted together to make a yarn, which may then be woven into a glass cloth or coarser mat. Alternatively they may be chopped into short lengths (2-5 mm) and sprayed onto a flat surface to form a kind of coarse felt, held together by small amounts of adhesive binder. These "chopped strand mats" are obviously not as strong as woven material, but are cheaper to produce and may be handled in much the same way.

Contact moulding is the oldest and simplest method used in laminate production. A mould (previously covered with release agent or polythene) is coated with cement paste and a sheet of glass reinforcement is placed over it. Further cement is brushed or sprayed on and impregnated into the sheet using a split-washer roller, and layers are built up to the required thickness of product.

Matched die moulding is expensive, but provides a good finish on both surfaces. A glass mat is placed onto the male die of a shallow mould and cement slurry is pressed in by the female die. Thick sheets may be progressively impregnated with cement paste by lifting the die periodically to delaminate the mat where the paste has not yet penetrated and adding more of it.

The mandrel winding method (see Section 2.2.2) may be

adapted to wind on mats: excess paste is removed from the mandrel by a small roller which simultaneously densifies and smooths the surface of each layer.

2.2.4 Chopped strands

Roving may be fed through a chopper unit which sprays out strands of uniform length. These strands may be premixed into cement paste (cf. asbestos-cement technology) and the resultant mixture applied direct to the mould. However, for any reasonable volume fraction (above 50%) or length of fibre (above 40 mm) the fibres ball up around the mixer blades, so that high strength composites cannot be made by this method.

Workers at the B.R.S. have solved this problem by spraying permeable simultaneously onto a/mould chopped strands and a cement slurry which is very dilute: thicker pastes gel too easily under pressure. Removal of excess water and compaction of the laminate is then achieved either by pressing at up to 3 MNm^{-2} or by suction at 80 kNm^{-2} (B.R.S. 1963, N.R.D.C. 1970).

2.2.5 Finishing methods

The 'green' product from one of the above methods may be further formed by bending or cutting before curing. Optimal curing of HAC-based laminates is achieved with 100% humidity

and low temperatures (below 15°C), commonly obtained by covering the 'green' product with a wet cloth or polythene sheet. E-glass /HAC laminates may be demoulded only 10 hours after moulding, when they will have acquired up to 50% of their final strength; and after 24 hours, when they are hard, it is best to post-cure them under water for several days,

Hardened products may be milled, planed, drilled or sawn, and may be repaired by layers of glass mat and rather fluid paste. They may be joined together by bolts or rivets, steel clamps or artificial glues. The strength of the finished product depends more on the distribution of the glass reinforcement than on the production method used, and extra strength may be secured by careful design features, such as sandwich construction or integrally moulded ribs. Where ribs are added afterwards they are best bonded onto laminates by means of layers of E-glass / HAC.

2.3 COMMERCIAL APPLICATIONS

2.3.1 General economic considerations

The dangers of oversimplifying materials economics have been pointed out in Section 1.2.3. It is, however, possible to make qualitative comparisons of GRC with other materials on a basis of properties.

GRC composite panels make up for much of their high production expense by virtue of the low transport and handling costs due to their lightness, which in turn may make possible considerable economies in design. Furthermore, the low density enhances their utilisable strength on a strength/weight basis (see Table 1.3).

Again, although they possess a lower elastic modulus than most metals, GRC composites have a lower (i.e. more advantageous) weight/stiffness parameter. In addition to this, it has been calculated that in the fabrication of complex panel shapes, where double curvature can be incorporated more easily into fibre composites than into steel, the ratio of forming to materials costs for steel is roughly triple that for fibre composites (Fibreglass 1964).

Biryukovitch (1964), basing his estimation on a superior type of GRC composite, quotes the following economic advantages of GRC for assembled products:

Total cost	$= \frac{1}{20} - \frac{1}{100}$ cost of GRP.
Cost for use in tension	$= \frac{1}{6} - \frac{1}{12}$ cost of concrete.
Cost of completed roof shell	$= \frac{2}{7}$ cost of comparable roof in reinforced concrete.

2.3.2 Applications

Unlike GRP composites, GRC materials are not only non-

flammable, but have considerable thermal stability up to 500°C, and are finding considerable use in sandwich panels, thin cladding panels, shuttering and utility building sections with zero fire hazard (Elkalite 1968). They do not, however, provide as great a thermal insulation as asbestos-cement, but are nevertheless used as cladding for railway points heaters and as silage containers (Peters 1970). They have greater water resistance than GRP's (especially at high temperatures) and are non-toxic, and so are ideal for water-containing uses: GRC tanks, pipes and water-panels, troughs, dams and sluice-gates have been manufactured in the U.S.S.R. (Biryukovitch 1964).

The possibility of making large and light mouldings of fairly intricate shape without using expensive moulding machinery has led to the manufacture of curved shells and domes, of and/cellular panels capable of taking relatively large loads with broad spans, such as the factory or pavilion roofs in Kiev (Biryukovitch 1964). Such structures utilise the weight/stiffness advantage of GRC's to the maximum - as do box-beams and T-beams. Trusses may be made exceptionally strong, as individual strut members may be fabricated by the winding method (see Section 2.2.2).

The high impact strength of GRC's relative to concrete suggests possibilities of improving the resistance of precast concrete products to accidental damage by cladding. However, glass fibres are probably not the best reinforcement for impact

strength, and sheets of polymer fibre/cement may give better protection (see Section 1.4.3).

2.4 IMPROVEMENT OF THE PROPERTIES OF E-GLASS/HAC COMPOSITES

2.4.1 Existing data

Table 2.1 lists typical properties of GRC composites as found in the literature: values for other composite systems are included for comparison. The Biryukovitch data is part of a study of the stress-strain characteristics of unidirectionally reinforced laminates in tension which gives mechanical properties at the limit of proportionality, at cracking and at failure over a range of V_f values. In general it was found that $\sigma_c \propto V_f$, but strain did not reach expected values at higher glass contents.

Further information is to be found in the Biryukovitch monograph (1964), including an outline of the results of investigations of the effect on tensile, compressive and flexural strength of the following parameters: water/cement ratio (optimum 0.5), age and fatigue. (It is interesting to note that a similar optimum was found by Pashchenko (1965) in a study of the variation of adhesion between glass and cement with w/c ratio.) Similar effects have been studied by Grimer & Ali (1969), Patterson (1970), Fulton (1968), and Cousins (1970). The significance of these investigations is discussed in greater detail in the relevant chapters.

Typical properties of fibre composite materials

Material type (see Table 2.2)	Tensile stress			Tensile modulus		Tensile strain			Flexural strength ϕ_c (MNm^{-2})
	σ_c^u	σ_c^{σ}	σ_c^e	E_c^e	E_c^r	ϵ_c^u	ϵ_c^{σ}	ϵ_c^e	
	(MNm ⁻²)			(GNm ⁻²)		(%)			
1	17	8	-	15	2	0.3	0.5	-	-
2	25	10	5	20	-	-	0.4	0.03	-
3	92	85	32	30	-	-	0.9	0.1	-
4	125	125	48	50	-	-	0.3	0.1	-
5	61	47	-	29	-	0.8	-	-	85
6	43	33	-	37	-	0.4	-	-	76
7	9	-	-	-	-	-	-	-	28
8	12	-	-	-	-	-	-	-	35
9	17	-	-	-	-	-	-	-	45
10	15	-	-	-	-	-	-	-	34
11	(28)	(25)	8	11.2	2.6	1.4	1.0	0.1	56
12	6.8	-	-	-	-	-	-	-	15
13	7.8	-	-	-	-	-	-	-	27
14	10.3	-	-	-	-	-	-	-	25
15	14	-	-	-	-	0.4	-	-	28
16	11	-	-	-	-				25
17	12	-	-	-	-	1	-	0.1	22
18	14	-	-	-	-				34
19	17	-	-	-	-				36
20	313	-	110	18.6	-	1.8	-	0.6	-
21	274	-	60	14.3	-	1.6	-	0.4	-
22	67	-	18	4.7	-	1.6	-	0.4	-

Table 2.1

Composite material types

Material type	System	Type of reinforcement	η	V_f (%)	References
1	E-glass/ HAC	Random mat	$\frac{1}{8}$	11*	Fulton (1969), Ch n & Patterson (1970)
2	E-glass/ HAC	Unidirectional	1	2*	Biryukovitch (1964)
3				10*	
4		Unidirectional	1	15*	
5				6*	
6		Random mat or woven cloth	$\frac{1}{8}$	7*	
7	E-glass/ HAC	Random chopped mat - vacuum compacted	$\frac{1}{8}$	3*	Grimer & Ali (1969)
8				5*	
9				8*	
10	E-glass/ HAC	Random mat	$\frac{1}{8}$	7	Kendellstone (1968)
11	E-glass/ OPC	Random mat	$\frac{1}{8}$	9	Krenchel (1964)
12	E-glass/ OPC	Pressed slurry random mat	$\frac{1}{8}$	4*	Grimer & Ali (1969), Majumdar & Ryder (1968)
13				6*	
14				9*	
15	Asbestos-cement	Pressed slurry random mat	$\frac{1}{8}$	9*	Grimer & Ali (1969)
16	α -gypsum	Pressed slurry random mat	$\frac{1}{8}$	4*	Ali & Grimer (1969)
17	GRG			8*	
18	β -gypsum			5*	
19				10*	
20	GRP : polyester	Rovings	1	25	Krenchel (1964)
21		Woven cloth	0.58	32	
22		Random mat	$\frac{1}{8}$	10	

* values of V_f estimated from W_f (see Equation 4.19)

Table 2.2

2.4.2 Areas for Improvement

It is worthwhile at this stage to summarise some of the ideas discussed above with respect to possible improvements to E-glass/HAC composites. Suitable areas for further research will be dealt with in greater detail in later chapters.

The toughening of cementitious materials with organic polymer fibres of low strength and modulus has already been considered (1.4.3). As this type of reinforcement may prove useful in conjunction with glass reinforcement (Mullin 1968, Allen 1970), mechanisms of toughening will be considered further in Chapter 5.

In glass/cement systems, where fibres and matrix have similar moduli of elasticity, the most efficient transfer of stress to fibres is likely to occur by plastic deformation (Baker 1966) or shear (Corbett & Walton 1966) of the matrix (see Chapter 4). Attempts to increase the "ductility" of cement usually take the form of adding latex (Biryukovitch 1964) or organic plasticisers such as p.v.a. (Krenchel 1964), but these reduce the strength of the matrix (Allen 1970) and do not increase composite strength significantly.

Theoretically, load transfer could be increased by prestressing the fibre, but this would be almost impossible to effect in practice. However, a similar result can be achieved by precompressing the matrix (Plant et al. 1961) or by

using expanding cement (Krenchel 1964).

Allen (1970) has shown that increasing fibre strength improves the failure strength of GRC composites but not their cracking strength, which is the effective working limit. Stronger and stiffer glass fibres do in fact exist (see Section 3.1.1), but their extra cost is unlikely to be justified in the small improvements achieved in composite properties. Raising the glass content as far as cost increases will permit is much more effective, but upper limits are set by the ability of cement paste to impregnate the reinforcement properly (see Table 1.4). Lower limits are governed by the critical volume fraction of fibres: see Section 4.2.2.

The role of the interface in the fracture of fibre composite materials has been considered in great detail by Cooper & Kelly (1969), and in view of the importance of matrix-to-fibre load transfer this subject is developed further in later chapters. Thus Cook & Gordon (1964) consider that in all brittle systems, if the ratio of interfacial adhesive strength to matrix cohesive strength is in the right range, then large increases in strength and toughness of the composite may result, as cracks will be deflected by cleavage planes. Mullin (1968) has come to a similar conclusion.

CHAPTER THREE: GLASS AND CEMENT: BACKGROUND

3.1 GLASS AND GLASS FIBRES

3.1.1 Composition and Properties of Bulk Glass

The theoretical strength of glass has been calculated by various workers as up to 30 GNm^{-2} (Marsh 1964, Sugarman 1967), and experimental strengths of fused silica fibres under ideal testing conditions (low temperature, vacuum) of up to 12 GNm^{-2} (Morley 1964, Proctor 1967), 14 GNm^{-2} (Hillig 1961) and 24 GNm^{-2} (Anderegg 1939) have been obtained. Most glasses possess an elastic modulus up to their breaking point of about 70 GNm^{-2} (see Table 1.1), but the expected high strains to fracture are seldom realised in practice, when the strength of the glass depends very much on its surface state. Griffith,

in 1920, proposed a theory of propagation of cracks to account for this which, with modifications to allow for plasticity (Orowan 1944), gives realistic calculated strengths. Marsh (1964) has developed an alternative elastic-plastic theory, in which plastic flow stresses (determined by network modifiers such as absorbed water) play an important role in fracture and can explain the high fracture energy of bulk glass.

The elastic modulus of a glass can be increased 50% by filling the interstices of the silicate network with ions of a high field strength ("network modifiers" such as Mg^{2+} , Ca^{2+} ,

Ti⁴⁺, Be²⁺, Li⁺) and by reducing the content of network formers (Si, Al, B): see Table 3.1 (Loewenstein 1961, 1967). But since the strength of glass depends so little on its bulk composition (Bartenev 1969), most attempts at raising it take the form of introducing compressive forces into the skin layers in order to reduce the likelihood of breaks in tension. Thus although substitution of an ion with a large volume such as Pb²⁺ for Ca²⁺ and Mg²⁺ into the bulk composition of a glass has no significant effect on its strength (Mitchell 1969), surface ion exchange with molten salts of Pb²⁺ (Loewenstein & Parvin 1962, Sonders et al. 1950), Ag⁺ and K⁺ (Ray et al 1967, Ray & Stacey 1969, Cooper & Krohn 1969), all of which are larger than the displaced Na⁺, results in a permanent increase in strength accompanied by a reduction in surface tension. Krohn & Cooper (1969) have achieved surface compression of borosilicate glass by cladding it with a silica glass of higher thermal expansion.

3.1.2 The Glass-Water Interface

Most glasses are very sensitive to the presence of water, which probably exists as a layer about 100 molecules thick on glass fibres under normal humidities as an extension of the oxygen network in the glass (Kawasaki et al. 1964, Loewenstein & Parvin 1962). The dynamic equilibrium of water on glass surfaces has been studied in relation to the isotherms of physical or H-bonded adsorption by Lange (1965), whereas Yates & Trebilcock (1961) have developed a chemical model of the

Glass fibre compositions

	SiO ₂	CaO	Al ₂ O ₃	B ₂ O ₃	Na ₂ O + K ₂ O	MgO	ZrO ₂	Li ₂ O, BeO, TiO ₂ , CeO ₂	References
	(%)								
E-glass	55.2	17.7	14.8	7.3	0.5	4.3	-	0.2	"FGRE 2" (Fibreglass Ltd)
U.S.S.R. non-alk. glass	54.4	16.4	14.8	9.4	0.5	4.4	-	-	Pashchenko et al. (1965), Budnikov et al. (1965)
A-glass	72.0	9.0	2.5	0.5	14.0	0.9	-	-	Loewenstein (1967)
U.S.S.R. alkaline glass	71.8	7.5	3.1	-	12.9	4.1	-	-	Pashchenko et al. (1965)
B.R.S. alkali- resistant glass	71	-	1	-	11	-	16	-	Majumdar & Ryder (1963)
High- modulus glass	53.7	12.9	-	-	-	9.0	2.0	22.0	Loewenstein (1961)

Table 3.1

surface in terms of polymeric acidic silanol groups. Adsorbed water may then diffuse into the interior of the glass (Haller 1963), where it may modify its structure and hence mechanical properties (Hetherington & Jack 1962, Jelli 1965).

Although water is capable of leaching a considerable amount of matter from glass (Das & Douglas 1967), the commonest etchant used to increase the strength of glass by smoothing out surface cracks and asperities is hydrofluoric acid (Proctor 1962, Symmers et al. 1962), which may increase the tensile strength of bulk glass by an order of magnitude, but at the same time making it very sensitive to surface damage and heating (Ray & Stacey 1969). Recently, however, the etching ability of alkalis have been investigated, and Lesnikov & Bykodorova (1968) have found that NaOH, KOH and NH_4OH are particularly efficient at strengthening quartz glass. With alkali silicates the rate of etching appears to depend on the $\text{SiO}_2:\text{Na}_2\text{O}$ ratio (Ray & Johnson 1967), a maximum being obtained at 2:1 possibly because of the formation of a more soluble surface layer on the glass (Smith & Corbin 1949). With both acid and alkali etching, the strength varies in a similar fashion with the amount of glass removed, and with subsequent heat treatment: Ray & Johnson (1967) consider that water must be the common factor responsible.

3.1.3 Glass Fibres

When drawn from melts into fibres (see Section 8.1.1)

glass acquires properties slightly different from those it has in bulk. The reduction in density of about 2% and in elastic modulus (Loewenstein 1967) has been ascribed to orientation of the whole fibre structure (Bartenev & Bovkumenko 1956), and Otto (1961) has observed that on subjecting fibres to heat treatment these properties return to normal as the structure rearranges itself into a lower energy state - a phenomenon known as compaction.

It is more likely, however, that the exceptionally high strengths observed in glass fibres are due to their near-perfect surfaces (Sugarman 1967), and studies in the electron microscope by Zarzycki & Mezard (1962) and by Sterman & Bradley (1961) and in the scanning e/m by Bott & Barker (1968) have shown that surfaces are smooth to the order of a few nm. Bartenev (1969a&b) has investigated the strength distribution of both bulk and fibrous glass and has found statistical and topographical evidence for the existence of five discrete strength levels in glass depending on the severity of various flaws which may be present: see Fig. 3.1.

Thomas (1960) has shown that the strength of 'virgin' fibres is independent of diameter in the range 5-15 μm (i.e. that of most reinforcements) and that previous work by a number of authors showing that strength was approximately proportional to diameter was due to poor control of experimental factors such as melt temperature (Cameron 1966), humidity and surface damage (see Fig. 3.2(a)). Hagen (1956) supports this view and considers that the diameter dependence will always be observed under all but the most rigorous testing conditions (see Loewen-

Strength Levels in Glass

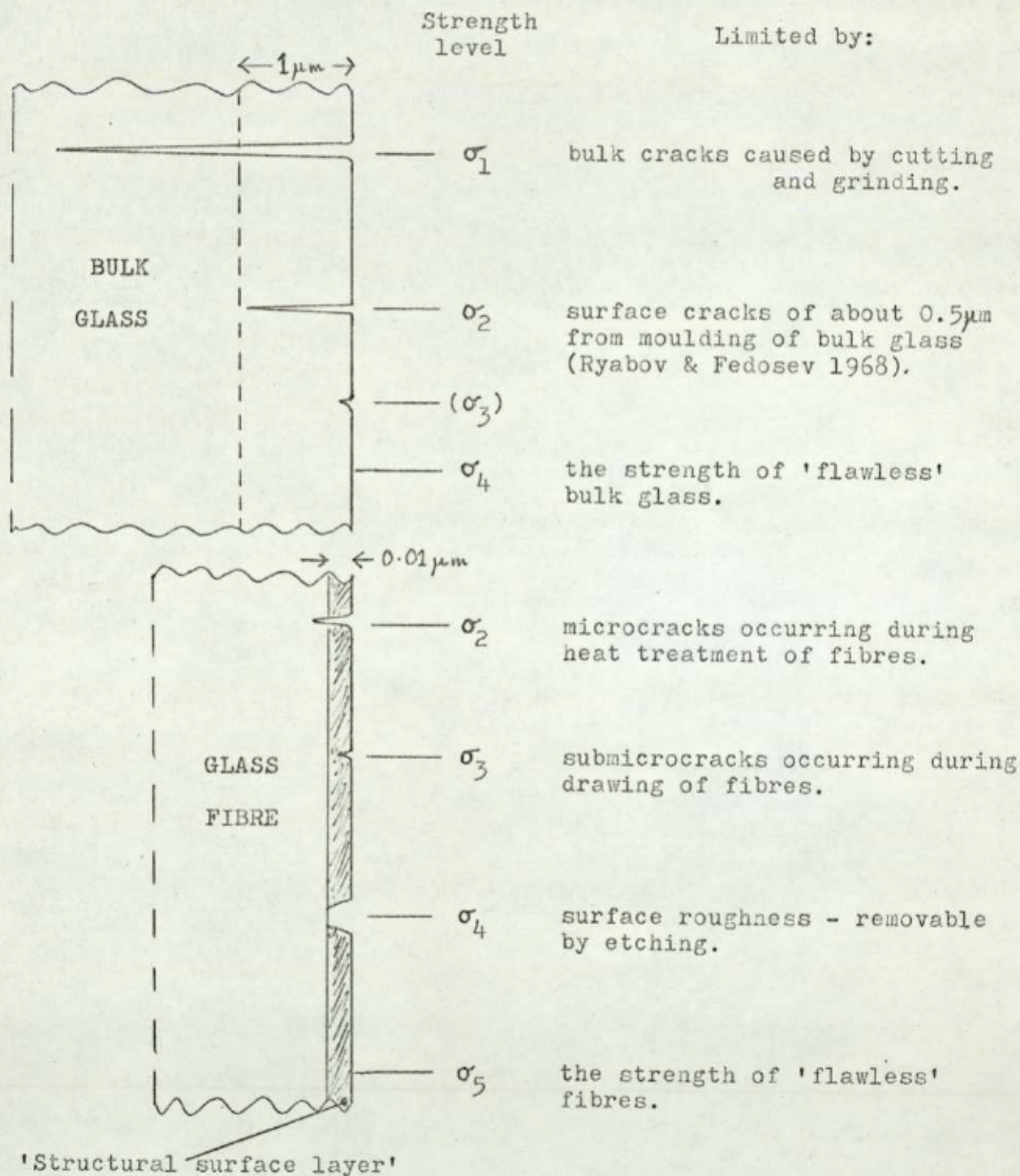
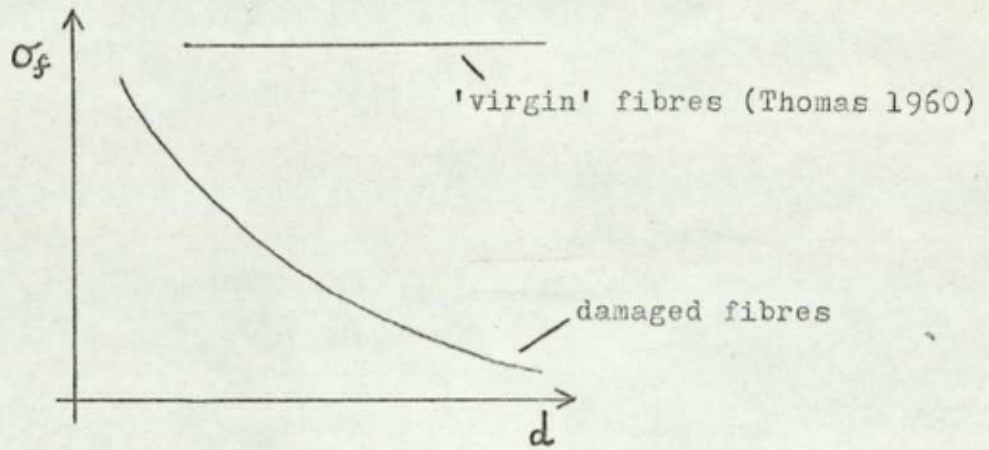


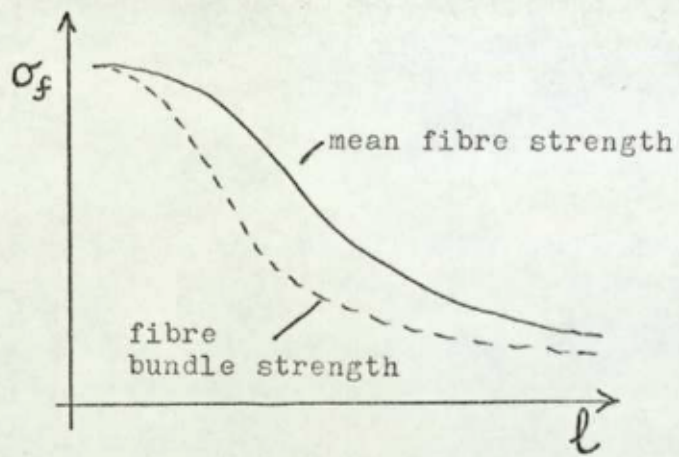
Figure 3.1

Fibre strength distributions



vs. diameter

(a)



vs. length

(b)

Figure 3.2

stein & Dowd 1968).

Metcalf & Schmitz (1964) have investigated the effect of length on the strength of fibres and found that it could be explained by a distribution of flaws similar to Bartenev's (1969). Weibull's (1951) original "weakest link" theory has been modified by Kies (1958) to take account of the upper limiting strength of virgin glass (σ_5 in Fig. 3.1), and theoretical strength/length distributions agree well with those obtained experimentally. Both are similar to strength/diameter distributions, so that fibre strength ^{should} vary inversely with the product of flaw density and surface area.

Fibre strength statistics (Wallhaus 1962, Rosen 1965, Robinson 1970) may be extended to explain why the strength of bundles is lower than the mean fibre strength (see Fig. 3.2(b)), and decreases with increasing dispersion in the strength of its constituent filaments (Coleman 1958). This may be because the probability of fracture of the weaker fibres increases as the stress is raised (Parrat 1960).

3.2 HYDRAULIC CEMENTS

3.2.1 General Properties

The physical and chemical properties of cements are so well documented that we need be concerned only with those properties, especially of high alumina cement, which are likely

to be of importance to a composite matrix.

The tensile strength of brittle materials such as cement and concrete is not easy to measure as specimens have to be suitably shaped to avoid point stresses. Three- or four-point bending, indentation and diametral compression tests all give more reliable results than most (Berenbaum & Brodie 1959), but Roper & Bryden's (1964) centrifugal force test is claimed to distribute the stresses as evenly as possible. However, Malhotra (1965) has suggested that a ring tensile test is even more practicable and has shown (Malhotra & Zoldners 1967) that reproducibly high values of strength can be obtained from it.

Observed strengths may be correlated mathematically with the structure of concrete, and many structural models have been proposed (Hansen 1960a, Dougill 1967, Popovics 1967). Concrete is an extremely complex material, and the cement-paste /aggregate interface in particular merits detailed attention (see Section 5.2.1). X-ray diffraction (Grudemo 1960, 1965, 1966), and transmission and scanning electron microscopy (Mills 1969) have revealed Portland cement to be a porous mass of interlocking needle- and plate-shaped crystals bound together by a continuous gel of calcium silicate hydrates (Chatterji & Jeffery 1967). But there are so many divergent interpretations of the fine structure of set cement that it is possible that more than one microstructure is characteristic of the pastes (Midgley 1969).

3.2.2 High Alumina Cement

Table 3.2 gives the compound composition of typical British high alumina (HAC) and ordinary Portland (OPC) cements, which were used in the practical part of this investigation. A Russian HAC of the type used for E-glass/HAC compatibility studies is included for comparison, where it may be seen that only the iron and alkali contents may be significantly different. In fact no chemical composition is given for the HAC used in composite studies by Biryukovitch and his school, but although the alkali content (a rather crucial parameter in this case - see Chapter 6) is still not known, the iron content of some Russian HAC's can be as high as in British ones (Biryukoviych 1964).

The early hydration of OPC and HAC pastes is dealt with from a point of view of ionic concentrations and chemical attack on silicates (e.g. aggregate minerals or glass fibres) in Chapter 6, but in setting cement paste it is the phase structure which largely determines the morphology and hence strength development. At temperatures below about 22°C the main products of hydration of HAC are the hexagonal hydrates CAH_{10} and CA_2H_8 , contained in a hydrated alumina gel (Chatterji & Jeffery 1963): these hydrates are only metastable, however, and slowly change to the cubic C_3AH_6 and gibbsite ($\gamma-AH_3$) (Jones 1960, Percival 1960, Wells & Carlson 1956, Cooper 1965). This phenomenon is known as conversion and is accelerated by higher temperatures and water/cement ratios: it usually causes

Chemical compositions of cements

compound	British HAC	Russian HAC	British OPC	Calcium aluminate cement
SiO ₂ (S)	4.6	11.7	20.2	0.4
Al ₂ O ₃ (A)	39.5	45.4	5.9	71.9
CaO (C)	37.5	39.2	64.5	26.4
Fe ₂ O ₃ (F)	9.0	1.7	2.1	-
FeO (f)	6.0	-	-	-
MgO (M)	1.0	1.0	1.2	-
TiO ₂ (T)	1.6	1.5	0.3	-
Na ₂ O + K ₂ O (N)	0.3	?	0.7	0.3
SO ₃ (s)	0.1	0.3	2.7	-
Free lime	?	?	3.0	-
H ₂ O (H)	-	-	-	-
Reference	Lafarge "Ciment Fondu"	Pashchenko et al. (1965)	CMC "Blue Circle"	Lafarge "Secar 250"

Table 3.2

a reduction in strength due to a volume loss accompanied by the creation of voids. Some Hungarian workers consider the strength loss and void formation to be a serious drawback to the use of HAC under any conditions (Schwiete et al. 1965, Talaher 1967, Dolezsai & Revay 1966), but there is evidence to show that controlled hydration at elevated temperatures and low w/c ratios may produce a high strength converted product (Tseung & Caruthers 1963, Midgley 1967). The effects that conversion may produce in composite materials are dealt with in Chapter 5.

The changes in phase composition of a hydrating cement may be followed by infra-red spectroscopy (Lehmann & Dutz 1960) or by microscopy (Cottin 1969, Chatterji & Jeffery 1968). Lehmann & Dutz (1960) showed that individual phases in HAC hydrated at rates $C_3A > C_{12}A_7 > CA$, the rate of total cement hydration being intermediate between the first two in the series. Chatterji & Majumdar (1966a) found $C_{12}A_7 > CA > CA_2$, Buttler & Taylor (1959) $CA > CA_2$, and Tseung (1960) $CA > \text{Secar 250 (65\% CA, 25\% CA}_2, 10\% A) > CA_2$, so it is fairly conclusive that hydration rate increases with increasing C/A ratio in the calcium aluminate series. In the alumino-ferrite series the rate decreases with increasing F/A ratio (Majumdar & Chatterji 1966b), and Chatterji & Majumdar (1966c) and Buttler & Taylor (1959) conclude that Ca^{2+} ions accelerate or that Al^{3+} ions retard the hydration process. It should thus be possible to estimate $\frac{\text{relative}}{\text{hydrate phase growth}}$ $\frac{\text{rate}}{\text{from initial dry cement phase composition}}$, enabling some correlation to be made with such factors as bond strength development of E-glass / HAC composites.

In addition to chemical composition, the physical composition of HAC is likely to be of particular significance to fibre reinforcement. The particle size distribution of HAC powder is typically as in Figure 3.3 (Robson 1962, Cooper 1965): i.e. the median size is about $50\mu\text{m}$. It seems that although hydration changes the morphology of the crystals significantly, their size changes little, as evidenced by surface area measurements (Cooper 1965). A scanning electron micrograph of Secar 250 after 1 week's hydration at room temperature (Figure 3.4: Chatterji & Jeffery 1968) shows hexagonal plates (C_2AH_8 , carboaluminate?) and needles (CAH_{10}) separated by what appears to be a fair amount of space, although the porosity of HAC (as measured by vacuum drying) is usually of the order of only a few percent (Midgley 1967), and increases with decreasing water/cement ratio.

Typical particle size distribution of HAC powder

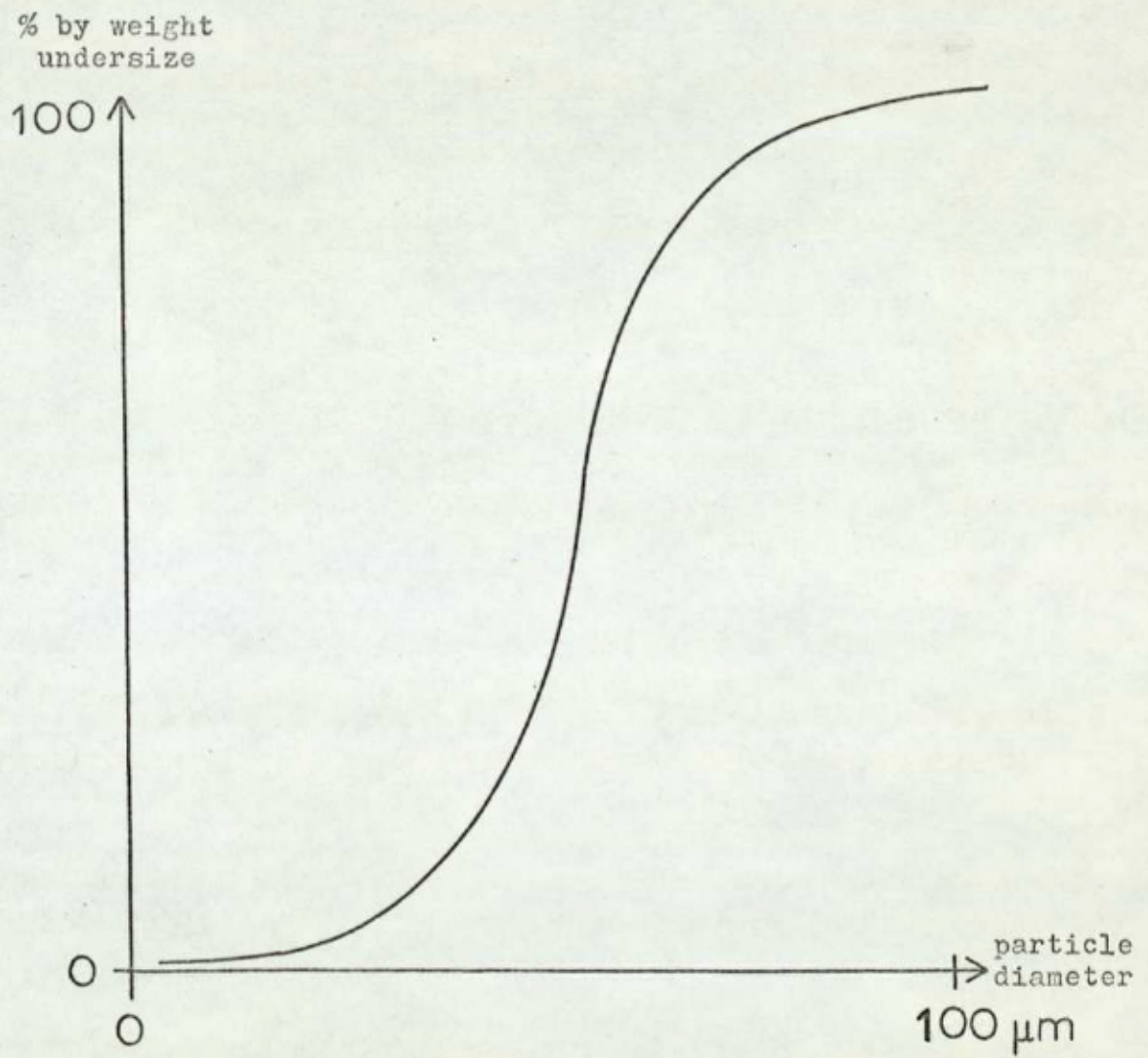


Figure 3.3

Morphology of hydrating calcium aluminate cement

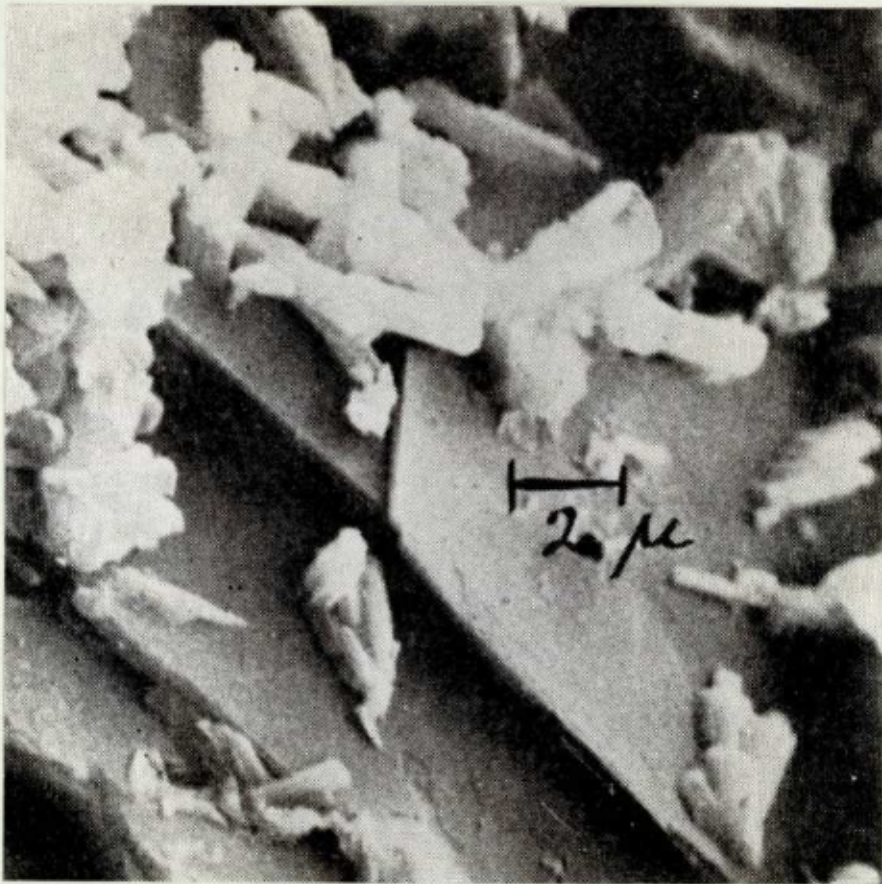


Figure 3.4

CHAPTER FOUR: THEORETICAL COMPOSITE STRENGTH

4.1 CALCULATION OF THE MECHANICAL PROPERTIES OF COMPOSITES

4.1.1 General Materials Considerations

The original theory of Griffith (1920) for the critical stress necessary to initiate crack growth has proved to be very adaptable, especially when ways of absorbing energy other than by creation of new surfaces are considered (McLean 1969). It has formed the basis for many theories of strength of brittle (Pugh 1967) and porous (Biggs 1967b) materials such as concrete (Kaplan 1965), as well as for fibre-reinforced (Romualdi 1965) or microfissured (Jenkins 1969) materials. The increase of toughness and arrest of cracks afforded by fibre reinforcement will be discussed further in Section 5.1.

However, although the tensile strength of materials is generally the easiest strength parameter to investigate mathematically, this is not always so experimentally, especially for brittle materials. But tensile strength may be deduced from indirect measurements of bending or splitting strengths (Berenbaum & Brodie 1959) if it cannot be measured directly (see Section 3.2.1), and since it represents a more 'absolute' criterion than other strengths, it will be used in this chapter as the principal means of comparison between experimental and theoretical strength values.

4.1.2 Theories of Fibre Reinforcement

Generalised theories of the distribution of stress round inclusions in a plastic, elastic (linear or non-linear) or viscous matrix are well documented in the literature (Biggs 1967b). In the case of cylindrical inclusions with a large aspect ratio $\frac{l}{d}$, the problem tends to one of matrix to fibre stress transfer, and the solutions obtained on this micro-level may be applied to the whole composite. Thus Rosen (1964) has shown how a statistical distribution of fibre 'link lengths' (calculated by a shear-lag type analysis - see Section 4.4) may be used to estimate composite failure stress, and he has evaluated the internal failure process by microscopic examination of test specimens. Finite-element analysis is ideally suited to fibre composites, and has been compared with other analytical methods by Carrara & McGarry (1968): on the experimental side, photoelastic analysis of epoxy models reinforced with aluminium alloy bars has been used to verify the validity of finite-element and shear-lag analyses of interfacial stress fields by Chen & Lavengood (1969) and Tyson & Davies (1965).

These methods of elastic analysis may be adapted to take into account some plastic deformation (Biggs 1967b, Piggott 1966), but they tend to assume ideal stress transfer conditions, and the low fibre/matrix modulus ratio, discontinuity of interfacial bond and complex porous microstructure of the matrix in cement systems preclude their application to GRC composites.

4.1.3 Rule of mixtures

Upper and lower bounds for the elastic moduli of hetero-phase materials may be established in terms of their constituent phase moduli by considering the two possible extreme arrangements of phase. For the parallel model, where each phase receives a constant strain, the composite modulus E_c is

$$E_c = E_1 V_1 + E_2 V_2 + \dots \quad (4.1)$$

whereas for the series model (constant stress)

$$\frac{1}{E_c} = \frac{V_1}{E_1} + \frac{V_2}{E_2} + \dots \quad (4.2)$$

(For a full explanation of the nomenclature used for these and subsequent mathematical expressions see Appendix 1)

In general the parallel model represents the upper bound, and the series model the lower, and these bounds are closest when E_1 and E_2 are equal (cf. Figure 4.1, which applies to composite stress rather than to modulus).

This basic concept has proved useful in simple composite systems with similar phase moduli (Biggs 1967b) and even in concrete systems (Newman 1967), and closer bounds may be derived from more rigorous approaches based on variational principles (Hashin & Shtrikman 1963, Hill 1964, 1965). While such methods may yield extremely accurate values of composite moduli (bulk, elastic and shear), they do not take into account maximum permissible stresses or strains for each phase

Variation in tensile strength of GRC composites with glass content

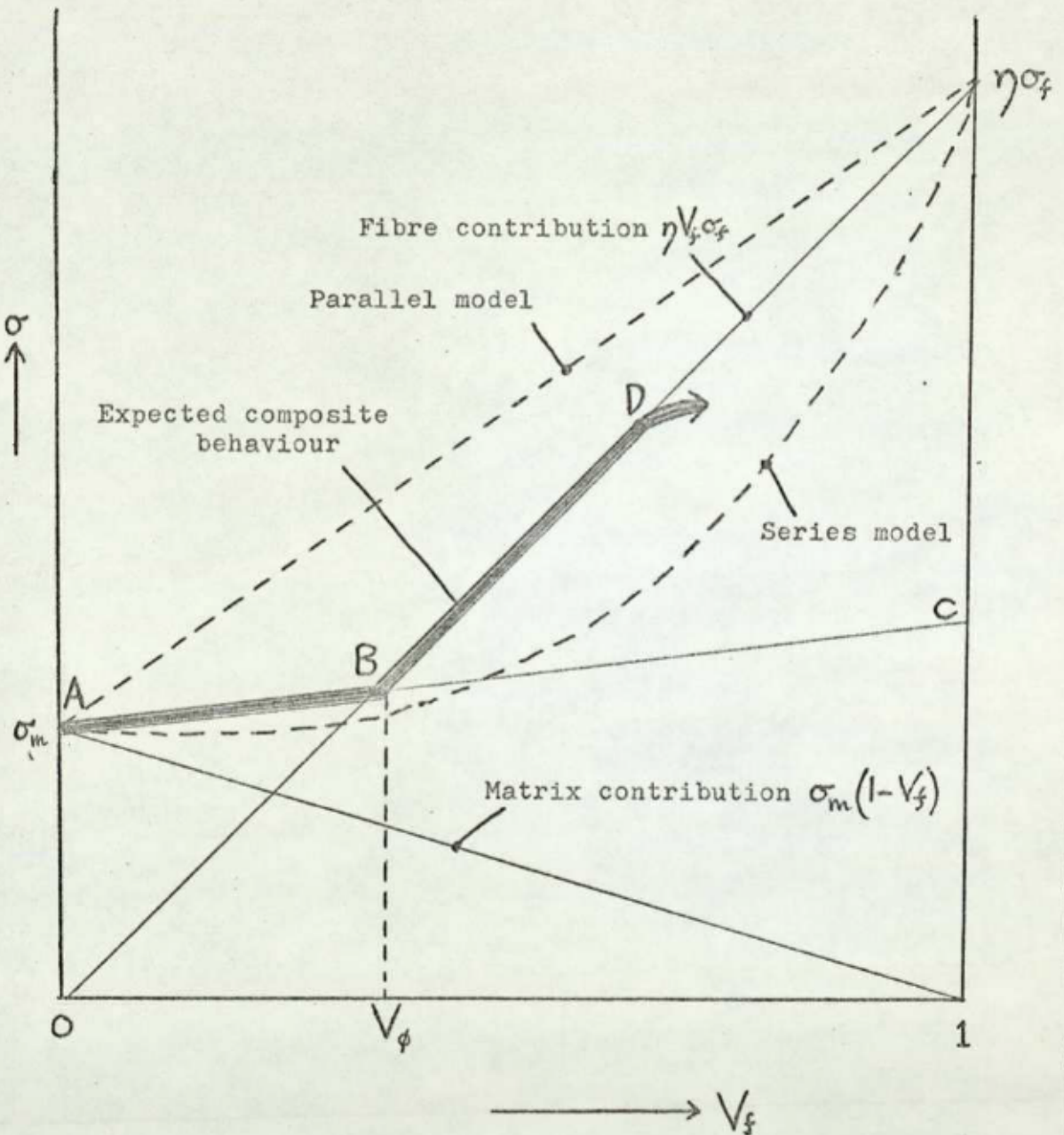


Figure 4.1

and therefore cannot be reliably used to predict failure strengths. In order to do this it is necessary to investigate possible modes of failure each with its own limiting value of stress or strain, and to incorporate these values into simple mixture equations.

Each equation used in the following analysis has been derived from a particular literature source where the author was interested in only one aspect of composite failure. The novelty of our approach is in applying one of these failure limits to a law of mixtures type of equation to get a value for composite ultimate strength, and in comparing the set of values thus obtained for different failure modes.

4.2 MODIFICATION OF THE RULE OF MIXTURES FOR DIFFERENT

FAILURE MODES

4.2.1 Efficiency of reinforcement

As the essence of our approach is the use of simple algebraic manipulations rather than of complex initial boundary conditions, we shall start with the simplest model of a fibre/matrix system governed by the following conditions:

(i) The fibres are aligned parallel to the tension axis and are not in contact with each other, being uniformly distributed in the matrix.

(ii) The fibres are all of continuous length across the model, and are uniform in diameter and fully bonded to the matrix.

- (iii) Both fibre and matrix materials are fully elastic.

These conditions satisfy the constant strain model (Equation 4.1) and we may therefore write

$$E_c = (1-V_f)E_m + V_f E_f . \quad (4.3)$$

If we now have as a further condition that

- (iv) The strains to failure of the matrix, fibres and hence composite are all equal, the ultimate composite strength is then

$$\sigma_c^u = (1-V_f)\sigma_m^u + V_f \sigma_f^u . \quad (4.4)$$

If the fibres are not all aligned parallel to the tension axis they may be treated as groups of parallel fibres of volume fraction V_θ lying at an orientation θ to the axis.

Krenchel, in a detailed treatise on both theoretical and practical aspects of fibre reinforcement (1964), has shown that the load-carrying capability of the fibres is reduced by a factor η (the "efficiency of reinforcement") where

$$\eta = \sum \cos^4 \theta \quad (4.5)$$

The following values of η may be derived for various geometries of reinforcement:

- $\eta = 1$ tension along parallel fibres
- $\eta = \frac{1}{2}$ tension along weave of equally woven cloth
- $\eta = \frac{1}{8}$ random fibres in a plane
- $\eta = 0$ tension perpendicular to parallel fibres.

Equation (4.4) may thus be written more generally as

$$\sigma_c^u = (1 - V_f) \sigma_m^u + \eta V_f \sigma_f^u \quad (4.6)$$

This simple equation ignores the Poisson effect of lateral contraction which Krenchel included in his derivation of theoretical properties of GRP systems, but this may be justified by the fact that in GRC systems the fibre content is small and both Poisson's ratio and strain to failure of the matrix are low (ca. 0.2 and 10^{-4} respectively), and the simplification does not affect the results by more than a few percent. Moreover, deviations from linearity are far more likely to be caused by variations in the macro-homogeneity of the composite.

4.2.2 Composite strength limited by the tensile strength of either phase

As the practical upper limit to fibre content for a particular type of reinforcement is approached (see Table 1.4) it becomes difficult to impregnate the fibres thoroughly with cement, and voids are formed. The consequence of this is to reduce the effective modulus of the matrix by an amount roughly proportional to the void concentration, with a resultant decrease in the value of σ_c^u : this effect is shown at values of V_f above point D in Fig. 4.1 (cf. Allen 1969).

If, at lower values of V_f , the strain to failure of the

matrix is below that of the fibres, the stress in the fibres at failure of the matrix is

$$\sigma_f = \epsilon_m E_f = \sigma_m^u \frac{E_f}{E_m} \quad (4.7)$$

Substituting this value for fibre stress into Equation (4.6) we get a composite strength at matrix failure of

$$\sigma_c^m = \sigma_m^u \left[(1 - V_f) + \eta V_f \frac{E_f}{E_m} \right] \quad (4.8)$$

This composite cracking stress is shown as the line ABC in Figure 4.1. At values of V_f greater than V_ϕ , however, the concentration of fibres is sufficient to hold the composite together even though the matrix has started to crack. The value of V_ϕ , the critical fibre volume fraction, is given by

$$\eta V_\phi \sigma_f^u = (1 - V_\phi) \sigma_m^u + \eta V_\phi \frac{E_f}{E_m}$$

$$\text{or} \quad V_\phi = \frac{1}{\eta \left(\frac{\sigma_f^u}{\sigma_m^u} - \frac{E_f}{E_m} \right) + 1} \quad (4.9)$$

Thus the expected behaviour of the composite at higher values of V_f lies below the upper bound and probably above the lower.

An argument analagous to that used to derive Equation (4.7) shows that if composite strain conditions allow the fibres to fail in tension then the composite failure stress is

$$\sigma_c^f = \sigma_f^u \left[(1 - V_f) \frac{E_m}{E_f} + \eta V_f \right] \quad (4.10)$$

4.2.3 Composite strength limited by interfacial strength

In the process of transfer of load from matrix to fibre, a certain portion of the fibre at each end is ineffective because it is unable to carry the full tensile load. It is reasonable to assume that to a first approximation the rate of stress transfer at the fibre ends is linear (Kelly 1964, Kelly & Davies 1965), and a stress distribution is obtained as in Fig. 4.2(a). The mean stress in the fibre, $\bar{\sigma}_f$, is related to the maximum stress σ_f by

$$\bar{\sigma}_f = \sigma_f \left(1 - \frac{\lambda}{2l}\right) \quad (4.11)$$

where $\frac{\lambda}{2}$ is known as the transfer length of the fibre. If we assume the interfacial shear stress τ_i to be constant over this length (see Section 9.3 for a more detailed exposition) we may equate the interfacial shear load along this transfer length with the fibre load.

$$\text{i.e. } \pi d \frac{\lambda}{2} \cdot \tau_i = \frac{\pi d^2}{4} \cdot \sigma_f \quad (4.12)$$

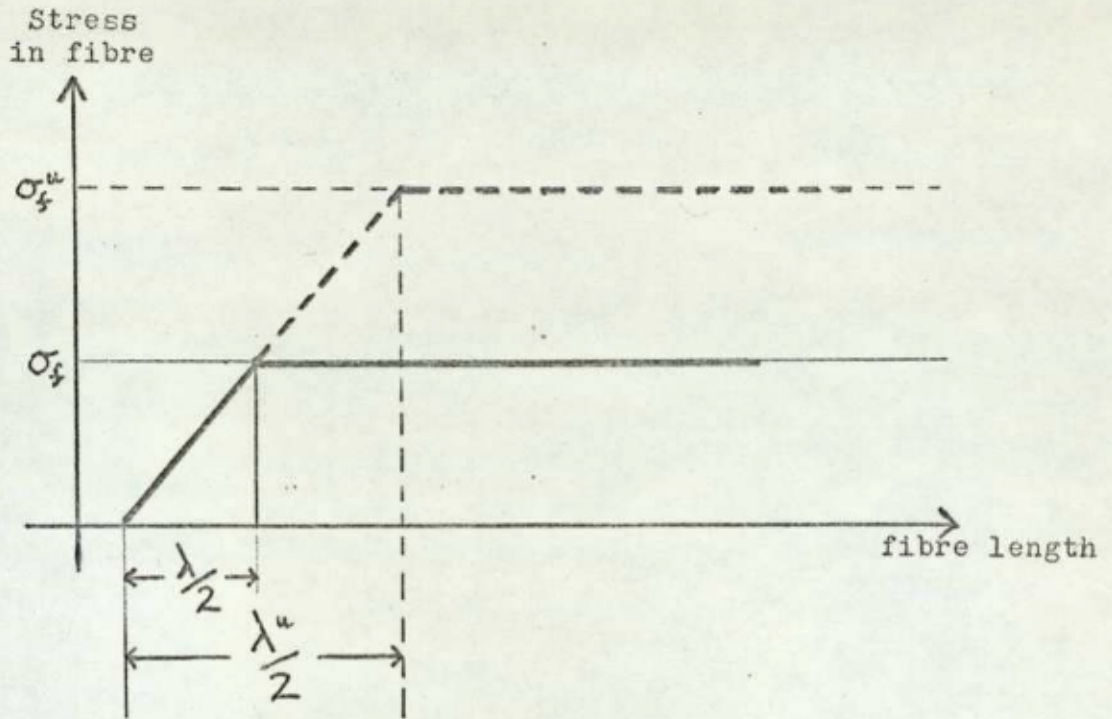
As the composite load is increased to the limit of fibre strength σ_f^u , we have

$$\lambda^u = \frac{\sigma_f^u d}{2 \tau_i^u} \quad (4.13)$$

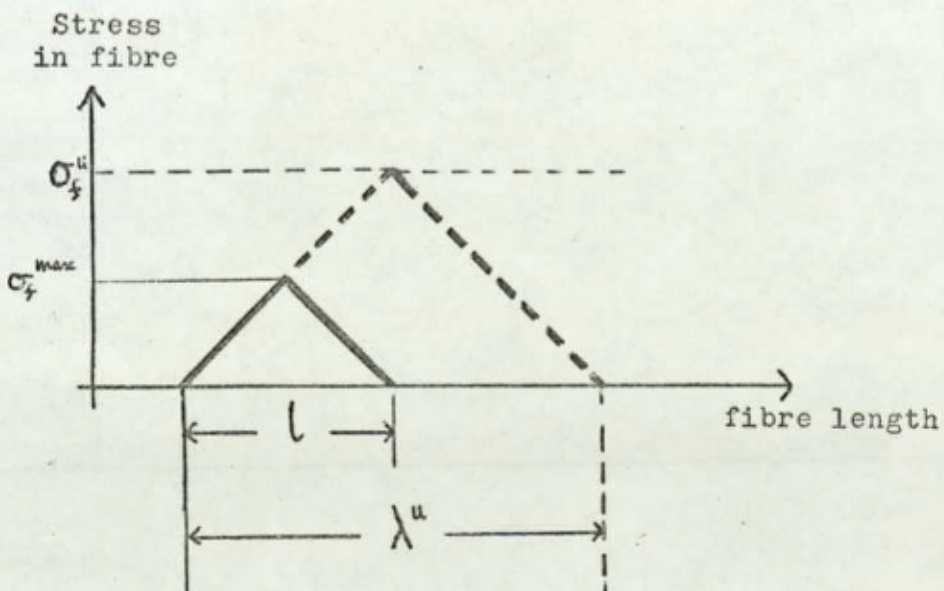
where λ^u is known as the critical length of the fibre, and τ_i^u is the shear stress at failure of the interface.

Combining Equations (4.11) and (4.13) produces an expression for the effective failure stress of discontinuous

Stress transfer at fibre ends



(a) Fibres longer than critical length



(b) Fibres shorter than critical length

Figure 4.2

fibres (of length greater than λ^u) in a composite which may be substituted into Eqn.(4.10) to give

$$\sigma_c^\lambda = \sigma_f^u \left(1 - \frac{\sigma_f^u d}{4\tau_i^u \ell}\right) \left[\left(1 - V_f\right) \frac{E_m}{E_f} + \eta V_f \right] \quad (4.14)$$

But if the fibres are shorter than the critical length ($\ell < \lambda^u$), the stress distribution in them will be as Fig. 4.2(b), where

$$\bar{\sigma}_f = \frac{\sigma_f^{\max}}{2} = \sigma_f^u \cdot \frac{\ell}{2\lambda^u} \quad (4.15)$$

or, substituting from Eqn.(4.13), the maximum stress which the fibres can sustain before pulling out is

$$\bar{\sigma}_f = \frac{\tau_i^u \ell}{d} \quad (4.16)$$

The composite will therefore fail at fibre pull-out when

$$\sigma_c^i = \frac{\tau_i^u \ell}{d} \left[\left(1 - V_f\right) \frac{E_m}{E_f} + \eta V_f \right] \quad (4.17)$$

Parrat (1960) has proposed a theory to account for the failure of composites by fibre pull-out even when the fibres are longer than the critical length.** He suggests that as the stress on the composite is increased, some fibres will break before others, and the newly fractured lengths will now be capable of sustaining greater loads before fracturing again because they are shorter and therefore stronger (see Fig. 3.2(b)). This continual fracturing of fibres continues until they are not long enough to sustain transfer of their breaking stress (i.e. the critical length is reached), and the composite finally fails when the fibres pull out of the matrix. This failure mechanism is essentially similar to

** which has been verified by Riley & Reddaway (1968)

simple pull-out, but with the value $\ell = \lambda^*$: substitution of Equation(4.13) into (4.17) then gives

$$\sigma_c^{f'} = \frac{\sigma_f^u}{2} \left[(1 - V_f) \frac{E_m}{E_f} + \eta V_f \right] \quad (4.18)$$

Equation (4.18) represents an upper limit to the pull-out criterion of Equation (4.17): it is interesting to note that at this limit the fibres are contributing only half their effective strength to the composite.

4.3 CORRELATION OF THEORETICAL WITH EXPERIMENTAL STRENGTH DATA

4.3.1 Collation of data

Table 4.1 summarises properties of fibres and matrices in systems where sufficient experimental data has been quoted to enable a realistic comparison of theory with experiment to be made using the measured composite properties listed in Table 2.1. Numerical values shown in Table 4.1 are governed by the following conditions:

(1) Values of V_f marked by * in Table 2.2 have been estimated from the weight fraction of fibres W_f and the respective densities of fibre and matrix by the relationship

$$V_f = \frac{1}{1 + \frac{(1 - W_f) \rho_f}{W_f \rho_m}} \quad (4.19)$$

Such values are not very accurate as the presence of air voids in cement matrices, especially at higher values of V_f (Grimer & Ali 1969) makes the exact determination of ρ_m difficult.

Properties of fibres and matrix in composite materials

Material type (see Table 2.2)	E_f (GNm ⁻²)	σ_f^u (GNm ⁻²)	E_m (GNm ⁻²)	σ_m^u (MNm ⁻²)	r_i^u (MNm ⁻²)	l (mm)	d (μ m)	V_f (%)	λ^u (mm)	ω_m	ω_f	ω_i ($\times 10^{-3}$)	
1	76	0.7	40	5	7	50	12.5	1.9	0.63	0.97	0.51	6.3	
2										1.02	0.56		
3						" "	11	0.4		1.08	0.60	-	
4	72	0.7	40	2.6	7				0.55	1.12	0.62		
5										1.05	0.58		
6						50	11	1.0		0.98	0.55	5.5	
7										0.98	0.54		
8	73	0.7	40	5	7	50	9	1.9	0.45	0.98	0.54	4.5	
9										0.97	0.53		
10	72	0.7	40	5	7	50	12.5	1.9	0.63	0.98	0.54	6.3	
11	75	0.7	30	12	7	50	10	3.3	0.50	1.00	0.40	5.0	
12						50				0.99	0.54	4.5	
13	73	0.7	40	5	7		9	1.9	0.45	0.97	0.53		
14						25				0.98	0.54		
15	165	3.0	40	5	3	4	15	0.5	7.5	1.05	0.25	10 ³	(5)
16				4	1.0			1.5	3.2	0.99	0.54	32	
17										0.97	0.53		
18	73	0.7	40	6	6.8	50	9	2.3	0.46	0.98	0.54	4.6	
19										0.97	0.53		
20								1.8		8.9	0.27		
21	68	1.4	2.1	45	10	" "	10	3.0	0.7	6.4	0.21	-	(7)
22	72	1.0				50		6.3	0.5	1.4	0.07	5	
													Notes (see text)

Table 4.1

(2) Values of E_m and σ_m^* in parentheses were not provided by the author, and averages were therefore substituted from Tables 1.1 and 1.2.

(3) Values of σ_f^* in parentheses were taken as lower than for virgin glass because of damage caused by mechanical handling and chemical attack by alkaline aqueous solutions (see Section 3.1). A figure of 0.7 G Nm^{-2} was chosen after a consideration of values given by authors who have investigated these effects (Thomas 1960, Urev et al. 1968, Bartenev 1969, Ryabov & Fedoseev 1970).

(4) The only literature values available for τ_i^* in cementitious systems are those of de Vekey & Majumdar (1968), who quote values of 6.38 MNm^{-2} and 9.25 MNm^{-2} for E-glass / OPC systems after 28 days curing at 25°C in moist air and under water respectively. An average value of 7 MNm^{-2} was therefore selected, and used for E-glass / HAC systems as well (cf. values of $2 - 4 \text{ MNm}^{-2}$ for aggregate / OPC systems: Farran 1956, Hsu & Slate 1963, Taylor & Broms 1964).

(5) Values of τ_i^* , l and d for asbestos reinforced cement (ARC) are average values from Hodgson (1965).

(6) Values of l quoted as " ∞ " are where very long fibre rovings or continuous woven mats were used.

(7) Values of τ_i^* for silane sized E-glass / polyester

in the literature vary from about 4 MNm^{-2} (Bennett 1964, Broutman 1969) to over 20 MNm^{-2} (Norman et al. 1964), presumably depending on the constitution and curing of the resin. A value of 10 MNm^{-2} was selected as representative.

(8) For GRP systems the use of Eqn.(4.9) to calculate V_ϕ leads to excessively high values. This is because V_ϕ is governed by fibre failure rather than by matrix cracking, and an expression of the type used by Bortz & Blum (1967) was employed in this case:

$$V_\phi = \frac{1}{1 + \frac{\eta \sigma_f^u}{E_m(\epsilon_m^u - \epsilon_m^f)}} \quad (4.20)$$

ϵ_m^f , the strain in the matrix at failure of the fibres, was taken as the strain of the composite at its elastic limit (Krenchel 1964) - see Table 2.1.

(9) Transformation coefficients ω (see Table 4.2) have been tabulated to facilitate the calculations of composite strength in Table 4.3.

4.3.2 Theoretical strength values

Data from Table 4.1 has been used to calculate composite strengths for the various failure modes discussed in Section 4.2, and the results of the calculations are shown in Table 4.3. Failure strains ϵ_c were calculated on the basis of an elastic modulus given as

Summary of tensile strength equations

Failure mode	Tensile strength equation
Simple mixture rule	$\sigma_c = (1-V_f)\sigma_m^u + \eta V_f \sigma_f^u \quad (4.6)$
Tensile failure of matrix	$\sigma_c^m = \sigma_m^u \left[(1-V_f) + \eta V_f \frac{E_f}{E_m} \right] \equiv \sigma_m^u \omega_m \quad (4.8)$
Tensile failure of fibres	$\sigma_c^f = \sigma_f^u \left[(1-V_f) \frac{E_m}{E_f} + \eta V_f \right] \equiv \sigma_f^u \omega_f \quad (4.10)$
Failure of discontinuous fibres	$\sigma_c^\lambda = \sigma_f^u \left(1 - \frac{\sigma_{f,i}^u d}{4 \tau_i l} \right) \left[(1-V_f) \frac{E_m}{E_f} + \eta V_f \right] \equiv \sigma_c^f (1-\omega_i) \quad (4.14)$ [$l \gg \lambda^u$]
Fibre pull-out	$\sigma_c^i = \frac{\tau_i^u l}{d} \left[(1-V_f) \frac{E_m}{E_f} + \eta V_f \right] \equiv \frac{\sigma_c^f}{4 \omega_i} \quad (4.17)$ [$l \leq \lambda^u$]
Badly flawed fibres	$\sigma_c^{f'} = \frac{\sigma_f^u}{2} \left[(1-V_f) \frac{E_m}{E_f} + \eta V_f \right] \equiv \frac{\sigma_c^f}{2} \quad (4.18)$

Table 4.2

Calculated strength parameters for fibre composite materials

Material type (see Table 2.2)	Tensile strength (MNm ⁻²)						E_c	Strains at fracture ($\times 10^{-3}$)					
	σ_c	σ_c^m	σ_c^f	σ_c^λ	σ_c^i	$\sigma_c^{f'}$		ϵ_c	ϵ_c^m	ϵ_c^f	ϵ_c^λ	ϵ_c^i	$\epsilon_c^{f'}$
1	34	5	340	340	-	170	39	0.9	0.1	9	8	-	4
2	17		390			200	41	0.4					
3	73		420			210	43	1.7					
4	108	3	430	-	-	220	45	2.4	0.1	10	-	-	5
5	44		410			210	42	1.0					
6	21		390			190	39	0.5					
7	13							0.3					
8	18	5	380	380	-	190	39	0.4	0.1	10	9	-	5
9	26							0.7					
10	23	3	380	380	-	190	39	0.6	0.1	10	10	-	5
11	35	12	280	280	-	140	30	1.2	0.4	9	-	-	5
12	15							0.4					
13	28	5	380	370	-	190	39	0.7	0.1	10	9	-	5
14	20							0.5					
15	28	5	750	-	170	380	43	0.7	0.1	17	-	4	9
16	14	4						0.4					
17	25		380	380	-	190	39	0.6	0.1	10	-	-	5
18	19							0.5					
19	32	6						0.8					
20	380	400	380			190	19	20	21	20			10
21	290	280	290	-	-	150	14	21	20	21	-	-	11
22	78	62	64			27	5	16	12	11			5

Table 4.3

$$E_c = (1 - V_f)E_m + \eta V_f E_f \quad (4.21)$$

The physical properties observed experimentally for these composites are shown in Table 2.1, and comparison with Table 4.3 will illustrate some of the deductions which may be made from this type of calculation.

In general the observed ultimate tensile strength σ_c^u (see Table 2.1) shows the expected variation with V_f , and it lies just above that calculated from the simple mixture equation (4.6). This is surprising since Equation 4.6 represents an upper bound (see Figure 4.1), but the anomaly must be due to uncertainty in the value for matrix strength σ_m . Furthermore, the high strengths calculated from fibre failure (σ_c^f) are not attained in practice as the matrix is incapable of sustaining more than a fraction of the fibre strain σ_f^u/E_f (Equation 4.10), except in GRP composites where $\epsilon_f^e \sim \epsilon_m^e$.

Except for the asbestos-cement composite, fibre length ℓ is about two orders of magnitude higher than the critical length λ^u , so that in theory failure cannot occur by fibre pull-out. However, it is certainly observed experimentally, and this discrepancy indicates the necessity to investigate the pull-out mechanism more closely, and if possible to determine λ^u for GRC composites.

The calculated elastic modulus is not attained experimentally except in GRP systems and in GRC systems where V_f

is high. It is probable that this is due to partial bonding in the composite, for it can be shown that the effective modulus contribution of the fibres is reduced by an amount proportional to the degree of non-bonding (Greszczuk 1969). The presence of air voids would also lower the modulus by effectively lowering V_m to a value $V_m(1-V_p)$, where V_p is the volume fraction of pores, microcracks etc.

Whereas the strengths calculated above assume perfect elasticity right up to the point of failure, GRC composites generally exhibit high extensions to failure after the elastic limit has been reached (Grimer & Ali 1969, Fulton 1969). The similarity between the calculated strain in the composite at tensile failure of the matrix (ϵ_c^*) and observed strain at cracking stress (ϵ^*) or at the elastic limit (ϵ^*) suggests that GRC composite failure is not as straightforward as our simple model would appear to indicate. Moreover, examination of GRC fracture surfaces (see Section 7.1) reveals evidence not only of matrix failure, but of fibre failure and pull-out as well, although observed failure strengths do not reach the values calculated for the two latter modes of failure.

One possible explanation for these inconsistencies may be that the mode of failure of the composite can depend not only on the physical properties of its constituents but also on the geometry of the reinforcement. Stowell & Liu (1961) and Kelly and Davies (1965) have used a theoretical treatment to show that at low fibre-tension angle θ , fibre fracture is

the dominant mechanism of composite failure; at intermediate ϕ interfacial shear, and at high ϕ matrix failure in plane strain. Jackson & Cratchley (1966) and Cooper (1966) have verified this in metal systems reinforced by stiff metal or ceramic fibres, and Figure 4.3 illustrates the variation in σ_c with ϕ that is observed.

4.3.3 Conclusions

The main value of the attempt to correlate observed with theoretical strengths has been to show that simple failure equations may be applied to GRC systems, with certain reservations, and that the inconsistencies encountered have proved useful in suggesting suitable areas for investigation in the project.

The fact that in most systems fibre pull-out is observed experimentally but should not occur in theory seems to indicate that air voids and/or incomplete bonding may also explain the 'plasticity' observed in GRC composites after passing beyond a strain approximating to the matrix failure strain.

The effect of attack on glass fibres by the alkali released by hydrating cement has not been satisfactorily investigated in OPC systems, and very little study has been made in HAC systems. Krenchel (1964) has shown that this attack may weaken the composite not only by weakening the

Variation in U.T.S. of unidirectionally aligned
fibre reinforced composite with orientation

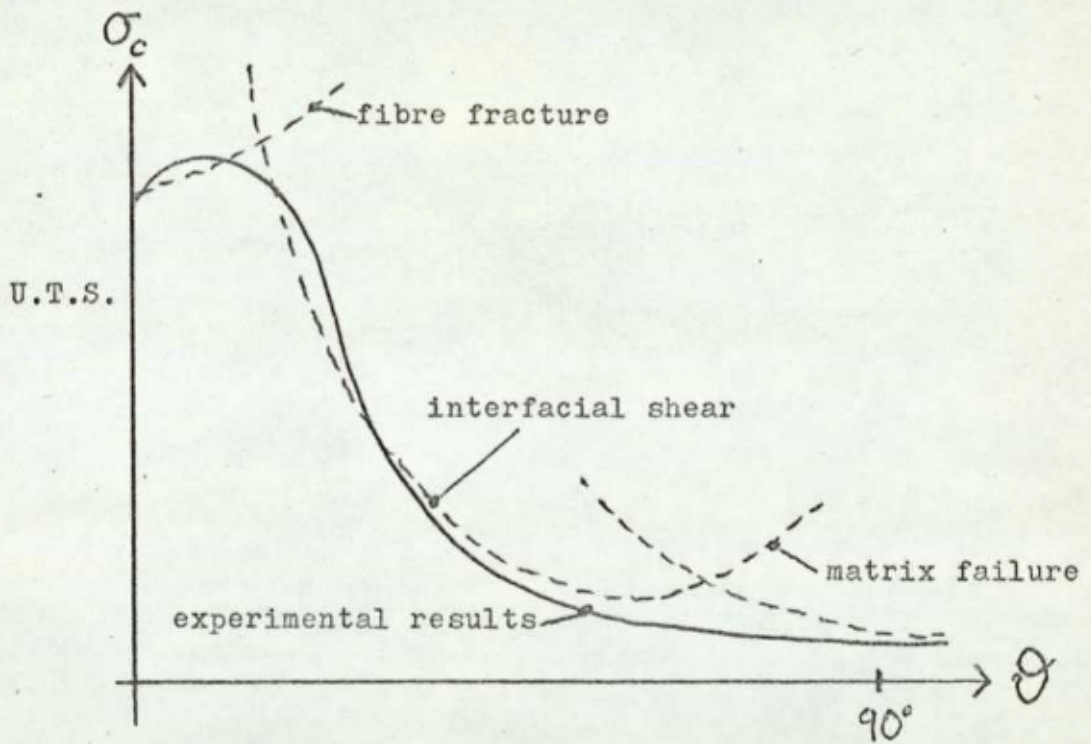


Figure 4.3

fibres, but also because a low value for σ_f^u increases the critical volume fraction V_ϕ (Equation 4.9 and Figure 4.1).

There is consequently enough evidence to justify a more detailed investigation of the fibre / matrix interface than has hitherto been attempted in GRC systems. Such an approach complies well with the experimental resources available for this project, which allow both mechanical and chemical tests to be carried out.

CHAPTER FIVE: THE GLASS / CEMENT INTERFACE

5.1 THEORETICAL ASPECTS

5.1.1 The importance of bond strength to composite properties

In order for a fibre-reinforced material to exhibit truly composite properties, there must be some sort of bond between the phases to enable stress transfer to take place. If the bond strength is too low the fibres will tend to pull out of the matrix before their full load-carrying capacity is reached, but on the other hand too high a bond strength may result in severe matrix-limitation of composite strength. For if it is greater than that needed to fracture the fibre, a weak enough matrix will crack at the fibre fracture site, propagating the crack to adjacent fibres (which are probably stronger), not allowing them to realise their potential strength (Mullin et al. 1968). Cook & Gordon (1964) have shown that if the interfacial adhesive strength is greater than about $\frac{1}{5}$ th of the matrix cohesive stress, cracks will propagate directly through matrix and fibre and the composite will behave as a homogeneous brittle solid with low fracture toughness.

This type of crack propagation may be retarded by interspersing load-carrying with ductile filaments (of thermoplastics

for instance), but from the point of view of combining strength with toughness in a composite the best solution seems to be to ensure that composite failure occurs by fibre pull-out (Bobalek & Evans 1960). As long as the fibre-matrix bond is sufficient to give a composite strength which does not deviate significantly from the rule of mixtures, the only strength properties which it influences directly are compressive and transverse strength. However, if fracture energy can be absorbed in the interfacial region, then composite toughness may be increased by several orders of magnitude.

It can be seen in Table 5.2 that impact strength is very much dependent on the volume fraction of fibres. Furthermore, in the carbon fibre reinforced silica system (where the degree of interfacial bonding can be controlled by heat-treatment to vary the amount of reaction between C and SiO_2), Crivelli-Visconti & Cooper (1969) have found that weakly bonded composites tend to have high strength and toughness, and low elastic modulus. The converse is true for strongly bonded composites, where matrix cracks tend to propagate across fibres, and this effect has also been noted by Majumdar & Ryder (1970) in glass-reinforced cement systems, and by Shah (1969) in concrete systems).

Thus the importance of the interfacial bond has prompted much research into fibre coatings in GRP systems, and it therefore seems logical to investigate the interface in GRC systems in much greater detail than has been done to date.

5.1.2 Fracture toughness and energy absorption

Toughness is a concept difficult enough to define quantitatively even in a homogeneous single phase material. Both the total elastic energy stored at fracture, U , and the work of fracture F (the amount of energy necessary to produce unit area of fracture face during controlled crack growth) are important criteria in determining whether or not a crack can propagate through the material, and attempts to construct toughness parameters have generally been based on combinations of U and F .

In fibre composite systems it might be expected that the work of fracture per unit area, F_c , would be given by a simple law of mixtures addition of the component parts. But in practice fracture energies may be several orders of magnitude higher than this because there exist additional mechanisms for the absorption of energy in such composites. These mechanisms depend on the fracture behaviour of the composite during impact (cf. ultimate tensile strength - see Chapter 4), and are enumerated below. The calculations assume a fracture plane perpendicular to unidirectional fibres, but since fracture energy may dissipate itself non-directionally, the results apply also to multidirectional laminates.

(i) Simple plane fracture. If the fibre-matrix interface contributed nothing to the fracture energy, then a simple law of mixtures according to the parallel model would apply:

$$F_c^s = V_f F_f + (1 - V_f) F_m \quad (5.1)$$

(ii) Fibre debonding. Outwater & Murphy (1969) argue that fibre debonding is an important step in the fracture process of composites, and must certainly precede any pull-out of the fibres: furthermore, they have detected this phenomenon in transparent matrices. By using a fracture mechanics approach they derive an expression for the strain energy release rate in terms of the length of debonded filament. It is reasonable to assume that this length is about twice the mean pull-out length (Kelly 1966, Harris et al. 1971), i.e. is about $\frac{\lambda^u}{2}$, and hence the work of debonding per unit c.s.a. is

$$F_c^d = \frac{V_f \sigma_f^2}{2E_f} \cdot \frac{\lambda^u}{2} \equiv \frac{\sigma_f^2 d}{8E_f} \cdot \frac{V_f}{\tau_i^u} \quad (5.2)$$

(iii) Fibre pull-out. It is possible for fracture energy to be absorbed by fibre pull-out even when fibres are longer than the critical length λ^u . Cottrell (1964) and Kelly (1966) have shown that fibres which have ends within a distance $\frac{\lambda^u}{2}$ of the fracture plane will pull out of the matrix instead of fracturing, and this has also been confirmed experimentally in GRP systems by Hancock & Cuthbertson (1970). These fibres constitute a fraction $\frac{\lambda^u}{\ell}$ of the total number $\frac{4V_f}{\pi d^2}$ per unit c.s.a.

Now the work done in pulling out a single fibre embedded to a depth x would be

$$\tau_i \int_0^x x \cdot \pi d \cdot dx = \frac{\pi d}{2} \cdot \tau_i x^2 \equiv \frac{\pi d^2}{4\lambda^u} \cdot \sigma_f x^2 \quad (5.3)$$

where τ_i is the average shear force between fibre and matrix during pull-out. Thus for the total number of fibres $\frac{\lambda^u}{\ell} \left(\frac{4V_f}{\pi d^2} \right)$ with ends within a distance $\frac{\lambda^u}{2}$ of the fracture plane the

pull-out work will be

$$F_c^p = \frac{\lambda^u}{\ell} \left(\frac{4V_f}{\pi d^2} \right) \frac{\int_0^{\lambda^u/2} \frac{\pi d^2}{4V} \sigma_f \cdot x^2 dx}{\lambda^u/2} = \frac{V_f \sigma_f}{\ell} \cdot \frac{2}{\lambda^u} \cdot \frac{\lambda^u^3}{24} = \frac{V_f \sigma_f}{12} \cdot \frac{\lambda^u^2}{\ell} \quad (5.4)$$

(iv) Crack size limitation. If the fibre-matrix interface is stronger than the matrix itself it will effectively increase the toughness of the matrix by diverting cracks, since a tortuous fracture path requires more work to be done than plane fracture (Cook & Gordon 1964, Clarke 1966). This effect is difficult to quantify as it depends so much on crack size and direction: but if the average fibre spacing S is of less than the order/^{of} the critical crack length C in Griffith's (1920) simple elastic strain theory, we may expect an increase in the apparent value of matrix toughness.

Now for a hexagonal array of parallel fibres

$$V_f = \frac{\pi}{2\sqrt{3}} \cdot \frac{d^2}{S^2} \simeq \frac{d^2}{S^2} \quad (\text{as for a square array}) \quad (5.5)$$

and the simplest form of the Griffith theory gives

$$\sigma_m \simeq \sqrt{\frac{E_m \gamma_m}{c}} \quad (5.6)$$

The order-of-magnitude calculations in Table 5.1 show that this toughening mechanism may be of much greater significance in GRC than in GRP composites.

Table 5.2 compares the measured impact strengths of composite materials with contributions to fracture energy

Crack limitation as a contribution to the toughness of
fibre composites

System	V_f (%)	d (μm)	$s \approx \frac{d}{\sqrt{V_f}}$ (mm)	E_m (GNm^{-2})	σ_m (NMm^{-2})	γ_m (kJm^{-2})	$c \approx \frac{E_m \gamma_m}{\sigma_m^2}$ (mm)	c/s
GRP (polyester)	0.4	11	0.017	2	40	0.1	0.125	6
GRC	0.1	11	0.035	40	5	0.01	16	500
						(McLean 1969)		

Table 5.1

Fracture energies: calculated and experimental

Material type (see Table 2.2)	F_f (Jm ⁻²)	F_m (kJm ⁻²)	F_c^s (kJm ⁻²)	F_c^d (kJm ⁻²)	F_c^p (kJm ⁻²)	F_c^{π} (kJm ⁻²)	Measured Impact Strength I (kJm ⁻²)
1	5	1.8	1.6	0.12	0.05	4.0	-
2	5	1.8	1.8	0.02	0.01*	0.64	-
3	5	1.8	1.6	0.09	0.04*	3.20	-
4	5	1.8	1.5	0.14	0.05*	4.80	-
5	5	1.8	1.7	0.06	0.02*	1.92	65-83
6	5	1.8	1.7	0.07	0.02	2.24	-
7	5	1.8	1.8	0.02	0.01	0.79	6
8	5	1.8	1.7	0.04	0.01	1.31	15
9	5	1.8	1.7	0.06	0.02	2.10	25
10	5	1.8	1.7	0.08	0.03	2.58	19
11	5	1.4	1.3	0.08	0.03	2.62	10
12	5	1.4	1.4	0.03	0.01	1.05	3.3
13	5	1.4	1.3	0.05	0.01	1.58	16.5
14	5	1.4	1.3	0.07	0.05	2.36	14.2
15	-	1.4	1.3	9.2	169	169	2.5
16	5	2.5	2.4	0.21	0.47	7.45	31
17	5	2.5	2.3	0.43	0.95	14.90	50
18	5	2.5	2.5	0.04	0.09	1.34	30
19	5	2.5	2.3	0.08	0.17	2.38	52
20	5	0.2	0.15	1.25	0.03*	20.4	50-100†
21	5	0.2	0.14	1.61	0.04*	26.2	
22	5	0.2	0.18	0.18	0.004	4.2	

* l taken as 50 mm for rovings

† (Harris et al. 1971)

Table 5.2

Experimental values for matrix fracture energy F_m are taken from Grimer & Ali (1969) for cements, Ali & Grimer (1969) for gypsum, and Harris et al. (1971) for polyester resin. The fracture energy for glass fibre F_f is the generally accepted value for bulk glass (Wiederhorn 1969): unlike tensile strength, which depends on surface state, it should be no greater for fibres.

from the mechanisms discussed above.

It is apparent that a law of mixtures approach is very inadequate, and that except in ARC composites the contribution from fibre debonding, F_c^d , is negligible. Impact strengths show a marked dependence on fibre content (cf. nos 7, 8, 9: 12, 13: 16, 17: 18, 19), which must be due to a debonding / pull-out type process. Now if the fracture path were such that all the fibres (rather than a fraction λ_x^u , which is integrated of the order of 1%) pulled out, values of the (pull-out contribution F_c^π are no longer insignificant, and the total contribution to fracture energy, $F_c^s + F_c^d + F_c^\pi$, does show a dependence on V_f .

However, calculated fracture energies are still a long way short of experimentally observed values, especially in GRC composites, and this suggests that values of τ_i^u (measured using carefully cleaned glass rods - see Table 4.1) are much greater than their "apparent" values in the composite. Alternatively, crack size limitation (mechanism (iv) above) may play quite an important role during the fracture of GRC's.

5.2 INTERFACIAL PHENOMENA IN CEMENT AND CONCRETE

5.2.1 The aggregate-cement bond

The strength of the bond between aggregates and cement or mortar has received surprisingly little attention in view of its importance to the strength of concrete. The tensile strength appears to lie between 2.5 and 4 MNm⁻² (Farran 1956,

Hsu & Slate 1963) for commonly used aggregate and mortar compositions, while the shear strength (at zero normal stress) is in the region of 3 MNm^{-2} (Taylor & Broms 1964).

Alexander & Wardlaw (1960) have found that dimensional changes occurring during the hardening of mortars upset the bond with larger aggregates, but this is unlikely to happen on the scale of glass fibre reinforcement. However, some of the influences involved here on bond strength are of general interest to fibre reinforcement. Aggregates with rough surfaces adhere more strongly to cement paste than those with polished surfaces, because cement hydrate crystals are able to key into the microscopic corrugations of their surfaces. This 'frictional' adhesion appears to be the dominant factor in shear strength, and the decrease in tensile bond strength that occurs with increasing w/c ratio is not observed here. Bond strength increases with age, possibly because of the development of chemical bonding. This so-called "alkali-aggregate reaction" is discussed in greater detail in Section 6.1.2, but it seems that the reactivity of the aggregate is not necessarily associated with an increase in the rate of bond strength development (Alexander 1959). Moavenzadeh & Bremner (1969) have noticed that Ca(OH)_2 exhibits poor bonding properties in OPC pastes.

Although bond strengths are generally lower than cement strengths, it is possible to explain the observed increase in tensile strength of mortar over cement paste, even though the sand/paste bond σ_{sp} is weaker than the paste/paste bond σ_p . The force needed to break a hemispherical interface between a sand particle of radius r and the cement paste is

$2\pi r^2 \sigma_{sp}$, whereas if the particle were not present the equivalent area of cement would have required a force of $\pi r^2 \sigma_p$ to break it. Now in 1:2 mortar, for instance, the volume fraction of sand particles V_s is about 83%, and σ_{sp} is about $0.6 \sigma_p$ (Hsu & Slate 1963), so the increase in mortar strength

is
$$\frac{[2\pi r^2 \sigma_{sp} V_s + \pi r^2 \sigma_p (1 - V_s)] - \pi r^2 \sigma_p}{\pi r^2 \sigma_p} = \frac{V_s (2\sigma_{sp} - \sigma_p)}{\sigma_p} = 0.2 V_s \approx 17\%$$
 compared with 15% observed experimentally.

There seems to be no reason why mortars, instead of neat cement pastes, could not be used as a cheaper matrix in GRC composites.

5.2.2 Adhesion in hydraulic cements

Chatterji & Phatak (1963) have shown that the variation in hydration rate of different components of cement clinker may be linked with the position of Fermi levels in these crystals. They consider aggregate-cement adhesion to be a donor-type (p→n) semiconductor action, so that those oxides which hydrate fastest (i.e. have the highest Fermi levels) adhere best. We may therefore expect adhesion to be improved by

- (i) using HAC rather than OPC, since Fermi levels are higher in calcium aluminates than in silicates
- (ii) enriching the CaO content of the clinker (hydration is faster at the Ca-rich end of the calcium aluminate series - see Section 3.2.2)
- (iii) introducing donor impurities (e.g. ZnO)

- (iv) reducing the hydrate crystal size (this raises the Fermi level).

The significance of this electrostatic component in adhesion is arguable, but Deryagin and co-workers have shown that it can account for adhesive forces as high as several MNm^{-2} (Smilga 1961). The mechanism would provide an interesting extension to Chatterji & Jeffery's (1967, 1968) theory of cement strength being due to hydrate spline overlap, and should presumably apply to reinforcement by glass fibres as well as by aggregates.

5.3 GLASS FIBRE - MATRIX ADHESION

5.3.1 Reinforced plastics

A major problem encountered with GRP laminates is their sensitivity to attack by water, especially at elevated temperatures. It seems that water seeps up the glass fibre - resin interface, creating pressure which prises the resin from 'islands' of silica, while dissolving certain areas of the silicate surface (Eakins 1969). However, so-called "coupling (or keying) agents" are in common use which not only strengthen the interfacial bond (Broutman 1969) but also increase its life in aqueous environments (Stone 1969). They may also help in the wetting of glass by liquid resin and assist in its polymerisation (Johannson et al. 1969).

There are two main types of coupling agent: unsaturated chromo-organic compounds such as methacrylato chromic chloride, and unsaturated organo-silanes such as vinyltrichlorosilane. Although it is possible to devise chemical formula linking the silanol groups on the glass surface (see Section 3.1.2) to unsaturated bonds in the resin via the coupling agent (Loewenstein & Parvin 1962), it seems likely that this is not the sole mechanism by which the bond is improved.

McGarry (1959) considers that no special chemical affinity is necessary to ensure good adhesion to glass, but only the removal of foreign substances and air. Keying agents do not improve dry bond strength directly (Bikerman & McGarry 1959), but facilitate the wetting of the glass by liquid resin, and bond failure tends to occur at the resin/keying agent interface rather than on the glass surface (Norman et al. 1964).

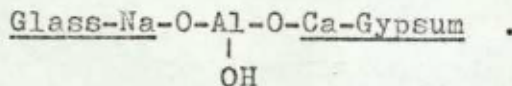
With polyester laminates the bond appears to be mainly frictional on account of the high shrinkage of the setting resin (ca. 7%): coefficients of friction of up to 0.3 have been measured (McGarry 1959). The bond is weak because adsorbed water on the glass surface upsets the curing of the resin even when a keying agent is applied. The glass-epoxy bond, however, is much stronger as curing is less affected by water: shrinkage of the resin is less, and frictional forces are not as important. Nevertheless, with all resins there will be considerable pressure exerted on the fibres by differential thermal contraction on cooling from the curing temperature: Bowden (1970) has found a compressive stress of 7 MNm^{-2}

in steel wire/epoxy resin systems.

5.3.2 Reinforced cements

Whereas the primary aim of keying agents in GRP systems is to protect the interface from the effects of extraneous water, in GRC composites the problem becomes one of ensuring that the attack on the glass surface by the alkalinity of hydrating cement is minimised: suitable coupling agents have been discussed in Section 1.4.4.

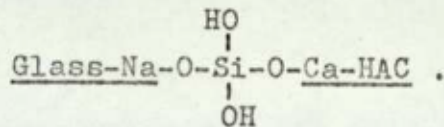
However, even the strength of glass reinforced gypsum (non-alkaline) may be increased by adding AlCl_3 as a coupling agent (Owens-Corning 1961), when it is claimed to form a chemical linkage such as



Other metallic salts proposed, such as those of Ca, presumably have similar actions, but the sequestering agents suggested by Owens-Corning (1962) probably act by increasing wettability and improving penetration of gypsum slurry into the fibres (cf. the 'mineralising' of organic pulp by impregnation with a metallic salt solution prior to adding cement: Novocrete 1924).

Certain types of coupling agents such as organic silicates appear merely to provide mechanical protection for the fibres; in addition the formation of a hydrophobic layer on the glass surface may diminish attack by alkali.

There is a possibility that some keying agents may enhance the strength of glass fibres by an etching action, although close mechanical contact with the matrix could well counteract this effect. The hydrofluoric acid produced in the hydrolysis of MgSiF_6 (Owens-Corning 1961) is well known to increase the strength of glass (Proctor 1962). Ray & Johnson (1967) noted a similar strength increase with particular compositions of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2$), which seems promising as a chemical coupling agent on account of the possible linkage



The importance of volume changes in setting cements to bond strength with fibrous reinforcement is unclear, as they depend very much on water/cement ratio and curing conditions. External expansion under water and contraction in air of 1 or 2% are generally observed (Slate & Matheus 1967, Cromarty & Bryden 1967), but the internal processes are complicated by the formation of voids. Thus in the conversion of HAC, where the cubic hydrates have a lower density than the hexagonal hydrates they are formed from, we would expect shrinkage: but expansion is usually observed, accompanied by increased porosity (Robson 1962). Gypsum, like expansive portland cement, expands on setting.

Mielenz & Benton (1958) have suggested that the pressure developed in cement pastes by osmotic forces may exceed 1 MNm^{-2} , which would contribute towards a frictional bond with any fibres present. Specimen size might well be important here.

CHAPTER SIX: THE CHEMICAL STABILITY OF GLASS IN HYDRATING CEMENT

6.1 INTRODUCTION

6.1.1 Scope of the problem

There is general agreement in the literature that ordinary E-glass fibres are not compatible with portland cement in the conditions found in GRC composites (Biryukovitch 1964, Owens-Corning 1964, Budnikov et al. 1966, Nurse 1967), but that they are with high alumina cement (Biryukovitch 1964, Nurse 1967).

Chan & Patterson (1971) have found no deterioration in the strength of E-glass/HAC composites after nearly 2 years of ageing, but a recent Building Research Station publication (Grimer & Ali 1969) has allegedly shown that even these composites are not as stable as was previously thought. Unfortunately some of the evidence presented in the B.R.S. work is of dubious value as air-cured samples are considered together with water-cured ones, and in many graphs 'trend' lines bear little relation to the means of measured parameters.

It was therefore thought that a more thorough investigation of the alkalinity of hydrating cements and of the resistance or otherwise of glass to chemical attack was called for.

6.1.2 The alkali-aggregate reaction in concrete

The reliability of concrete depends very much on the compatibility between the mortar and aggregate of which it is composed. The term "alkali-aggregate reaction" covers generally any interaction (not necessarily chemical) between the components of concrete, and it has been extensively studied over the past few decades in portland cement concrete (Bredsdorff et al. 1960, Mielenz & Benton 1958: see also Section 5.2.1).

Chemical reaction between alkalis (Na_2O , K_2O) in setting portland cement and silica in the aggregate, followed by osmosis (with the cement hydrates acting as a semi-permeable membrane) can cause expansion in the concrete, very high pressures being developed in the mortar (Pike et al. 1955, Hansen 1960b). Hansen (1959) has also shown that other mechanisms, such as the hydration of periclase, can also cause expansion.

Inhibition of this alkali-aggregate reaction can be effected by adding any ion with a soluble hydroxide and insoluble silicate such as Ba^{2+} , Li^+ , and to some extent Ca^{2+} , and many impurities both organic and inorganic have similar actions (Mielenz & Benton 1958). But complete elimination of any reaction may not be entirely beneficial, as some workers (e.g. Kartunnen & Sneek 1958) consider that a mild alkali-aggregate reaction actually improves bond strength.

6.2 ATTACK ON E-GLASS BY HYDRATING CEMENTS

6.2.1 Stability of glass in alkaline solutions

In their study of the progressive loss of strength of E-glass / OPC composites, workers at the Building Research Station have found some correlation between the resistance to attack of glass fibres of various compositions by alkaline solutions and their ability to sustain composite strength over a period of time (Majumdar & Ryder 1968). They tested weight and strength loss of fibres in a typical 'OPC filtrate' solution (i.e. presumably corresponding approximately to the conditions in hydrating cement: $\text{NaOH} = 22 \text{ mmol/l}$, $\text{KOH} = 63 \text{ mmol/l}$, $\text{Ca(OH)}_2 = 13 \text{ mmol/l}$, $\text{pH} = 12.5$) at elevated temperatures (80°C) in order to accelerate the tests. E-glass fibres, for instance, lose 50% of their strength after 12 hours under these conditions, but it should be borne in mind that the rate of attack is several hundred times that at room temperature. Significant reductions were also observed in the diameter of E-glass fibres after immersion in molar NaOH for 1 hour (60% reduction) and saturated Ca(OH)_2 for 4 hours (10% reduction);
as
but/no attempt was made to correlate these diameter reductions with the weight losses the results are somewhat inconclusive.

While tests of this nature are suitable for comparing the alkali resistance of different types of glass, the immersion of fibres in a vast excess of aqueous and completely mobile alkali gives a rather exaggerated impression of the

scale of attack which would probably occur in a composite. However, we can estimate the total possible weight loss of the fibrous reinforcement by assuming that all the alkali produced by the hydrating cement reacts with the silica in the fibres. For this particular reaction destroys the silicate network of the glass, which may therefore be considered as 100% SiO_2 (molecular weight = 60).

Now there is $\frac{W_f}{60}$ mol SiO_2 in unit weight of composite. But if M_m is the molarity of alkali liberated (as OH^-) by the cement, unit weight of composite will produce $\frac{1-W_f}{\rho_m} \cdot \frac{M_m}{1000}$ mol alkali. If this alkali reacts on a 1:1 molar ratio (an upper limit) with the silica in the fibres, their fractional weight loss δW_f is given by

$$\delta W_f = \frac{1-W_f}{\rho_m} \cdot \frac{M_m}{1000} \cdot \frac{W_f}{60} \quad (6.1)$$

$$\text{Now } V_f = \frac{W_f/\rho_f}{W_f/\rho_f + \frac{1-W_f}{\rho_m}} \simeq \frac{W_f/\rho_f}{(1-W_f)/\rho_m} \quad (6.2)$$

at the low values of V_f found in GRC composites, and for E-glass $\rho_f = 2.5$.

Hence the maximum possible fractional weight loss of the fibres is approximately

$$\delta W_f \simeq \frac{1}{V_f \rho_f} \cdot \frac{60 M_m}{1000} = \frac{0.024 M_m}{V_f} \quad (6.3)$$

Since both the load strength and weight of a given fibre depend on its cross sectional area, this expression also holds for strength loss, if we assume that the remaining

fibre structure is not weakened (Budnikov et al. 1966).

Now in terms of virgin fibre diameter d_1 and corroded diameter d_2 , the fractional weight loss is given by

$$\delta W_f = \frac{d_1^2 - d_2^2}{d_1^2} \equiv \left(\frac{d_1 + d_2}{d_1}\right) \left(\frac{d_1 - d_2}{d_1}\right) \simeq 2\delta d \quad (6.4)$$

since $\delta d = \frac{d_1 - d_2}{d_1}$ represents the fractional diameter loss, and for small losses $d_1 \simeq d_2$. This means that diameter reductions will be approximately one half weight or strength losses.

Substituting values for M_m of 0.1 and for V_f of 8% from a typical composite, it is seen that the maximum possible strength loss of the fibre (purely from chemical corrosion) is of the order of 3%, with a corresponding 1½% diameter reduction.

But Majumdar & Ryder (1968) found percentage losses of tensile load in E-glass of up to 90% and diameter reductions of up to 60% after prolonged treatment of the fibres in hot alkali solutions. So while these tests form a very convenient quick method of comparing the alkali resistance of various types of glass, it would be dangerous to use them as a basis for assessing the long-term stability of fibres in a cementitious matrix.

6.2.2 Petrographic studies

A different approach to the stability of glass fibres

in hydrating cements has been made by the Kiev school (Budnikov & Goryainov 1955). They immersed fibres in water or cement and studied the effect on their surfaces with both optical and electron microscopes. After immersion in water a layer of crystalline products was formed onto the fibre surface which then became irregular in finish, and thermogravimetric studies showed this to be calcium aluminate and silicate hydrates. Immersion in hydrating cement gave substantially the same results, and the chemical attack was to a depth of less than $1\text{ }\mu\text{m}$ (i.e. diameter loss $\sim 8\%$) on fibres with a composition similar to E-glass (see Table 3.1). Calcium ions from the cement combined with silica from the glass to give CaCO_3 , Ca(OH)_2 and calcium hydrosilicates and hydroaluminates. Later work (Budnikov et al. 1966) confirmed this, and also showed that the centre of the fibre remained "optically intact", with a polycrystalline sleeve growing out round the fibre. In HAC composites these growths were less extensive and it was concluded that the deterioration of E-glass/OPC composites with time was due to the formation of a new phase which weakened the fibre-cement bond and caused expansion (cf. the alkali-aggregate reaction) rather than to direct attack weakening the fibre. Thus the concentration of free calcium in the setting cement seems to be at least as important as its alkali content.

6.2.3 Correlation of chemical and petrographic evidence

The conclusions drawn from the above petrographic evidence have been confirmed by Urev et al. (1968), who have detected three stages in the fall-off in strength of glass fibres immersed in hydrating OPC. An initial, fast dissolution of the surface glass layer forms a thin coating of calcium hydrosilicates which substantially protects the fibre from further attack in the second stage (cf. Majumdar & Ryder's (1968) explanation of the action of their "alkali-resistant" fibres). But eventually crystals start to grow epitaxially from fibre defects, weakening the fibre by exerting pressure on these extra-sensitive points, and even in HAC (although the free lime and alkali contents of these Russian cements may be high - see Table 3.2) this can result in a 50% fibre strength loss after one year.

Further work by Urev & Mikhailov (1969) has shown that even "zirconia fibres" (similar to Majumdar & Ryder's (1968) composition?) are attacked extensively in HAC because of crystallisation at microdefects in the fibre surface. But they have found that coating any fibres with a mixture of fine silica particles (about 4 μm in diameter) in PVC caused crystals to grow from the particles rather than the fibres, ensuring good mechanical keying to the cement (verified by pull-out tests). This presents a further argument in favour of the use of mortars as composite matrices (see Section 5.2.1).

In view not only of the limited relevance of some of the British work but of the incompleteness (mainly lack of data) of the Russian work discussed above, as well as inconsistencies in their conclusions, there seems to be a need to investigate chemical compositions at the glass fibre / cement interface in greater depth. In comparison with hydrating cements, the surface of glass is relatively well understood, in chemical terms at least, and it was therefore thought that a comparison of ionic compositions of hydrating HAC and OPC might throw some light on the problem of 'alkalinity' in cements.

6.3 DETERMINATION OF THE CHEMICAL COMPOSITION OF THE AQUEOUS PHASE IN HYDRATING CEMENTS

6.3.1 Scope of the investigation

A fair amount of research into the ionic species present in hydrating OPC with or without various admixtures has been carried out (Lawrence 1966, Roberts 1968). The results from this work show great variation, mainly due to the use of different commercial types of cement, but certain factors (e.g. pH between 12.5 and 13) are reasonably constant. No such investigation of HAC has been carried out, and it was therefore decided to compare one sample of HAC with one commercial OPC under our own (arbitrary) conditions.

The aqueous phases of both HAC and OPC are supersat-

urated (Greenberg & Mehra 1960), but precipitates seem to form more quickly from filtrates of hydrating HAC. It was therefore necessary to be able to test filtrates quickly, and if all tests could be performed on the same aliquot this would save having to repeat the preparation of the very small quantities of filtrate obtained from nearly set low w/c ratio cements.

The filtrates were to be tested for pH, acid-titratable alkalinity, and for the ions Ca^{2+} and Al^{3+} , with possible interferences from Mg, $\text{Fe}^{2+}/\text{Fe}^{3+}$, and Ti. It was decided to develop a method of titrimetric analysis for the ionic concentrations using EDTA* as a reagent, since the established methods were slow and needed more than one aliquot.

6.3.2 Development of an analytical method

In practical terms the problem was one of determining Ca (+Mg), Al (+Ti) and Fe in concentrations of up to about 50 mmol/l in the same solution using EDTA. A thorough search revealed that no published methods existed which did not use complicated instrumentation (Wilson 1960, Flaschka 1964). Stability constants shown in Figure 6.1 (Ringbom 1963) suggest that the Al/Fe titration could be carried out at a pH low enough for the Ca-EDTA complex to be too weak to interfere, and a suitable procedure was developed by adapting the method of Cimerman et al. (1958).

* Ethylene diamine tetracetic acid

Some metal-EDTA conditional stability constants (K)

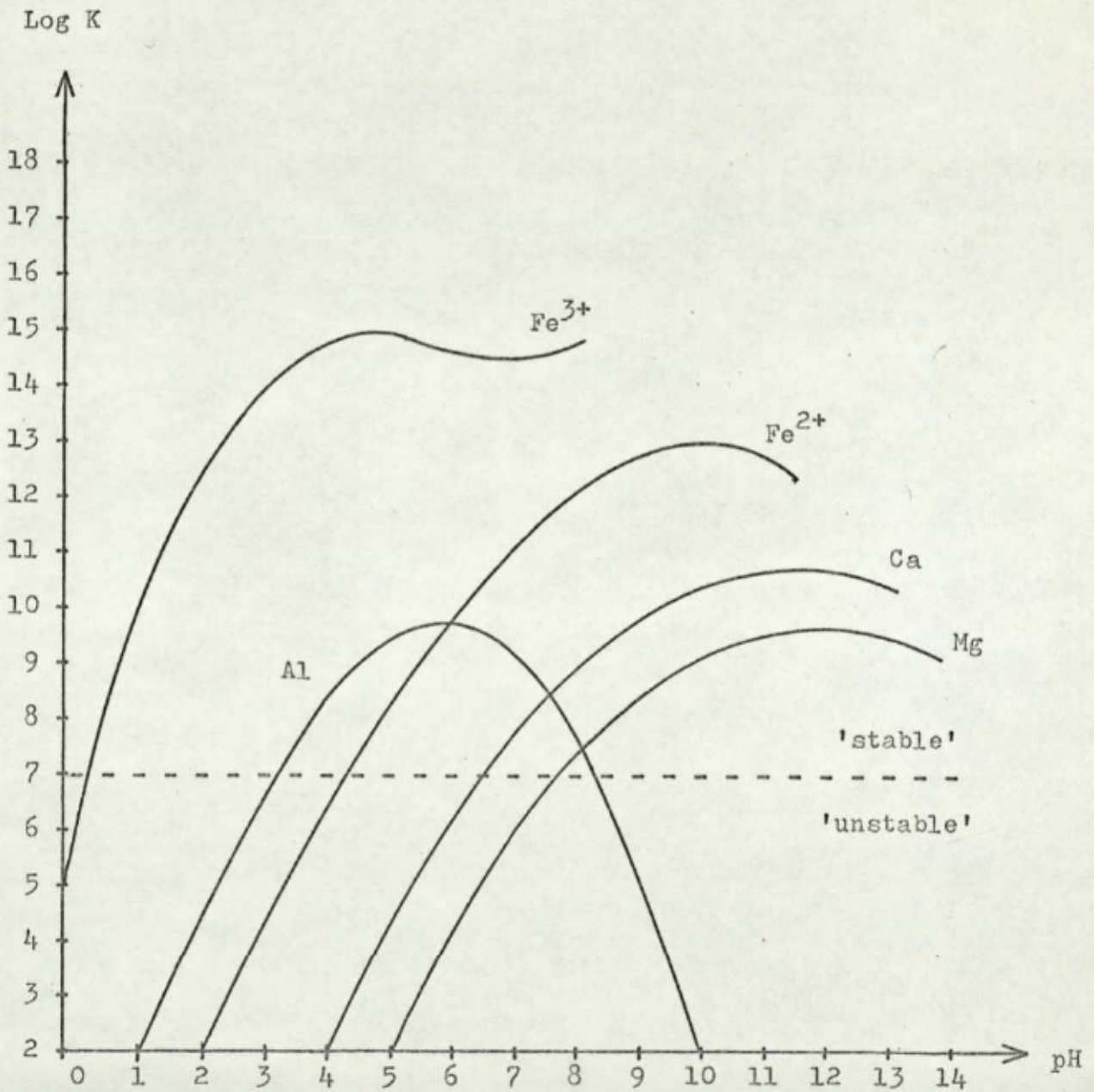


Figure 6.1

Excess EDTA added to the sample is backtitrated with Zn at pH 5 using xylenol orange as an indicator to give the sum of Al + Fe (backtitration is necessary because the Al-EDTA equilibrium is so sluggish at this pH): Al is then freed from its complex with EDTA by the addition of NaF to form the complex fluoride, and titration of the liberated EDTA with Zn gives Al, Fe being obtained by difference. It was originally intended to perform the analysis in the following sequence:

- (i) take pH of sample
- (ii) titrate with acid to phenolphthalein end-point
- (iii) perform Al / Fe analysis at pH 5 as above
- (iv) raise pH to 10 and titrate Ca with EDTA using Eriochrome black T as indicator (Wilson 1960).

But unfortunately it appeared to be impossible to titrate Ca after the Al / Fe analysis despite all attempts at masking interfering species. Alternative indicators were tried without success, but one of these, methylthymol blue (MTB), was found to be usable and to have other advantages (West 1969, Ringbom 1963). For not only is it a relatively interference-free indicator for Ca at pH 11, but it also undergoes a yellow - blue colour change at pH 7.2 (i.e. virtually at neutrality) and can be used as a metallochromic indicator in mildly acidic solutions.

Further investigations were carried out with the aid of a logical / analogue type computer program COMPLEX, which was capable of analysing whether or not a sequence of metal

determinations was possible on the basis of operating data fed into it. This data consisted of information on conditions under which a particular metal could be titrated or backtitrated with EDTA (pH and indicator) and what interfering reactions, if any, would upset the estimation. The program showed that the Al/Fe analysis could be performed with MTB as the indicator instead of xylenol orange if the pH was raised to 5.5 (still too low for Ca to interfere), and that this analysis could be performed after the determination of Ca.

After careful checks on accuracy, reproducibility and selectivity with known standards the following analytical scheme was selected for the analysis of the cement filtrate samples:

(i) Determine the pH of the filtrate with a glass electrode on an E.I.L. pH meter (model 46A) using a pH 9 standard⁽¹⁾: see Section 6.2.3). Hydroxyl was calculated from the relationship: $\text{OH}^-(\text{mmol/l}) \equiv \text{antilog}(\text{pH} - 11)$.

(ii) Pipette 10 ml of filtrate into a 250 ml conical flask and titrate with standard HCl⁽²⁾ using MTB⁽³⁾ as the indicator (blue to pale yellow at pH 7.2). This gives acid-titratable alkalinity.

(iii) Add one drop TriEthanolAmine (to reduce interference with the indicator by Fe, Al, Ti) and 10 ml pH 11 buffer⁽⁴⁾ to the solution: titrate against standard EDTA⁽⁵⁾ to a blue - colourless endpoint with MTB. This gives Ca⁽⁶⁾.

(iv) Run a known excess (i.e. greater than $\text{Al} + \text{Fe}$) of EDTA into the solution and boil to evolve ammonia until the indicator turns colourless (i.e. neutrality is reached). Add 10 ml pH 5.5 buffer⁽⁷⁾ and boil the solution for a further 5 minutes to ensure the complete formation of the Al-EDTA complex (above about pH 3 all Al equilibria are rather sluggish on account of the hydroxo-compounds in solution). After cooling and adding more indicator (MTB seems to lose its metallochromic specificity on boiling) titrate the solution against standard Zn ⁽⁸⁾ to a blue - yellow end-point to give the excess of total EDTA added over the sum of $\text{Al} + \text{Fe}$ ⁽⁹⁾.

(v) Add NaF ⁽¹⁰⁾ to the solution, boil for 5 minutes, cool, and titrate the EDTA liberated against Zn to give Al. Fe is calculated by difference.

The accuracy of the method using standard solutions is shown in Table 6.1.

6.3.3 Notes on the analytical procedure

(1) The BDH pH 9 buffer powder used gives a pH of 9.24 at 20°C (the average lab temperature). This was rather far below the pH of even hydrating HAC, but as the hydration pH of different cements was merely being compared, reproducibility of a standard point was thought to be more important. Higher pH buffers tend to be unreliable.

(2) Strengths of 0.1N, 0.05N and 0.025N were made up from $\text{N}/_{10}$ BDH 'CVS' hydrochloric acid.

(3) One spatula end (ca. 0.03g) of a 1:400 mixture of methylthymol blue powder:NaCl was used.

Standardisation of EDTA determination of Ca, Al, Fe

Ca $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 172.18$

Al $\text{AlKSO}_4 \cdot 12\text{H}_2\text{O} = 474.39$

Fe $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 404.00$

	known	found	error(%)
Ca	8.70	9.1	3
Al	8.59	8.6	0
Fe	10.95	11.0	0
Ca	30.8	29.1	6
Al	29.7	28.9	3
Fe	2.0	2.2	10

(m mol/l : average of 3 titres)

Table 6.1

(4) pH 11 buffer was prepared by diluting concentrated ammonia (s.g. = 0.880) to half strength and adding NH_4Cl (ca. 18g/l) to the required pH, using the meter.

(5) $\text{BDH } \frac{\text{N}}{50}$ (0.01 mol/l) EDTA concentrated volumetric solution.

(6) Under these conditions Mg is cotitrated with Ca, but no attempt was made to distinguish the two as Mg was found to be present at a concentration of less than 2% of Ca.

(7) pH 5.5 acetate buffer (ca. 2N) was prepared by dissolving 27g sodium acetate trihydrate in 1 litre water and adding concentrated HCl (ca. 5 ml) to the required pH.

(8) 0.01 mol/l $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$: the Zn and EDTA solutions were checked for equivalence.

(9) Ti can interfere in this backtitration, but it was in fact not found in significant amounts in either HAC or OPC. Fe^{2+} can be estimated by oxidising to Fe^{3+} with persulphate, added with the pH 5.5 buffer (Schwarzenbach & Flaschka 1969).

(10) ca. 0.3g NaF was added. Calculation showed that about 2.5 mg NaF was required per mmol of Al in the filtrate.

6.3.4 Sample preparation and analytical results

Cement powder / water mixtures were agitated by an

adapted Griffin flask shaker in sealed 250 ml polythene bottles in a waterbath held at 15°C ($\pm 0.2^{\circ}\text{C}$). The shaking speed was kept at around 500 cycles/min, as it was found that results were not very dependent on shaking speed as long as it was kept within certain limits (cf. Lawrence 1966). The slurry was then suction filtered through hardened filter paper (Whatman No 52) in a polythene Buchner funnel, and the filtrate was subjected to the analysis procedure detailed above. Filtration and complete analysis could be carried out within 15 minutes.

Figures 6.2 to 6.7 show the analytical results obtained from HAC and OPC pastes of three water/cement ratios: in practice most GRC composites have w/c ratios of between about 0.3 and 0.5. At the time interval after gauging indicated by 'set' on some of the figures, the paste had become so viscous that less than 5 ml of liquid could be extracted for analysis. The HAC and OPC used in these determinations were from ordinary commercial batches, and their chemical analyses are given in columns 1 and 3 of Table 3.2 respectively.

For purposes of comparison some of Lawrence's (1966) results from a commercial portland cement '242' of unknown composition are included in Figures 6.5 and 6.6: Ca was determined "by EDTA titration", and Na and K were presumably estimated photometrically. Alkalinity was measured by titrating with standard acid to an end-point with methyl red, which indicates at a lower pH (ca. 5.2) than MTB (pH 7.2). We would therefore expect Lawrence's 'alkalinity' to be greater than ours, so the observation that it is generally lower sug-

Aqueous phase composition in hydrating HAC at 15°C: w/c = 1.0

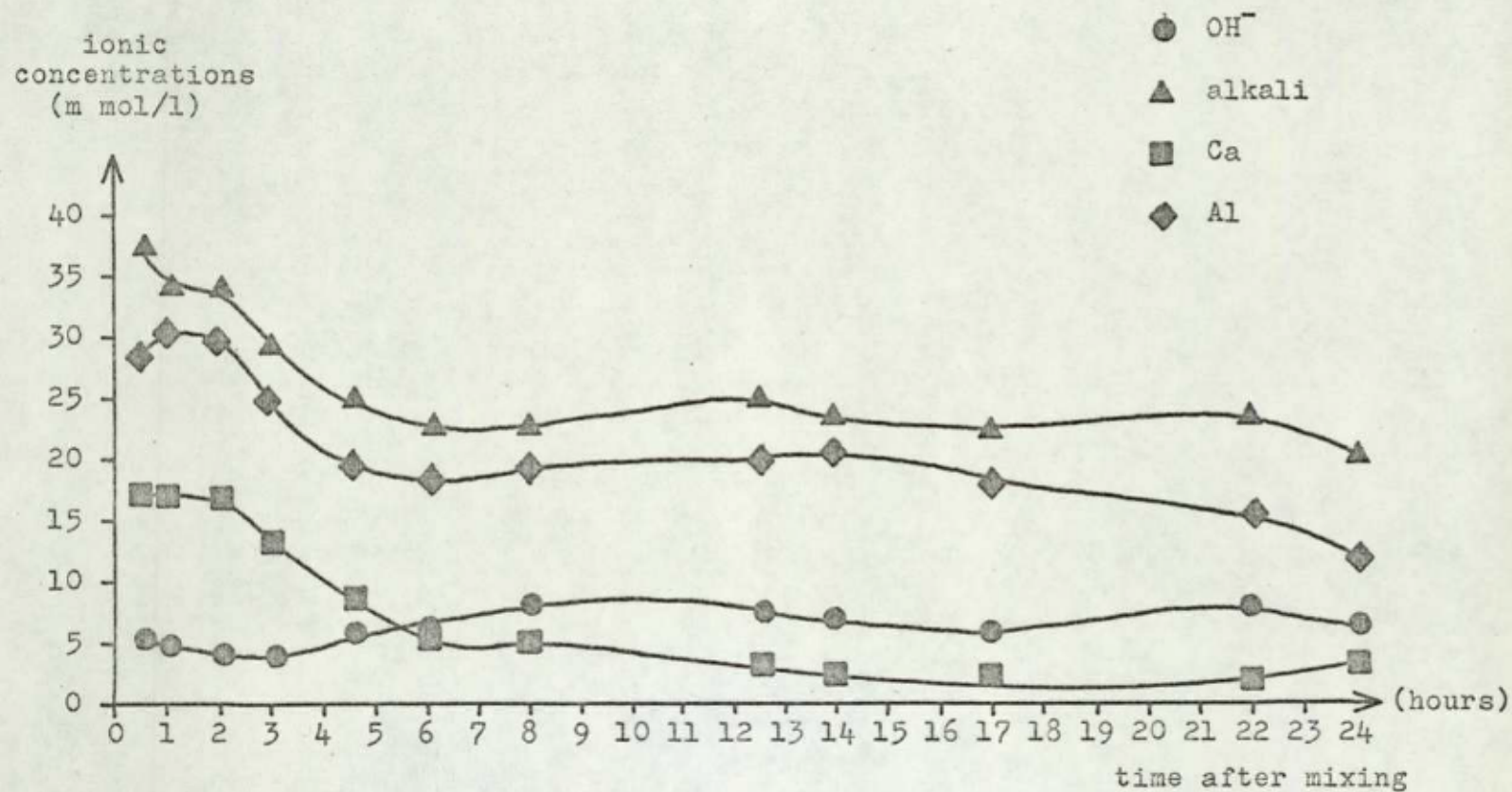


Figure 6.2

Aqueous phase composition in hydrating HAC at 15°C: w/c = 0.5

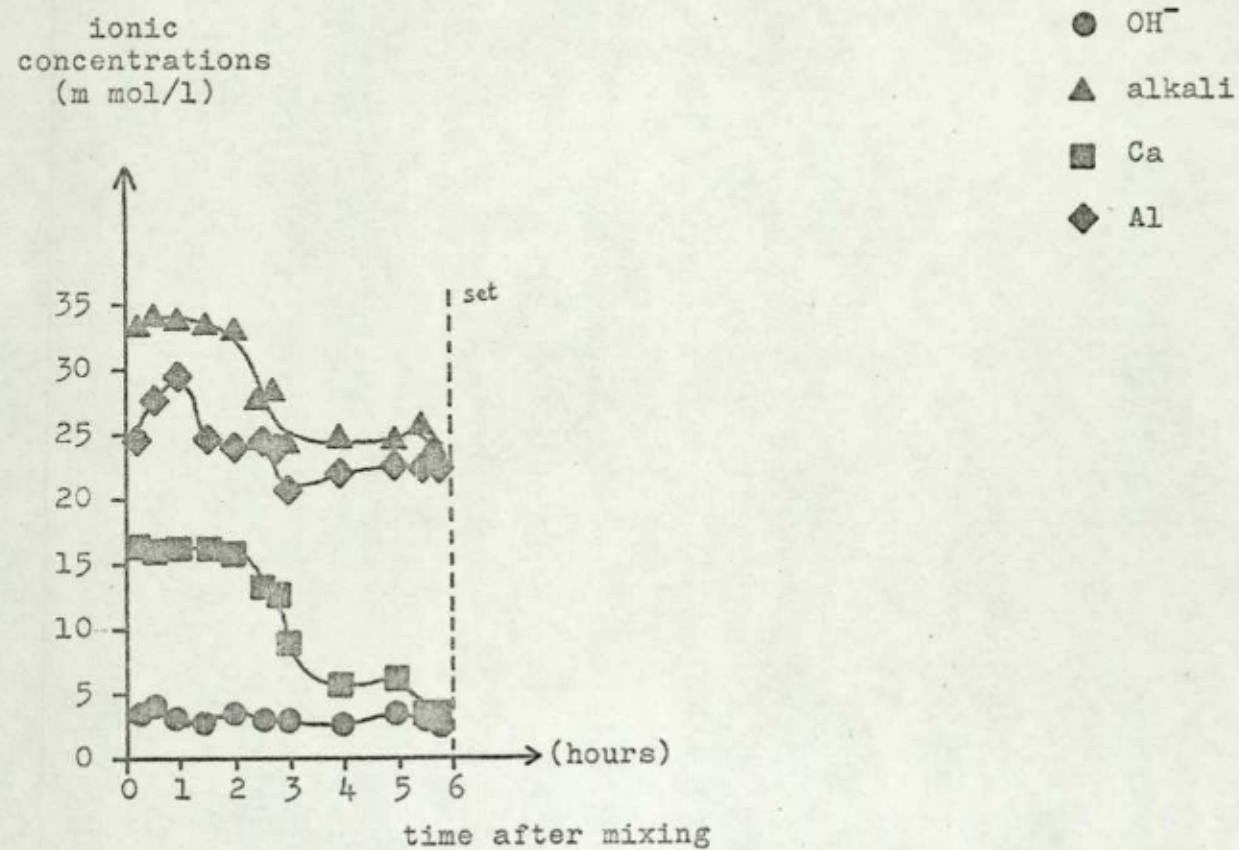


Figure 6.3

Aqueous phase composition in hydrating HAC at 15°C: w/c = 0.3

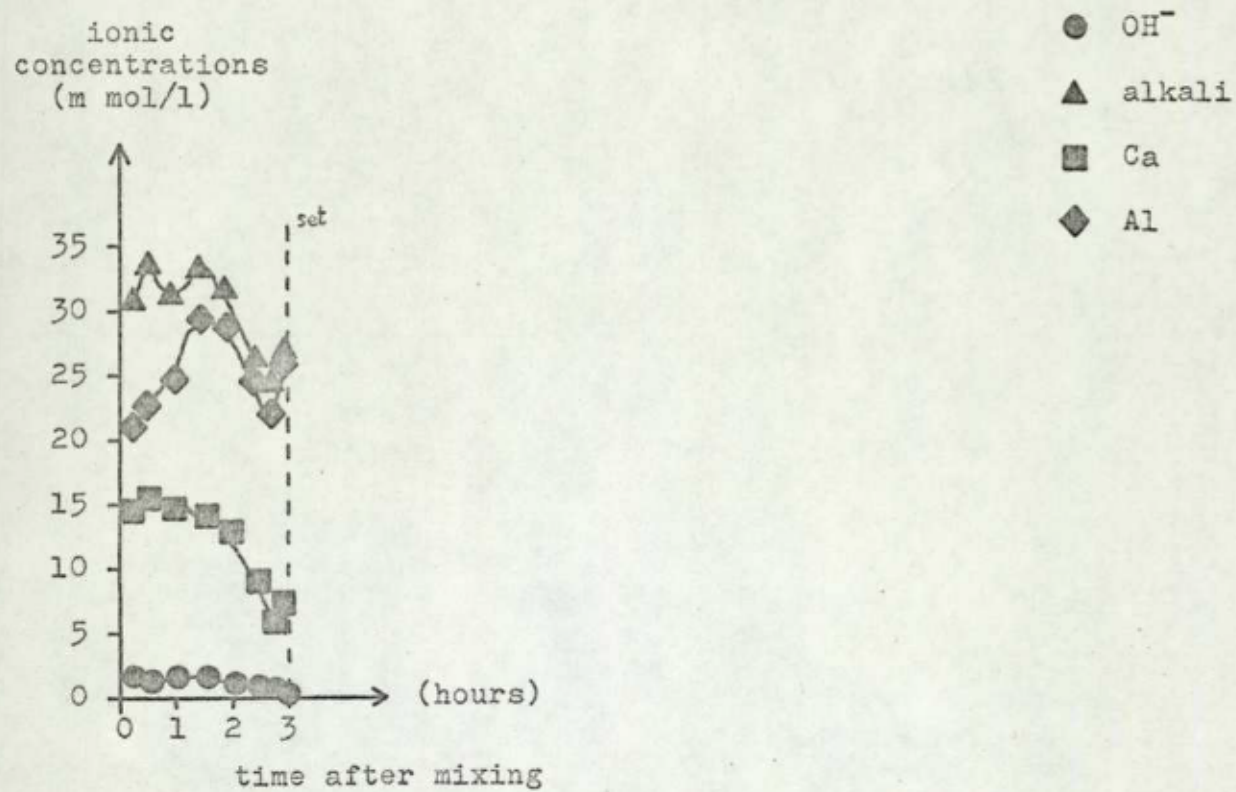


Figure 6.4

Aqueous phase composition in hydrating OPC at 15°C: w/c = 1.0

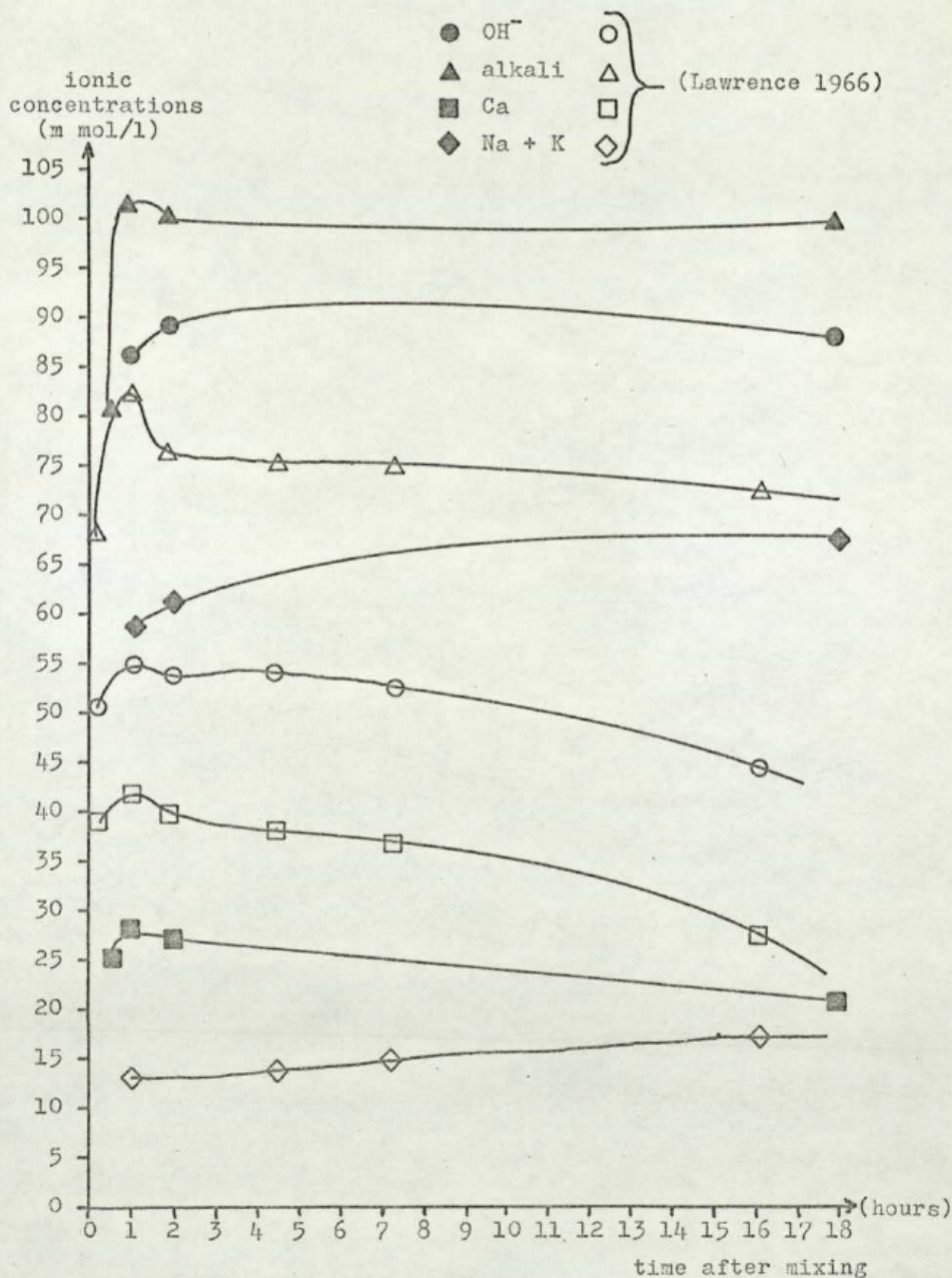


Figure 6.5

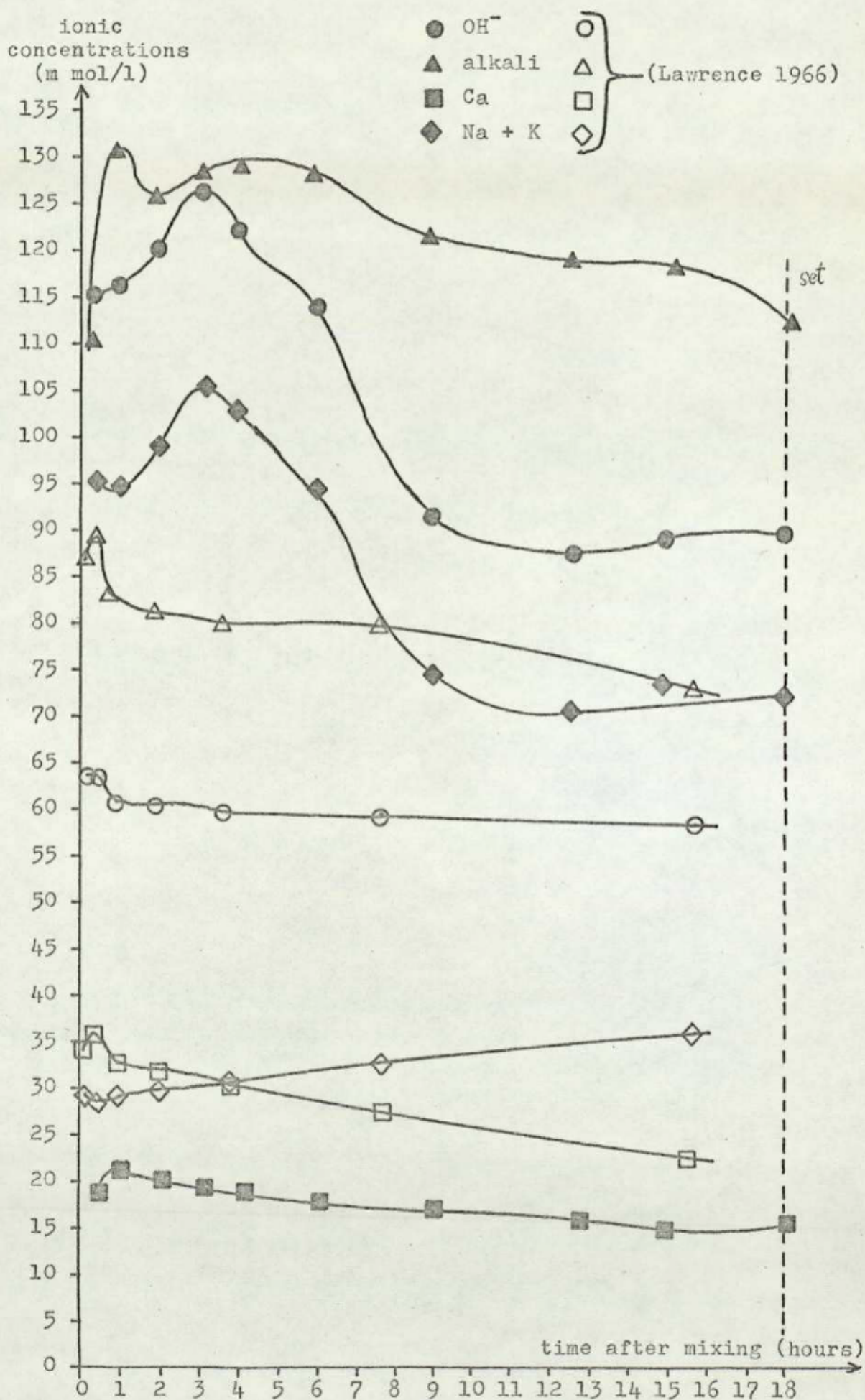


Figure 6.6

ionic
concentrations
(m mol/l)

-106-

Aqueous phase composition in
hydrating OPC at 15°C: w/c = 0.3

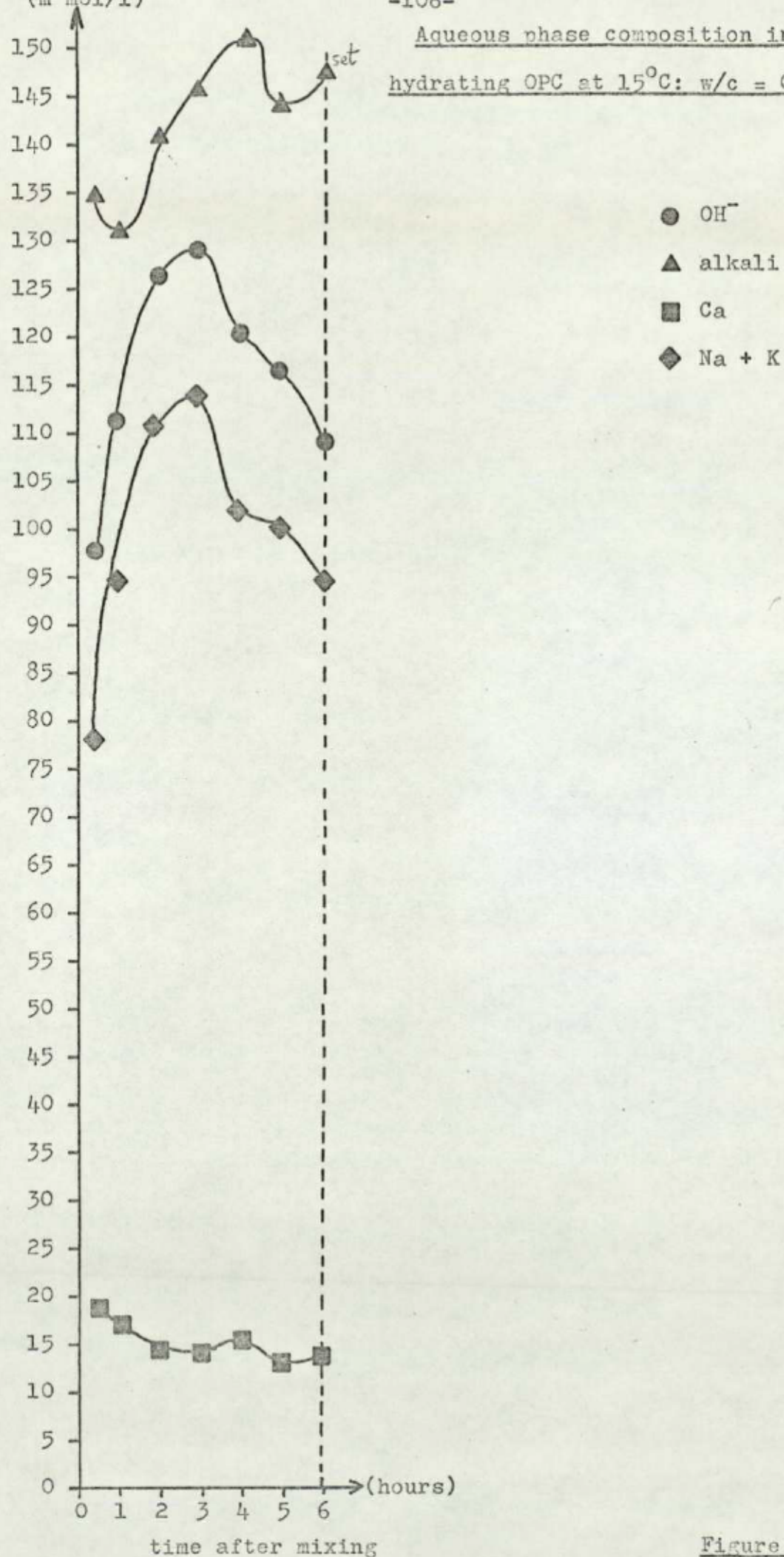


Figure 6.7

gests that cement '242' is considerably less alkaline than the OPC used in this investigation. Lawrence did not determine OH^- (measured as pH), and values for this have been taken as the sum of the three strong bases principally present in OPC: $\text{Ca} + \text{Na} + \text{K}$.

Values of $(\text{Na} + \text{K})$ have been estimated for our own analysis by the reverse procedure - subtracting Ca from OH^- - when it may be seen that these are quite high. For HAC filtrates Ca is mostly greater than OH, so that this estimation does not apply here, suggesting that $(\text{Na} + \text{K})$ is in fact extremely low in hydrating HAC.

6.4 ALKALINITY OF HYDRATING CEMENTS: CONCLUSIONS

Figures 6.2 to 6.7 show that the pH and ionic concentrations do not depend very much on water / cement ratio because both OPC and HAC filtrates are supersaturated. But hydroxyl ion concentrations in OPC filtrates (measured as pH) generally exceed those in HAC filtrates by a factor of about 30: with acid-titratable ("total") alkalinity this factor is about 4, and OPC filtrates do not exhibit the fall-off with time shown by HAC.

Following up the argument put forward in Section 6.2.1, we may estimate the magnitude of fibre diameter and strength losses by substituting values of M_m into Equation 6.3, assuming

V_f to be 8%:

δW_f

OH^-_{OPC}	0.12 mol/l	**	3.6%
OH^-_{HAC}	0.005 mol/l		0.15%
alkalinity _{OPC}	0.15 mol/l		4.5%
alkalinity _{HAC}	0.03 mol/l		0.9%

On this basis it seems that the attack on glass fibres in the aqueous conditions of hydrating HAC is not as significant as in OPC.

The hydroxyl ion concentration in HAC is almost an order of magnitude less than the total alkalinity (this is not so with OPC), suggesting that much of the alkalinity may be due to the presence of weakly dissociated bases such as aluminium hydroxide or aluminates. Dissolved silicates are negligible (a few $\mu\text{mol/l}$) in both OPC and HAC filtrates (Lawrence 1966), and the present work has shown that Fe^{2+} and Fe^{3+} are also.

In OPC the level of Al is low enough to be hidden by titration errors, and there is consequently a considerable excess of uncombined Ca. But although the level of Ca in HAC is not far below that in OPC, it falls with time and is always considerably lower than the Al level. As Greenberg & Mehra (1960) have shown that the ratio of solubility products of hydrated calcium aluminates to silicates is at least 30:1, we would expect glass fibres to be relatively immune

** Strictly the concentration in the aqueous suspension of cement, which is approximately equal to the concentration in the solid.

to attack by Ca in HAC composites (cf. a similar conclusion reached in Section 6.2.2).

We may therefore conclude from these preliminary chemical studies that because hydrating HAC has significantly lower aqueous concentrations of alkali and free Ca than OPC, it presents a much less hostile environment to glass fibres, from both the direct corrosive attack and crystal growth pressure points of view. However, it would be necessary to investigate the relative magnitude of the deleterious effects arising from these two theories before the present confusion of conflicting opinions could be resolved.

CHAPTER SEVEN: PRELIMINARY INVESTIGATION OF THE BOND BETWEEN
GLASS FIBRE AND CEMENT

7.1 EXAMINATION OF FRACTURE SURFACES USING A SCANNING ELECTRON
MICROSCOPE

The transmission electron microscope (TEM) has been much used in the past for determining the micro-morphology of hydrating cements - see, for instance, Chatterji & Majumdar's (1966) study of high alumina cement. But despite its high resolution (1 nm) it has two serious disadvantages with respect to the study of cement: poor depth of focus, and the necessity to use either replicas or else extremely thin specimens. 100 nm appears to be the limit of thickness with a conventional TEM (Midgley 1969), but Hale & Henderson Brown (1969) consider that 2 or 3 μm specimens may be used in a TEM with higher accelerating voltages (500-1000 kV).

Although a comparatively recent innovation, the scanning electron microscope (SEM) has already gained considerable use in the field of cements despite its low resolution (only 20 μm) on account of its high depth of focus (tens of μm). As it operates by diffracting a scanning beam of electrons from the surface under study no thin sections or replicas are necessary, but this surface must be electrically conducting in order to provide a current sink. Conductivity may be achieved by

vacuum depositing a thin film of metal on the specimen - gold/palladium, aluminium, or even carbon are commonly used.

Micrographs of fibre reinforced gypsum (Majumdar et al. 1968) show how valuable the SEM's increased depth of focus can be in a study of fracture surfaces in composite materials. The apparent irregularity of the glass fibre - gypsum bond in this GRG system prompted an investigation of some of our own reinforced HAC composites which had been fractured both in flexure and by delamination at an age of about one year. The surface coating was of vapour deposited aluminum.

Figure 7.1. shows a typical tensile fracture face: pull-out lengths vary up to almost 1 mm, and cement particles may be seen still adhering to pulled out fibres. Delaminated fracture surfaces (Figures 7.2 and 7.3), on the other hand, show how poor and intermittent the glass - cement bond can be. This must be partly due to the irregular coating of waxy binder and organic size on the glass as-received (Figure 7.4), which cannot be completely leached off with water.

In the event these micrographs proved to be of little value, except to highlight the non-uniformity of the fibre - matrix bond. In general the matrix was found to be mostly amorphous and rather uninteresting, which was not the case with Majumdar et al.'s (1968) highly characterised gypsum, suggesting that it would probably be more revealing to use a

Tensile fracture face in glass fibre reinforced HAC

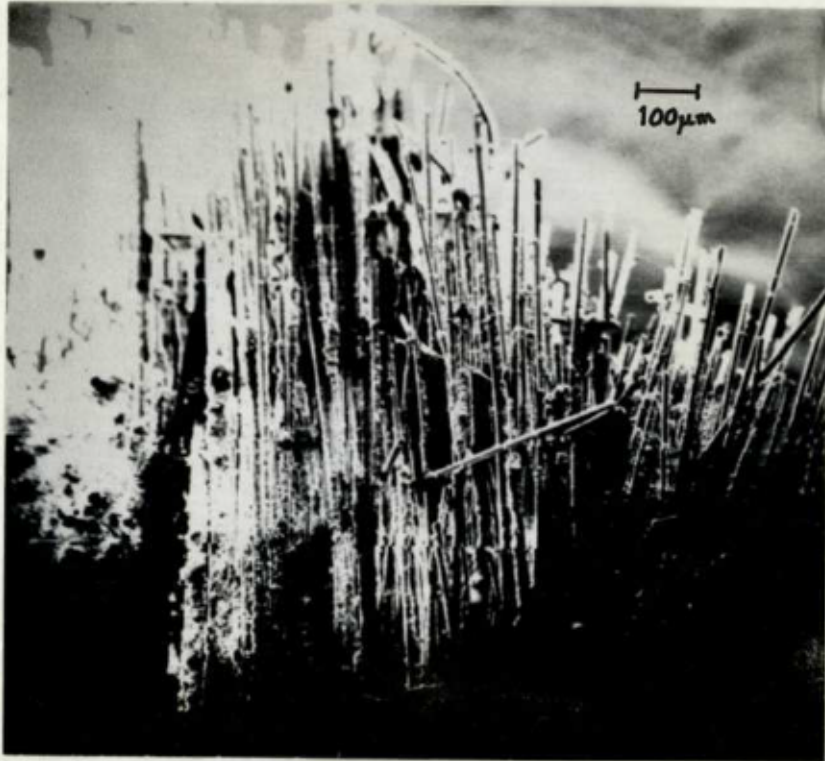


Figure 7.1

Delamination in glass fibre reinforced HAC

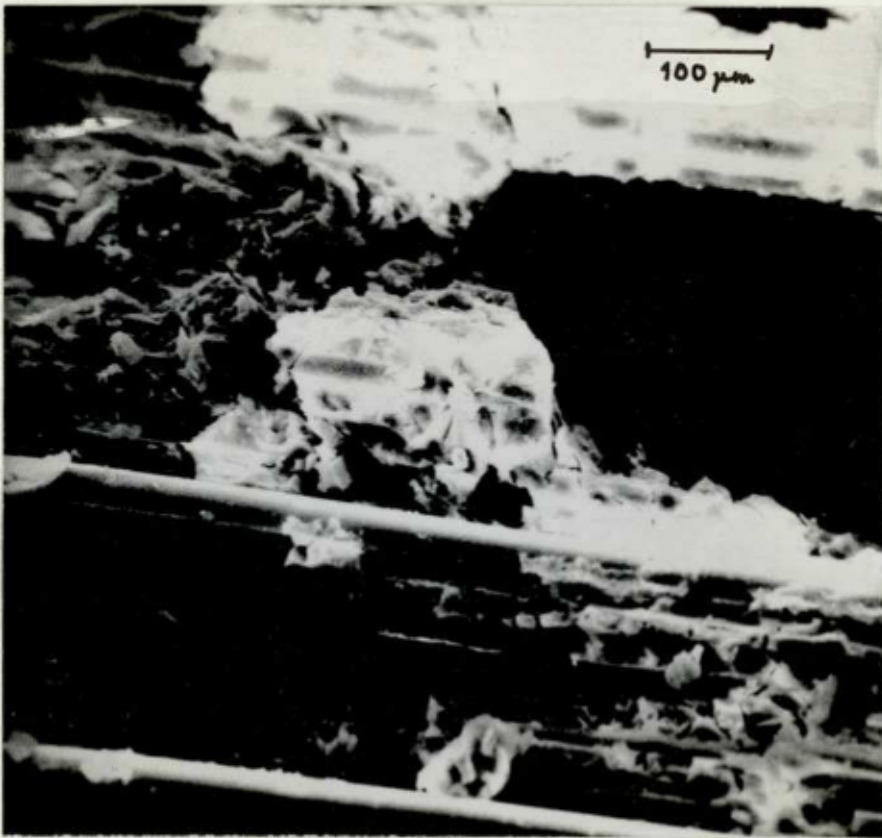


Figure 7.2

Delamination in glass fibre reinforced HAC

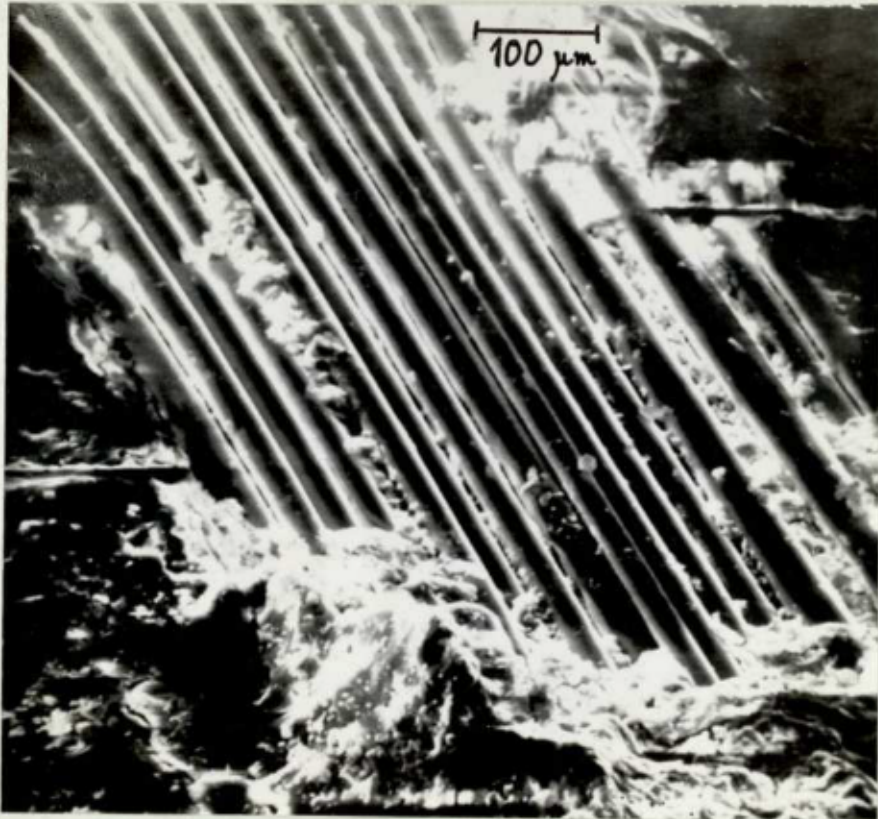


Figure 7.3

Commercial E-glass fibre: as-received

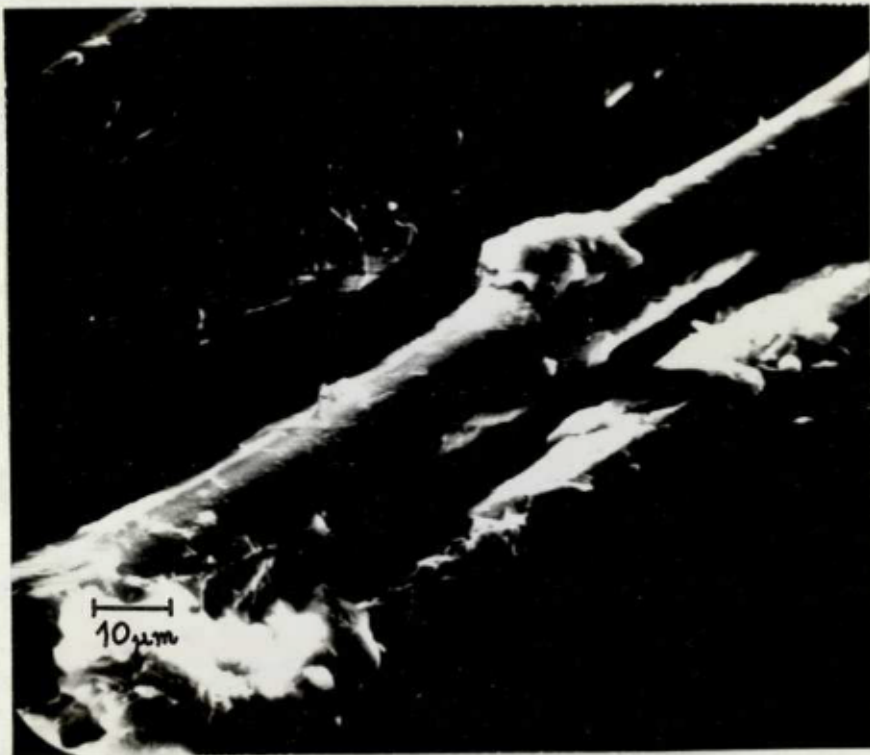


Figure 7.4

pure calcium aluminate cement such as Secar 250, where crystalline plates and rods are usually much more in evidence (see Figure 3.4, from Chatterji & Jeffery 1968). Their shape may then help to provide a clue to their composition and enable a comparison to be made with the crystals which Urev et al. (1967) have observed growing on glass fibres in a cementitious matrix (see Section 6.2.3).

7.2 GLASS / CEMENT BOND STRENGTH

7.2.1 Test method

The choice of a suitable method for measuring glass / cement bond strength was influenced largely by economic considerations: no large-scale testing apparatus was available, and glass was on hand in the form of lengths of fibre. It seemed sensible to adopt the 'fundamental' approach of pulling single glass fibres out of blocks of cement using the beam of a laboratory balance as the means of applying load. A rough idea of the magnitude of the bond shear strength would thus be obtained, and any variation caused by different surface treatments of fibre or of cement paste compositions observed.

In order to achieve continuous loading at a steady rate, the choice lay between hydraulic loading (Loewenstein & Dowd 1968, Gillet & Majumdar 1968) and chain loading (Thomas 1960, Kelsey & Krock 1965). Since it is easier to achieve a linear rate of stress increase with chain loading, an apparatus was constructed from a Griffin Quickway Chainindial Balance by making

the following modifications, illustrated in Figure 7.5.

A small synchronous mains-voltage induction motor was geared down with Meccano worm and cogs to give a very constant output speed of around 5 r.p.m. with a fairly high torque. This output was coupled to the chain dial mechanism via a cone-pulley / spring belt system which gave a range of 3 speeds and allowed easy return to zero load without the use of a clutch. The motor was mounted with rubber grommets on the base of the balance, and the belt drive further minimised the transfer of any vibrations to the loading beam: the motor was started by pressing a microswitch - a quick and shock-free operation.

The loading drum was modified to take up to two turns, and the point of attachment of the free end of the chain to the balance beam was moved outwards to about 130 mm from the fulcrum. This increased the effective capacity of the chain movement sevenfold, and the range over which the chain loading corresponded linearly with the dial reading was now found to be about 70 mN.

Vibrations in the loading beam were minimised by a damper consisting of a vane dipping into an oil dashpot. In order to ensure free beam movement it was therefore necessary to counterweight the beam with lead weights of about 150 g on each end.

Single fibre pull-out apparatus



Figure 7.5

The chain dial was initially calibrated on a weight basis, but in view of the linear relation between dial reading and time (due to the constant motor speed) it was decided to measure the time to failure with a stopwatch. The rate of increase of stress was found to be 0.778 mNs^{-1} . The end-effect of the time taken for the motor to reach a constant speed (ca. 0.1 s) was considered to be compensated by the reaction time between seeing the pull-out failure and stopping the watch, which moved in steps of 0.2 s. Thus the maximum error was estimated as 0.3 s, of the order of 1% of normal pull-out times: this was considered to be well within the limits of sample errors.

7.2.2 Design of sample-holder

It was planned to use 12 samples per run, and since hydration times of several weeks were envisaged, it was necessary to have enough sample-holders to enable several runs to proceed simultaneously. In view of this fact and the necessity to use a material unaffected by water, each holder was constructed from two polycarbonate weighing bottles (Griffin & George S16-222) whose polythene caps were cemented end to end with polythene cement (see Figure 7.6). Two polythene rings, cut from sample bottles, were cemented concentrically onto the base of the holder, the inner one to support the cement disc on the mercury pool, the outer one to separate the sample from the annulus of water which provides a curing

Design of sample-holder: cross-section

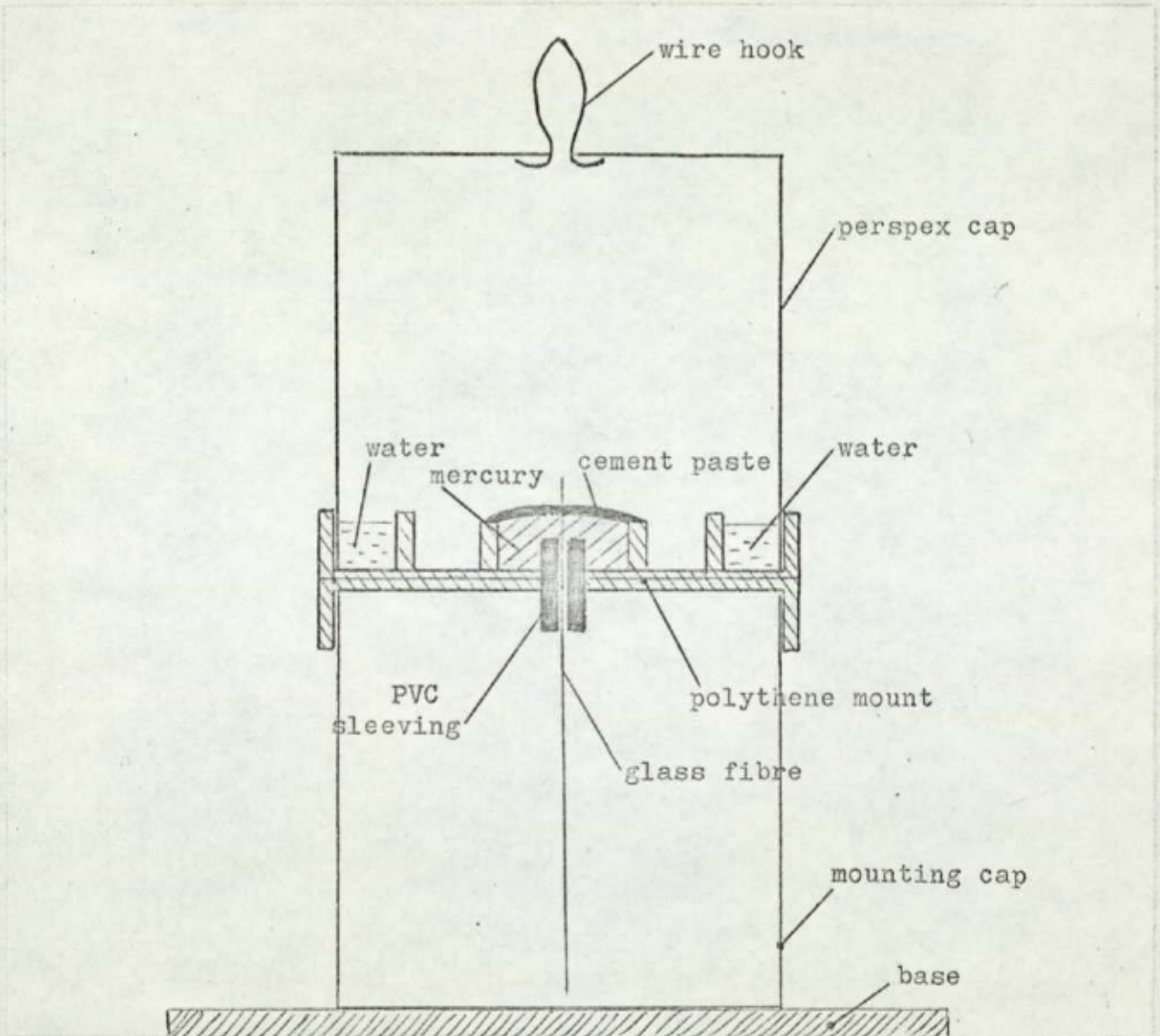


Figure 7.6

atmosphere saturated with water vapour. The difficulty of passing a fibre through the high energy surface of the mercury was avoided by enclosing the fibre in a guide-tube of PVC insulation sleeving around which an annulus of mercury was formed. The sleeving was then pulled down a little into the holder so that the mercury closed in over the fibre, and was left in place to ensure that the fibre remained in as vertical a position as possible while the cement set.

The sample was cured by semi-immersing the test holder in a set-temperature water-bath for a fixed period, after which it was taken out and the base cap removed to expose the free end of the fibre for attachment to the loading apparatus.

7.2.3 Measurement of sample dimensions

After fibre pull-out, cement discs were removed from the sampleholder and their central thickness ϕ was measured between the pointed anvils of a screw micrometer (Moore & Wright 947M). Cement surfaces were in general quite smooth and measurements were accurate to about 0.05 mm (i.e. ca. 5%).

Optical transmission microscopy was judged to be the quickest and most accurate method of measuring the diameter d of the glass fibres (Thomas 1960). A T&S microscope was used, fitted with a calibrated 10x Kellner crosswire micrometer eyepiece and a 40x objective. In order to minimise

edge diffraction effects a liquid of refractive index close to that of E-glass ($\mu=1.55$) must be used, and glycerol ($\mu=1.47$) was chosen as its high viscosity also helps to 'anchor' the fibres onto their glass slide. Despite this precaution fibre dimensions were sometimes rather indistinct and could be measured only to the nearest $0.5 \mu\text{m}$ (ca. 3% accuracy).

7.2.4 Preparation and testing of samples

For initial tests individual glass fibres were teased from Fibreglass FGRE 2 roving and used as received (see Table 3.1 for their chemical composition): their average diameter was found to be $12.5 \pm 0.5 \mu\text{m}$. The best information available on their surface condition was that they were coated with both PVA size and a chromo-organic wetting agent (see Section 5.3.1), probably rather irregularly: no attempt was made to remove this coating for the first 11 runs.

Ciment Fondu was used for all runs except for No 11, where Secar 250 was used: the chemical compositions of these cements are shown in Table 3.2. Cement powder was mixed by hand in 5 g quantities with the appropriate amount of water for one minute in a porcelain pestle and mortar: the paste was then transferred on a small spatula to each of the sample-holders in turn. The placing of this paste was carried out as quickly as possible to stop it drying out before reaching the water-saturated atmosphere of the sample-holder. The dozen

sample-holders were then transferred to a water-bath at the required temperature and were left there until just before testing.

The sample-holder was then hung from one arm of the chain balance, and the free fibre end was gripped between two screw-clamped flats of PVC-covered brass (see Figure 7.6). This was found to be an efficient clamping method, and it did not damage the fibre sufficiently to cause repeated breakage in or near the clamp.

Each sample was tested as detailed in Section 7.2.1. Average pull-out stress τ was calculated from the measured load P , cement thickness ϑ and fibre diameter d using

$$\tau = \frac{P}{\pi d \vartheta} \quad (7.1)$$

Given the accuracy of determination of P , d , and ϑ , as discussed above, τ should be accurate to about $\pm 6\%$, a value which is well within the limits of sample dispersion.

7.3 MEASUREMENT OF PULL-OUT STRESS

7.3.1 Experimental conditions

The first 15 runs were of an exploratory nature, and were intended to obtain a rough idea of the variation in pull-out stress with changes in certain experimental parameters. Laboratory working conditions were far from ideal, but it was

felt that some preliminary investigation was necessary in order to form a basis for later work.

Table 7.1 lists the experimental conditions used for these runs. The cements and glass fibre were as described above (Section 7.2.4). "a" indicates that the glass was used in the as-received condition; i.e. with the irregular coating of hard chrome size and waxy binder, whose exact composition could not be ascertained. Fibres designated "b", on the other hand, were boiled in water for 30 minutes, which removed a certain amount of this organic coating: it is not known how much was removed, but individual fibres were much more brittle to handle afterwards.

The use of higher curing temperatures than were thought desirable was necessitated by the lack of equipment to cool the water-bath below summer laboratory temperatures: as a result, the HAC pastes will have undergone a significant degree of conversion and will consequently be weaker. In runs 14 and 15, 25% by weight of cement powder of two additives were mixed in with the paste; aluminium chloride hydrate and sodium silicate (Crosfield "Pyramid" 125 solution: $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.07$) respectively, which were suggested in Section 5.3.2 as suitable coupling agents.

Preliminary investigation of pull-out stress: experimental conditions

Run number	cement	W/c ratio	Hydration time (days)	Curing temperature (°C)	Fibre condition	Additives (if any)
1	CF	.326	1	21	a	-
2	CF	.326	1	25	a	-
3	CF	.326	1	32	a	-
4	CF	.506	1	28	a	-
5	CF	.326	1	28	a	-
6	CF	.326	3	28	a	-
7	CF	.284	2	25	a	-
8	CF	.284	1	25	a	-
9	CF	.300	3	25	a	-
10	CF	.300	1	25	a	-
11	250	.352	1	25	a	-
12	CF	.300	1	25	b	-
13	CF	.300	1	25	b	-
14	CF	.300	1	25	b	see
15	CF	.300	1	25	b	text

Table 7.1

7.3.2 Results

Table 7.2 lists the individual pull-out stress results from each run in order of testing (as casting): rank correlation tests (see Table 7.3) established that there was no significant trend in τ with this order at a 20% level (Ractliffe 1967) except for runs 7 and 11. In both these runs casting the samples took longer than usual, and the cement paste was noticeably drier by the time the last specimens had been reached, and would therefore be weaker when set: hence the high negative correlation.

Because specimens were so small and delicate, not all of the original 12 survived until they were tested. Furthermore, of those that did, it was inevitable that some fibres would break before pulling out (in the event about 10% of the 151 specimens tested): but it was necessary to include these somewhat unreliable values (denoted by ">") in the analysis in order to prevent excessive bias towards lower, less prone to fibre breakage, values of τ . Since most of the runs were therefore irregularly distributed, with unusually high and low extreme values, the median rather than the mean was chosen as the best estimate of the "central tendency" of each run (Yule & Kendall 1964). Table 7.4 lists statistical parameters from each run for purposes of comparison: the coefficient of variation ($= \frac{\text{standard deviation}}{\text{mean}} \times 100 \%$) affords a convenient way of displaying the dispersion of results.

Individual values of pull-out stress (I)

Run No.	No. of samples	τ values												Ratio breakages : pull-outs
1	6	0.36	0.41	0.74	0.44	0.38	0.68							0:6
2	12	1.19	0.14	0.12	0.52	0.71	>0.45	0.09	0.70	1.31	1.17	1.02	0.26	1:11
3	11	1.25	>1.42	>0.26	0.50	0.67	1.15	>0.89	0.50	1.24	0.90	0.42		3:8
4	9	0.46	>1.60	0.23	0.95	>0.74	0.30	0.25	>0.68	0.42				3:6
5	8	0.11	0.70	0.52	0.30	0.44	0.63	0.46	0.54					0:8
6	10	0.92	>1.98	1.19	1.17	1.15	0.90	1.45	0.42	1.15	1.11			1:9
7	10	0.97	0.93	0.58	0.53	0.61	0.78	0.67	0.94	0.77	0.54			0:10
8	9	0.37	0.34	0.51	0.94	0.86	0.42	0.99	0.48	0.37				0:9
9	12	1.33	0.67	1.06	1.19	0.68	1.11	0.96	>1.97	1.13	0.53	0.99	1.35	1:11
10	10	>0.55	0.56	0.91	1.28	0.46	0.73	0.27	0.72	1.54	0.28			1:9
11	11	1.28	0.72	1.69	2.08	0.50	1.22	0.81	0.15	0.35	0.43	0.47		0:11
12	10	0.55	2.74	>0.32	1.63	1.18	0.35	1.48	3.40	0.57	1.48			1:9
13	11	1.16	>3.04	1.77	>1.37	2.02	0.86	>1.23	0.87	1.01	2.29	3.04		3:8
14	11	0.91	1.24	2.69	2.88	3.40	2.04	2.12	2.05	4.38	2.62	1.97		0:11
15	11	>2.36	2.10	1.85	1.27	0.92	1.50	0.86	0.77	0.49	0.99	3.21		1:10
	<u>151</u>													<u>15:136</u>

Table 7.2

Correlation between measured pull-out parameters (I)

Run number	Rank corrln. of τ vs. testing order	Product-moment coefft. of correlation	
		ρ vs. cement thickness θ	τ vs. ρ (time- to-failure)
1	+0.43	+0.72	+0.55
2	+0.20	+0.57	+0.91
3	-0.30	+0.83	+0.91
4	-0.27	+0.79	+0.99
5	+0.26	+0.30	+0.83
6	-0.31	+0.21	+0.87
7	-0.76	+0.86	+0.58
8	-0.14	+0.24	+0.97
9	+0.07	+0.27	+0.96
10	-0.08	+0.79	+0.93
11	-0.72	-0.02	+0.96
12	+0.13	+0.32	+0.99
13	-0.30	-0.08	+0.79
14	+0.25	+0.50	+0.48
15	-0.37	-0.44	+0.91

Table 7.3

Statistical parameters (I): values of τ

Run No.	No. of samples	Mean (MNm^{-2})	Coefft. of variation (%)	lowest value	median (MNm^{-2})	highest value
1	6	0.50	33	0.36	0.42	0.74
2	12	0.64	70	0.09	0.61	1.31
3	11	0.84	47	0.26	0.89	1.42
4	9	0.62	70	0.23	0.46	1.60
5	8	0.46	41	0.11	0.49	0.70
6	10	1.14	35	0.42	1.15	1.98
7	10	0.73	23	0.53	0.72	0.97
8	9	0.59	45	0.34	0.48	0.99
9	12	1.08	35	0.53	1.08	1.97
10	10	0.73	57	0.27	0.64	1.54
11	11	0.88	69	0.15	0.72	2.08
12	10	1.37	75	0.32	1.33	3.40
13	11	1.70	48	0.86	1.37	3.04
14	11	2.39	41	0.91	2.12	4.38
15	11	1.48	55	0.49	1.27	3.21

Table 7.4

In fact the rank correlation between medians and means in these 15 runs is extremely high (Spearman's coefficient = +0.97), and we may therefore use the mean as the criterion of comparison between runs as it is more amenable to algebraic treatment. Variance ratio F and student's t between the means were computed (program STATISTIC) for all 15 runs, and even where these tests established a significant (at a 5% level) difference between the means, which was in about 30% of the comparisons, this significance must be treated with caution because of small size of sample and probable skewness of its distribution.

Two of the runs (nos 12 and 13) were carried out on different days under identical experimental conditions. The medians are virtually identical, and the probabilities that both variance and mean of each run are random samples from the same population exceed 40% ($F^{10,11} = 1.62$; $t^{19} = 0.81$). Thus the reproducibility (of these two runs at least) seems to be fairly high.

7.3.3 Interpretation of results

Despite the reservations expressed above concerning detailed statistical analysis of the results, it should still be possible to observe certain trends in τ with change in experimental parameters, if only on a ranking basis, and these are considered below.

(i) τ increases with temperature from 21° to 32°C (runs 1, 2, 3): the reason for the anomalously low value at 28°C (run 5) may be that whereas HAC undergoes little conversion at 21° and 25° within one day, but a great deal at 32°C, at 28°C the process is incomplete and the cement is therefore in a weak state.

(ii) τ shows an expected increase with hydration time from 1 to 3 days at various different curing temperatures and w/c ratios (runs 5 and 6; 8 and 7; 10 and 9).

(iii) No significant trend can be established with increase in water/cement ratio (runs 5 and 4; 8, 10 and 2).

(iv) Removal of some of the hydrophobic coating on the fibres by boiling virtually doubled τ (runs 12/13 and 10).

(v) The addition of AlCl_3 increased τ by about 50% (runs 14 and 12/13), indicating that this compound might have some use as a coupling agent. However, there was no increase with sodium silicate (run 15), and this was thought to be caused by a decrease in the strength of the cement matrix due to the high alkalinity (pH ca. 13) of the additive. Pull-outs were not clean in run 15, a higher proportion of particles than usual adhering to the fibres in the contact zone after pull-out.

7.4 POSSIBLE IMPROVEMENTS IN EXPERIMENTAL TECHNIQUE

7.4.1 Statistical aspects

These preliminary results have demonstrated that single fibre pulling may be a feasible way of measuring glass/cement bond strength, only 10% of the specimens failing by fibre fracture. However, the spread of results is too great for any meaningful analysis to be made of the effects on bond strength of run conditions, as may be seen by referring to the coefficients of variation listed in Table 7.4, and we must therefore consider ways of reducing this dispersion.

Casting and testing orders have already been discounted as possibly significant sources of systematic error (see Section 7.3.1) but computation of product-moment coefficients of correlation (see Table 7.3) shows that there is generally a much higher correlation between τ and P than between P and θ , suggesting that the average shear stress as determined by Equation 7.1 is not the critical factor in bond failure. (Incidentally, the high positive correlation between τ and P , or time-to-failure, means that fatigue effects are relatively insignificant). It is possible that the non-uniformity of cement paste consistency through the discs is responsible for some of the dispersion in the results, but it seems that in further work we ought to consider stress concentration in the interface as a criterion for failure.

7.4.2 Testing apparatus

The capacity of the chain-loaded balance was used to the full with some of the specimens (γ ca. 2 MNm^{-2}), and it was felt that if longer hydration times and coupling agents were to be investigated, an instrument capable of applying greater loads would have to be employed to measure these higher values of γ . A water-flow loaded system (Gillet & Majumdar 1968, Loewenstein & Dowd 1968) could provide this increased capacity, but an Instron-type instrument would be ideal, with its low vibration, ability to record (permanently) load vs. time, and above all its constant strain- (rather than stress-) loading rate.

7.4.3 Specimen preparation

The techniques of preparation, curing and testing of specimens were thought to be adequate, with the exception of the high curing temperatures. In future experiments, a cooled water-bath at 15°C should be used to prevent conversion of HAC to cubic hydrates. Also, the design of the specimen holder in the testing apparatus should be improved to ensure that fibre pull-out is truly perpendicular to the plane of the cement disc.

However, while the constancy of diameter of glass fibre in Fibreglass FGRE 2 roving was advantageous in attaining a reasonable uniformity in bond area and in promoting cement hydrate

crystal growth of a fairly consistent magnitude, the lack of control over the nature of the glass surface was held to be a very serious drawback to achieving reproducible results. As a result it was decided to construct a furnace capable of drawing 'virgin' E-glass fibres of approximately the same diameter as commercial ones (i.e. ca. $12\ \mu\text{m}$): this is the subject of the following chapter.

CHAPTER EIGHT: GLASS FIBRE DRAWING

8.1 PRODUCTION OF GLASS FIBRES

8.1.1 Methods available

Glass fibre production is a fairly long-established art on an industrial scale, where several hundred fibres may be drawn simultaneously from one melt contained in a bushing with multiple forming tips. Laboratory-scale processes are less well documented in the literature, but two general methods seem to exist: rod-pulling and single fibre drawing.

It is possible to pull fibres from glass rods held in a flame which show very little variation in fibre strength and diameter (Morley et al. 1964). The disadvantage of this method, in which a fairly complicated timing apparatus takes the place of a costly furnace, is that continuous fibres cannot be produced. While this does not matter in single fibre experiments, it could prohibit further investigation calling for larger quantities of fibres. But it is worth noting that Chavet & Davidof (1961) have produced an ingenious continuous version of this apparatus.

However, E-glass is not readily available in rods, and it was therefore decided to melt crushed glass in a crucible and to pull fibres from a small orifice in its base onto

a rotating drum. Bushings of the type used by Thomas (1960) and Loewenstein & Dowd (1968) in which electrical power is fed through a step-down transformer and applied directly across the crucible at about 1 volt are difficult to obtain, so furnace-heating was chosen instead. It is possible to wind extremely long lengths of fibre from this type of apparatus, and various coatings may be applied easily to the fibre surface by passing it through liquid baths.

8.1.2 Operating conditions

It seems that for an apparatus in which a single fibre is drawn from a melt through a nozzle in the base of the crucible, the melt temperature should be about 100°C above the nozzle temperature (Cameron 1966) and that the fibre should be quenched rapidly (de Vekey & Majumdar 1967). Cameron (1966) and Thomas (1960) have found that a nozzle temperature of at least 1300°C is needed to produce fibres with a low scatter in tensile strength, around a mean value of about 3.5 GNm^{-2} . Thus our furnace should be capable of heating a crucible of glass up to at least 1400°C .

Fibre diameter is most easily controlled by varying the speed of the winding drum, since for a given nozzle size and melt temperature the rate of mass flow is independent of pulling speed N (Thomas 1960). Thus

$$\text{Mass flow} = \rho_f \cdot \frac{\pi d^2}{4} \cdot N = \text{constant} \quad (8.1)$$

and hence
$$d \propto \sqrt{\frac{1}{N}} \quad (8.2)$$

Under the correct operating conditions it should therefore be possible to vary the fibre diameter over at least an order of magnitude by changing the winding speed. A diameter of 12 μm was the initial aim as this is the size of most commercial fibres.

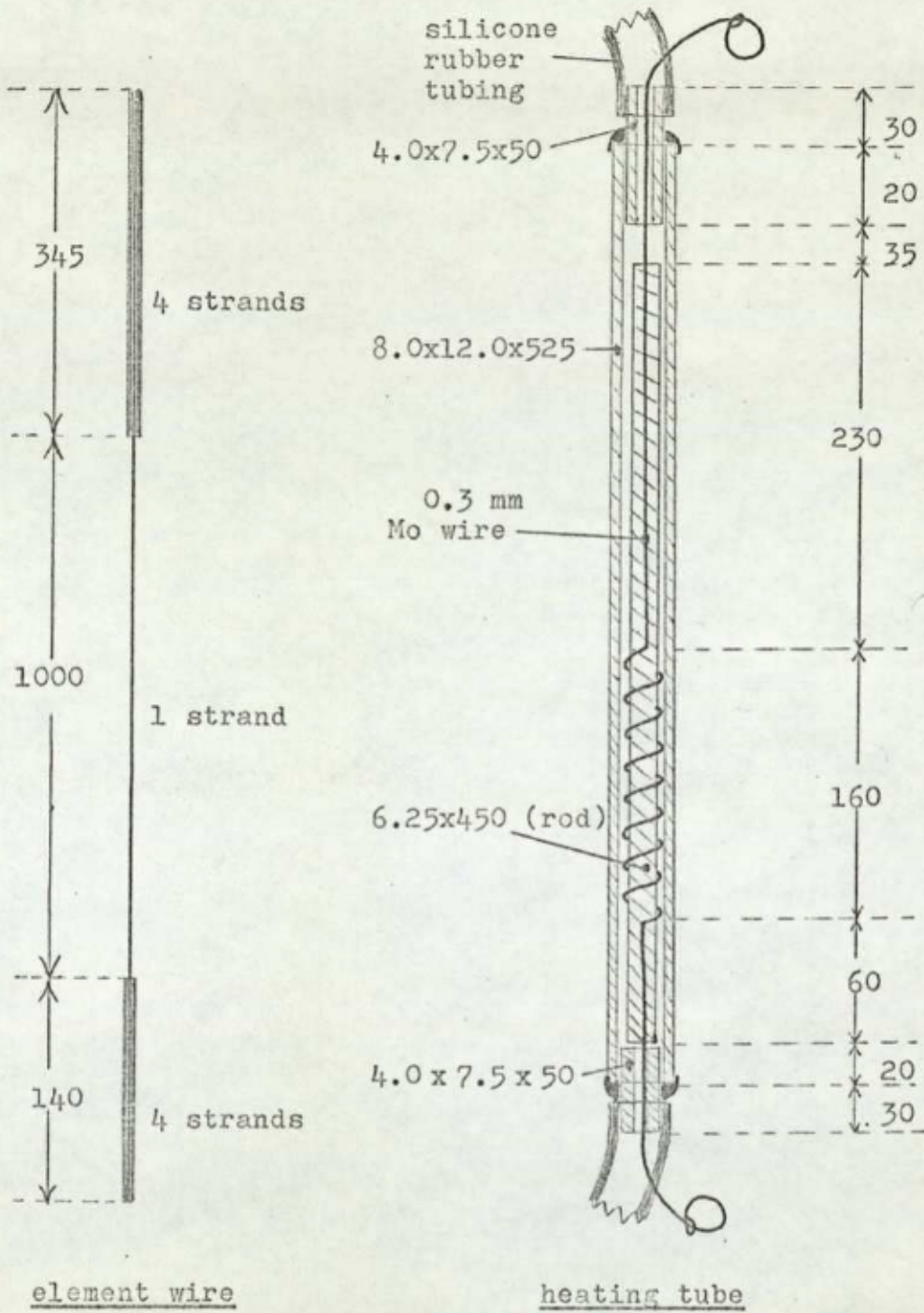
8.2 CONSTRUCTION OF APPARATUS

8.2.1 Furnace design

For reasons of economy a molybdenum-wound multi-element vertical tube furnace (Hayes & Roberts 1963) made of alumina was chosen in preference to a platinum-wound furnace (de Vekey & Majumdar 1967): it is more versatile (it may also be used in a horizontal position), and each element is cheap, easy to wind, and can be replaced quickly if it burns out.

The furnace consists of a central wide tube surrounded by eight narrow tubes, each containing 0.3 mm molybdenum wire wound round a rod, through which hydrogen can be passed to prevent oxidation of the wire. Figure 8.1 shows how each element tube was constructed: the low-resistance sections were made by twisting together four strands of wire on a specially adapted variable-speed laboratory motor, and were fixed to the rod with alumina cement. End-joints were sealed with 'Autostic', a proprietary silicate cement, and the tubes were

Construction of furnace heating elements



[All dimensions in mm (not to scale)
 Cross-hatching represents alumina
 Tube sizes: inner diameter x outer diameter x length]

Figure 8.1

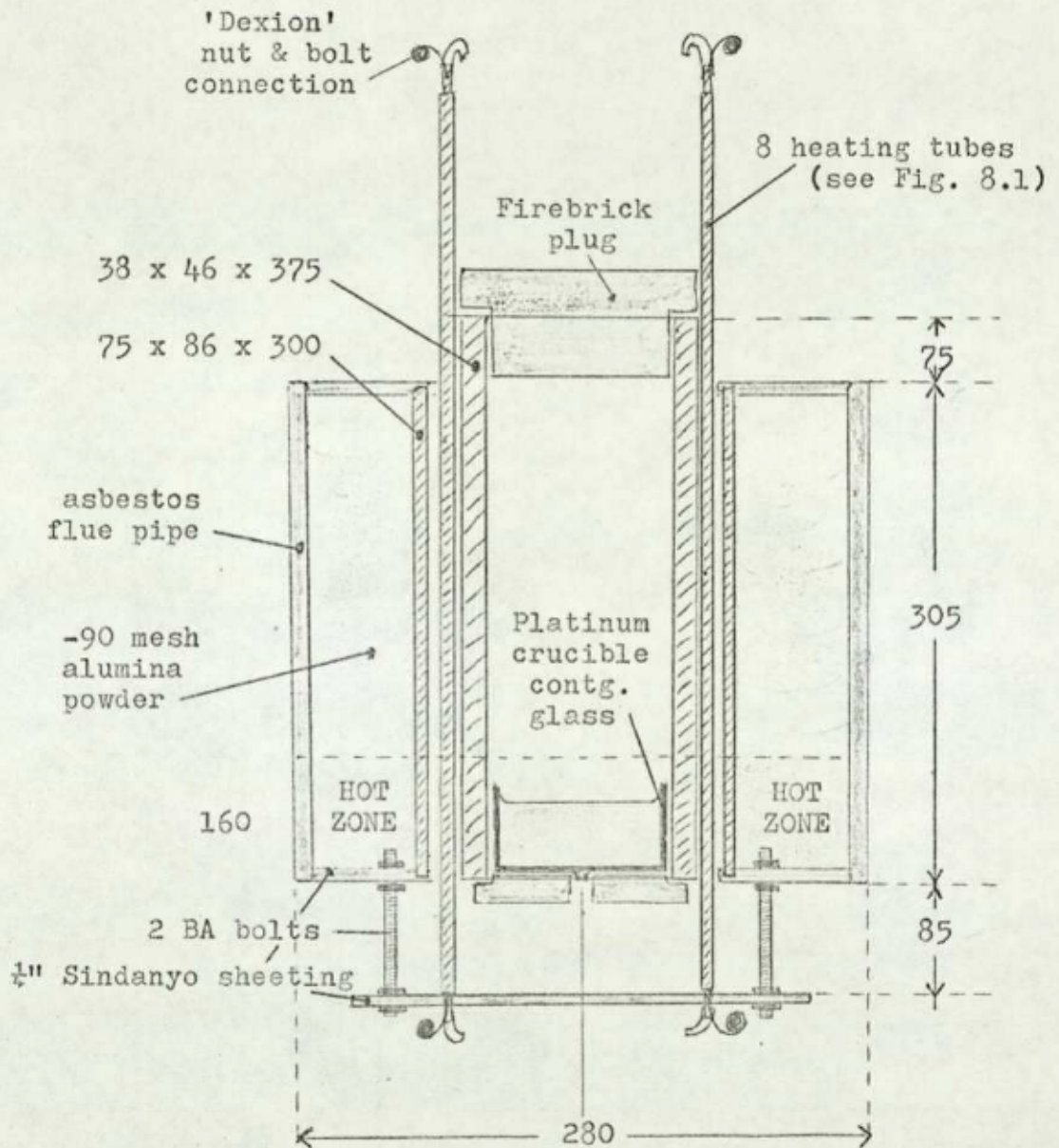
connected in series by silicone rubber tubing. Electrical connections, also in series, were made via 'Dexion' nuts and bolts, which acted as heat sinks.

Figure 8.2 illustrates the design and dimensions of the furnace. All ceramic parts were of T.S.L. "Recrystallised alumina" except for the outer casing and element tube base, which were cut from 'Sindanyo' sheeting, and the internal insulation, which consisted of -90 mesh T.S.L. fused alumina powder. Further external insulation was provided by three layers of aluminium foil wrapped round the outside of the furnace and by glass wool at the top and bottom.

Element tubes were flushed out with hydrogen prior to starting a heating run, and the flow through the tubes was kept between 250 and 500 mlmin⁻¹. A warning neon light, operated through probes inserted into a mercury manometer (see Figure 8.3), was extinguished if the flow-rate overran these limits, as a positive pressure in the tubes was necessary to prevent inward diffusion of air to form an explosive mixture inside the tubes. Equally, if too much hydrogen diffused out, an explosive mixture could have been formed in the insulation of the furnace.

The furnace was heated by connecting the eight elements in series directly across the output of a Eurotherm 10 A thyristor-operated temperature controller (type PID/SCR/PA), using a 5%-20% Rh/Pt thermocouple to sense crucible nozzle

Furnace design: cross-section



[All dimensions in mm (not to scale)
 Cross-hatching represents alumina
 Tube sizes: inner diameter x outer diameter x length]

Figure 8.2

Detail of furnace control

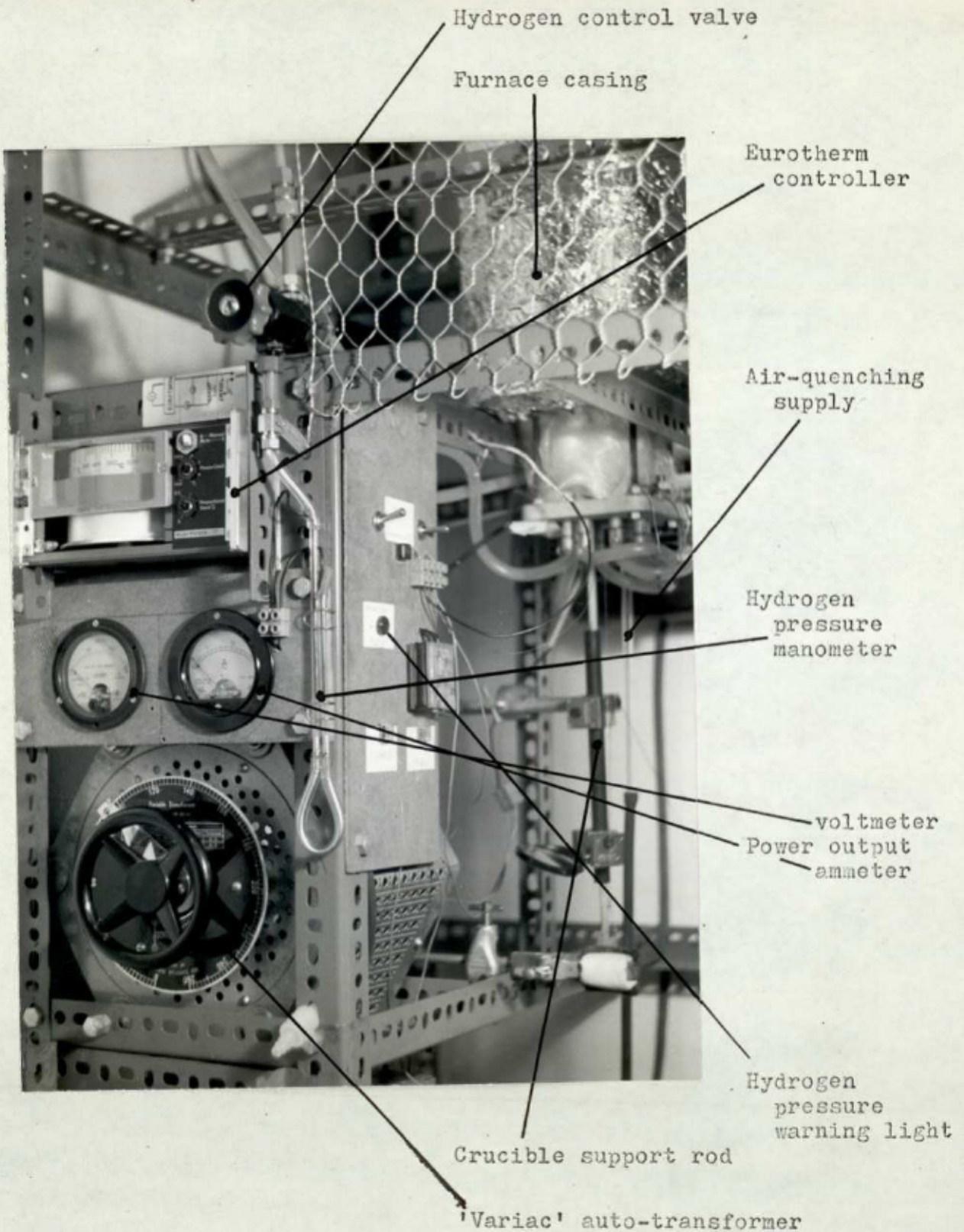


Figure 8.3

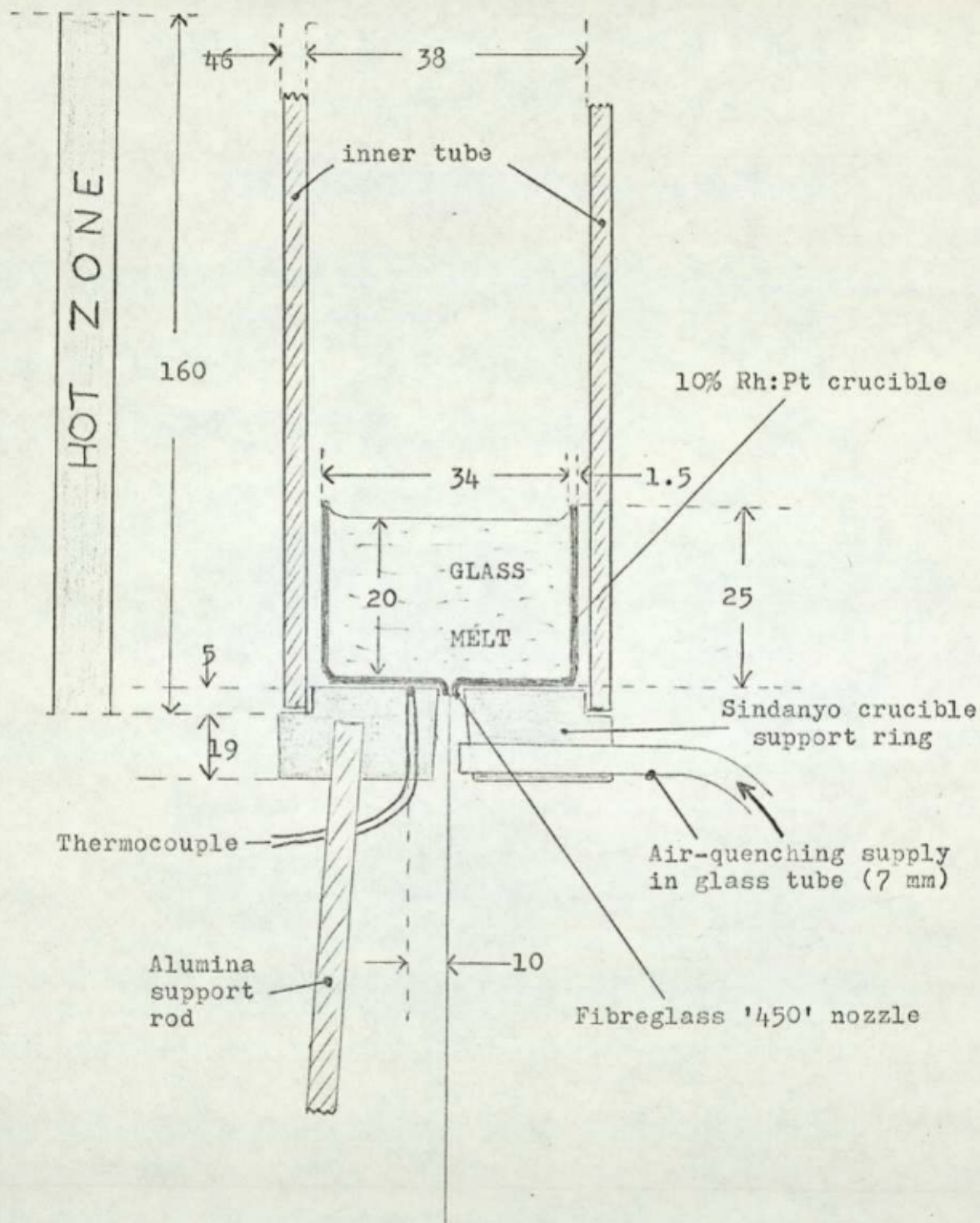
temperature. The position of this thermocouple on the crucible mounting is shown in Figure 8.4, where it measured effectively "drawing temperature". The crucible itself was made from 10% Rh:Pt and was fitted with a standard Fibreglass '450' nozzle (orifice diameter ca. 1.1 mm).

8.2.2 Attainment of suitable operating conditions

Owing to the high temperature coefficient of resistance of molybdenum the furnace impedance increased so much that it was found to be impossible to exceed about 1000°C at the power limit of the controller (10 A @ 240 V), and it became necessary to redesign the heating arrangement.

An obvious solution was to couple the controller output to the furnace via a variable transformer. However, the particular controller originally purchased was not designed to take inductive loads, and the quick-acting protection fuse was replaced by an inductive testing device which ensured that when the furnace was switched on from the cold, the power surge through the controller would not be unreasonably high. The modified power supply circuit is shown in Figure 8.5: if, prior to turning on the power, depression of the switch S to position 2 and back did not cause the neon bulb in the controller to flash, this indicated that the inductive coupling of the system was not close enough to avoid damaging the controller during switch-on. Likely faults were burnt-out furnace

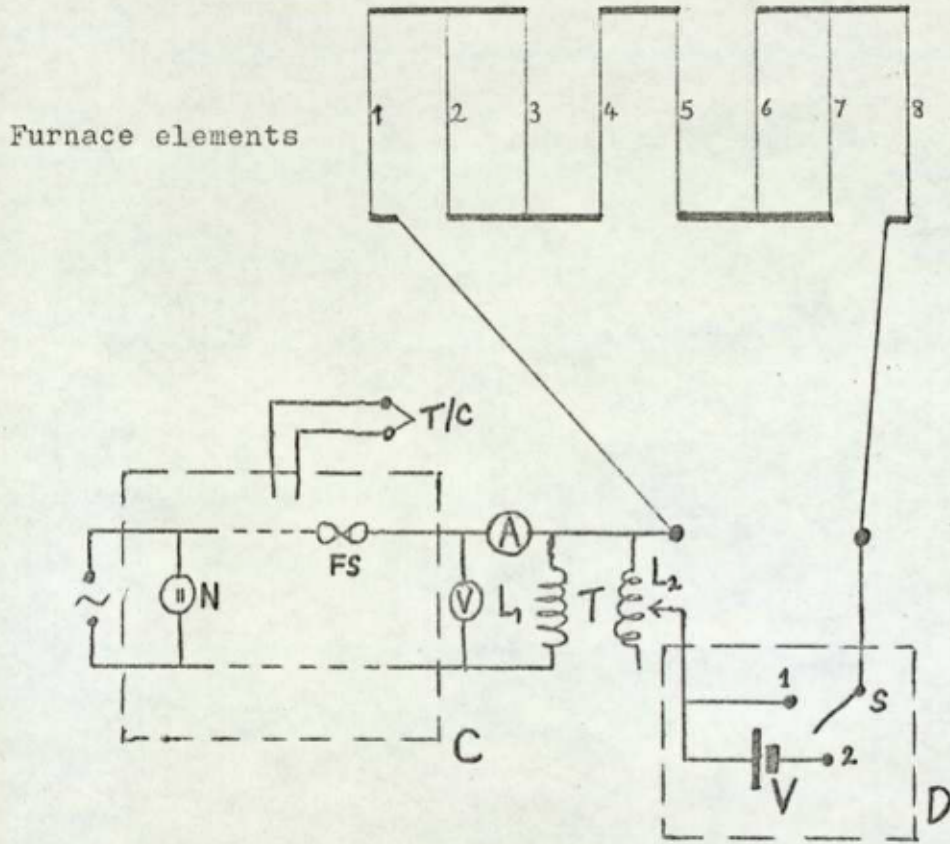
Detail of crucible mounting



Dimensions in mm (not to scale)

Figure 8.4

Power supply circuit: furnace element connections



- A ammeter
- C Eurotherm temperature controller
- D Inductive test device
- FS quick-acting 10 A fuse
- N mains voltage neon lamp
- S S.P.D.T switch biased to position 1
- T 'Variac' 12 A 240 V auto-transformer with variable tapping on secondary
- V $1\frac{1}{2}$ V cell

Figure 8.5

elements, poor electrical connections, or wrong Variac setting.

Figure 8.5 also illustrates the modified series/parallel connection of the furnace elements, which reduced the total furnace resistance to $\frac{1}{3}$ of its former value, thus permitting a 60% increase in power. As a result of these modifications the maximum crucible temperature was raised to over 1400°C , high enough (in theory, at least) for the satisfactory pulling of glass fibres.

A $\frac{1}{3}$ kW mains induction motor with a constant speed of 1490 rpm. was used to power the winding drum, and its axis could be tilted to enable fibres to be wound onto different parts of the drum (see Figure 8.6). The winding drum was a seamless copper calorimeter approximately 52 mm in diameter, so that the drawing speed was about 4.1 ms^{-1} . According to Thomas (1960) this should provide a variation of fibre diameters between 8 and $19 \mu\text{m}$ in the range $1200 - 1300^{\circ}\text{C}$ nozzle temperature. Since fibre diameter $\propto (\text{drawing speed})^{-\frac{1}{2}}$ (Equation 8.2) under stable operating conditions, errors in drawing speed due to non-circularity or eccentricity of the winding drum will appear halved in fibre diameter.

In view of the restricted space under the crucible (Figure 8.7), a quenching facility was provided underneath the nozzle by a stream of air directed at the crucible base through a glass tube 4 mm in diameter at a pumping rate of between 2 and 6 lmin^{-1} . As this tended to cool the crucible

General view of fibre-drawing apparatus

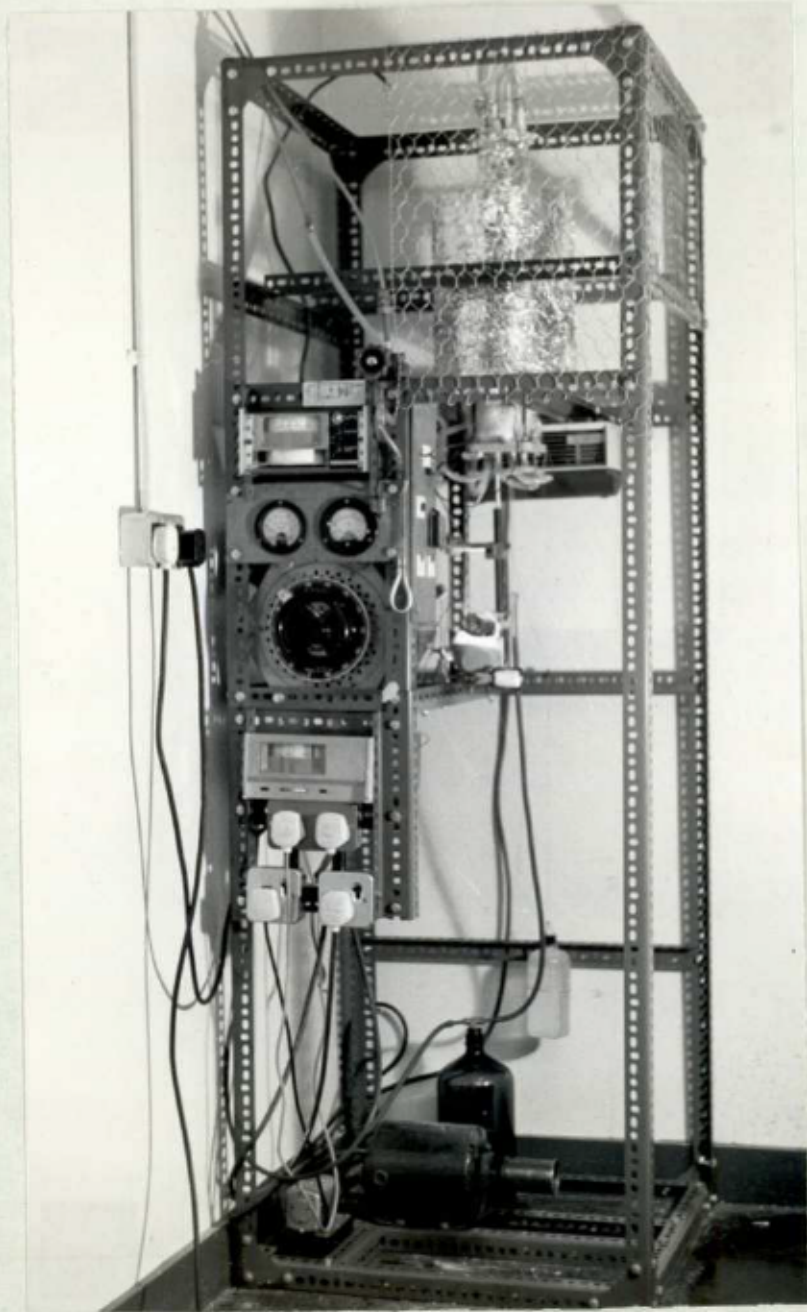


Figure 8.6

View underneath crucible mounting

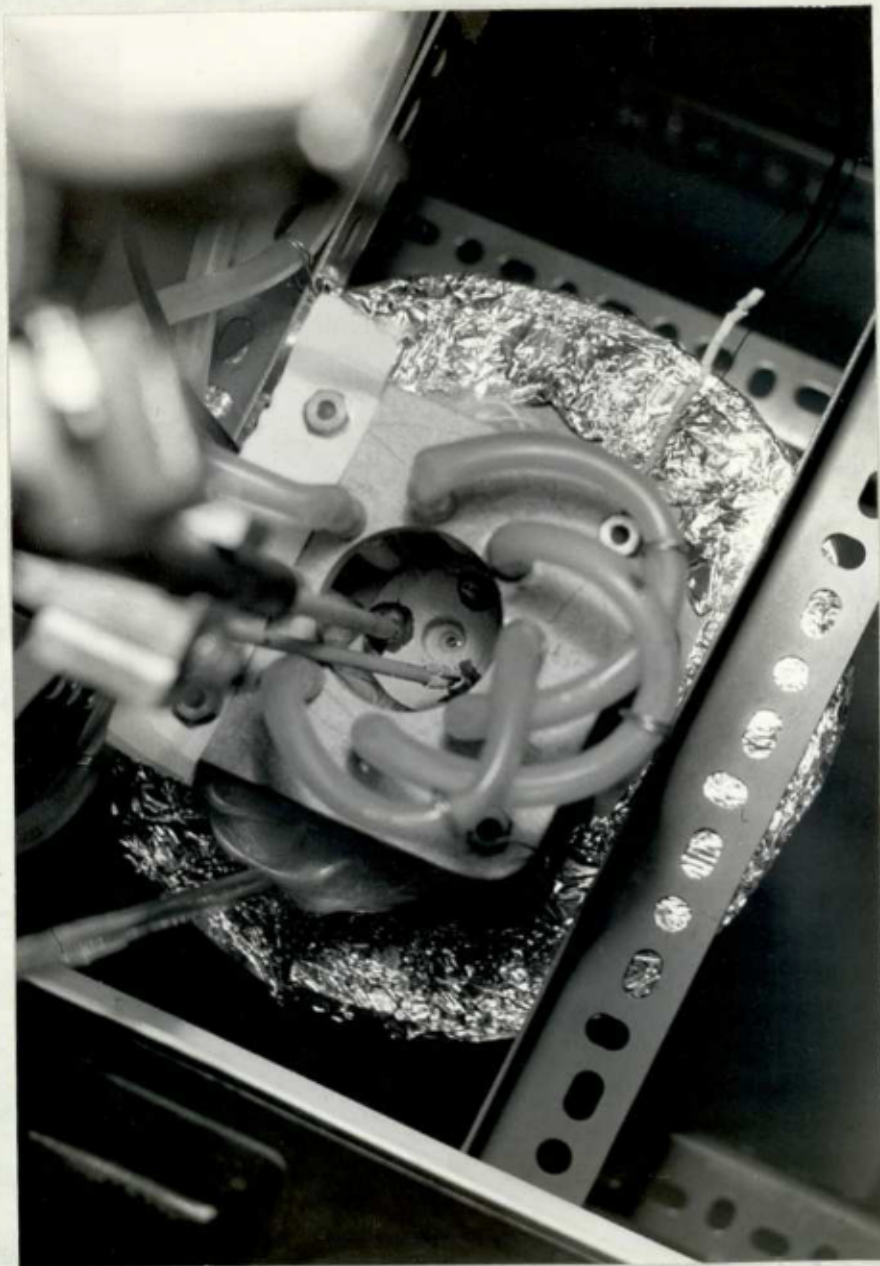


Figure 8.7

somewhat it was not switched on until just before fibres were to be drawn: this was accomplished by inserting a fine wire into the nozzle, withdrawing it quickly and winding the fibre so formed round a lightly greased section of the rotating winding drum.

8.3 FIBRE DRAWING

First attempts to pull fibres met with failure despite careful checks on suitable operating conditions, until it was discovered that the position and flow-rate of the air-quenching at the crucible base was extremely critical for successful fibre-pulling. The optimum flow-rate was about 3 lmin^{-1} , directed as close to the nozzle as the dimensions of the crucible would allow (See Figure 8.4).

The first batch of fibres drawn were too thin (about 7 mm in diameter), and even increasing the head of glass in the crucible to 20 mm did not cause much improvement. The winding drum motor was then changed to a slower (8 W) model rotating at 310 rpm, which resulted in a fibre drawing speed of 2.2 ms^{-1} . The desired diameter increase was thus achieved, and Figure 8.8 shows how the mean diameter varies with drawing temperature: Thomas (1960) has found a similar near-linear increase in diameter with temperature, but his greater head of glass ($>50 \text{ mm}$) prevents direct comparison with our results.

Variation of fibre diameter with drawing temperature

(glass head = 20 mm)

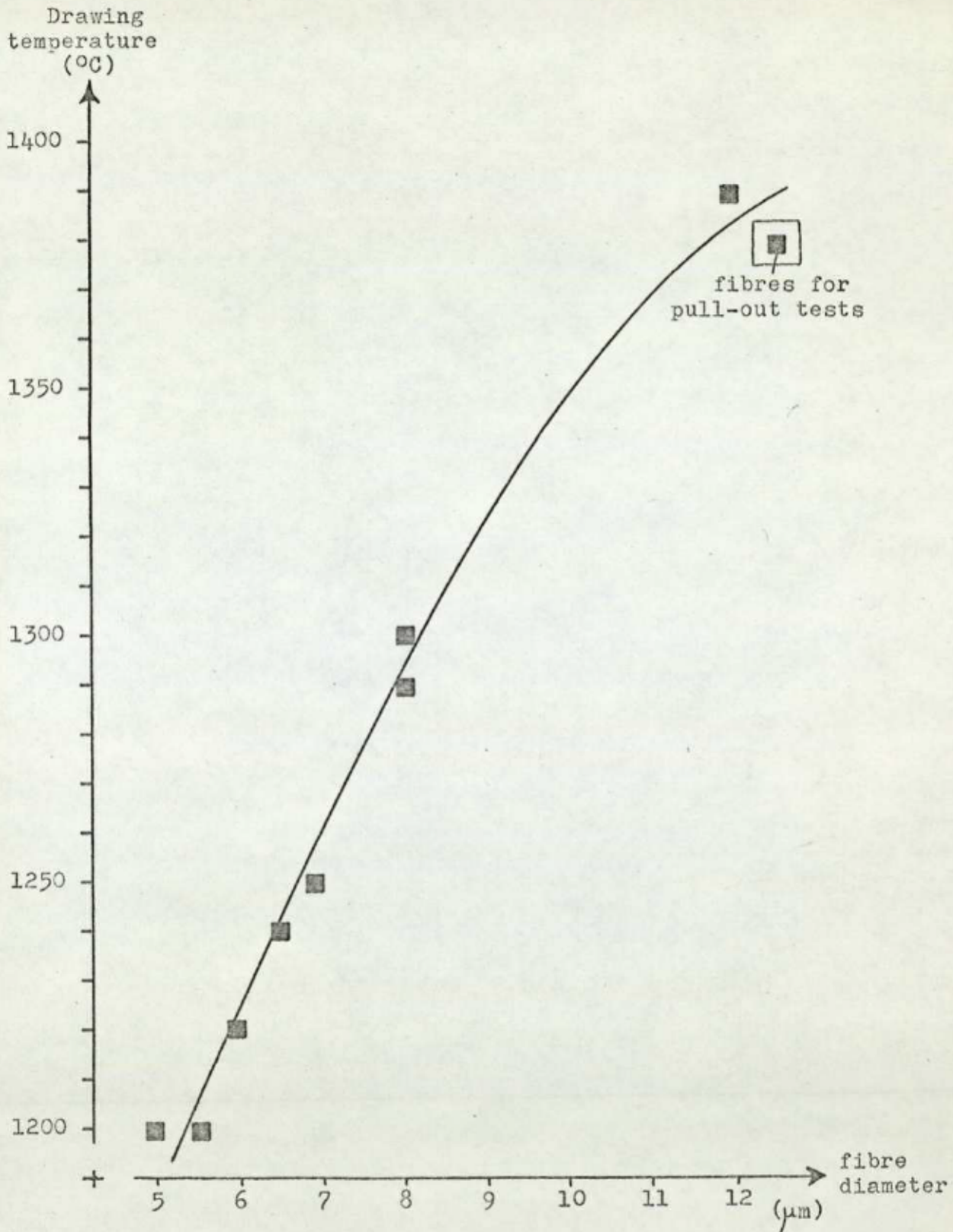


Figure 8.8

It was decided to use one batch of fibres drawn at 1380°C (circled in Figure 8.8) for the next set of pull-out tests (see Chapter 9). The mean fibre diameter was around $12.5\text{ }\mu\text{m}$, but no attempt was made to measure either the spread in diameters or fibre strengths, as it was considered that improvements to the drawing apparatus necessary to produce the most suitable fibres would not be justified in terms of the time involved. Furthermore, in pull-out tests the most important parameter to be optimised will be seen to be $\sigma_f \cdot d$, but under the conditions of sample curing, and this is best done by carrying out the tests and observing fibre breakages.

CHAPTER NINE: FURTHER PULL-OUT TESTS

9.1 MODIFICATION OF TESTING PROCEDURE

9.1.1 Improved sample-holder

The sample-holder (see Figure 7.7) was modified by replacing the fixed inner polythene ring by a removable one (a captive silicone rubber seal from $\frac{1}{4}$ " Drallim tube coupling) lightly cemented to the polythene base with sodium silicate cement. This had several advantages: the ring was available in quantity with fairly constant dimensions (i.d. 6.2 mm, o.d. 10.0 mm, wall thickness 3.5 mm), its shape permitted easy handling and measurement of cement thickness without risking damage to the disc, and, being black, the glass fibre was more visible against it.

In order to take advantage of the new sample-holder new test grips were made to ensure that the specimen was aligned vertically during pull-out (see Figure 9.1). The ring holding the cement disc could be moved laterally on the specimen cradle and the position of the fibre-gripping capstan could be adjusted until the alignment was correct. As long as the double-sided adhesive tape was renewed before testing each run, sufficient adhesion was developed with the fibre wrapped for only half a turn round the capstan to enable pull-out to be achieved without slipping. The capstan was racked up as close as

Mounting of specimen in Instron tester

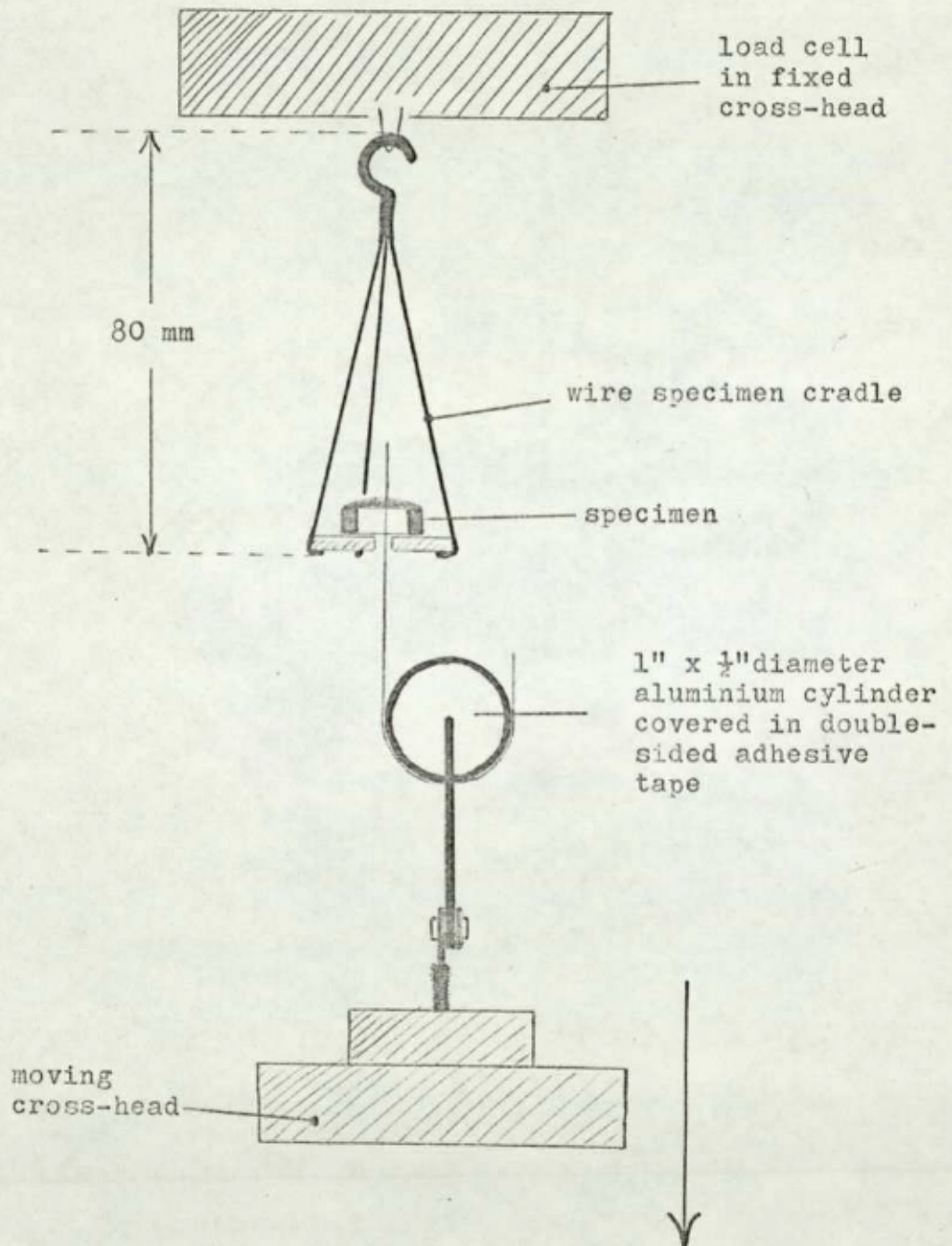


Figure 9.1

possible to the sample-holder before attaching the fibre to it, in order to reduce the probability of fibre breakage by keeping the length of free fibre as short as possible (see Figure 3.2(b)).

9.1.2 Use of Instron tensile test machine

The chain loading mechanism described in Section 7.2.1 was altered to accept two heavier chains on either side of the loading arm, when a maximum load of 160 mN could be applied at a constant rate of $2 \text{ mNs}^{-1} \pm 1\%$. This system eliminated sideways movement of the loading arm.

However, an Instron Tensile Test Machine (type TM-M) became available during the test programme, and it was decided to make use of it in view of its greater range and reliability than the chain balance: it operates on the principle of applying a steadily increasing strain to the sample while monitoring the load by means of strain-gauge, and it produces a chart-recording of the pull-out process as a function of applied stress against strain (see for example the pull-out traces in Figure 9.2).

The specimen cradle was hung on the fixed crosshead from the most sensitive load-cell available, which was calibrated to give a full-scale deflection of 200 mN (this could be switched instantaneously to 500 mN f.s.d. in the event of an

overshoot). The fibre-gripping capstan was screwed into a brass cylinder mounted on the downwards-moving crosshead (see Figure 9.1). The rate of this crosshead movement was adjustable over a wide range by means of replaceable gears, but a speed of 0.5 mm min^{-1} was found to correspond approximately to a 1.5 mN s^{-1} stress rate.

9.2 MEASUREMENT OF PULL-OUT STRESS

9.2.1 Experimental conditions

All samples in runs 16 to 34 were prepared as before (see Section 7.2), using the modified specimen holder described above, and experimental conditions for each run are listed in Table 9.1.

Runs 16 and 17 were carried out at a higher temperature on the old chain loading machine in order to assess the effect of using our own fibres instead of commercial ones, but thereafter the Instron machine was used, except for runs 22 and 24, which were intended to compare the two types of loading. The effect of changing the loading speed of the Instron was also investigated (runs 18, 19 and 20), and runs were carried out at differing cement curing times and water/cement ratios.

It was thought that limitation of the range of particle size in HAC (see Figure 3.3) might give more consistent pull-out strengths, and a batch of powder was sieved through B.S. 300 mesh and 350 mesh sieves to constant weight partition.

Pull-out tests (II): experimental conditions

Run No.	cement	w/c ratio	Hydration time (days)	Curing temperature (°C)	Crosshead rate strain (mm/min)	stress (mN/s)
16	CF	0.333	1	25	(0.7)	2.0
17	CF	0.333	4	25	(0.7)	2.0
18	CF	0.278	1	15	5	
19	CF	0.278	1	15	1.0	
20	CF	0.278	1	15	0.2	
21	CF	0.278	7	15	2.0	
22	CF	0.275	1	15	(0.7)	2.0
23	CF	0.275	5	15	0.5	
24	CF	0.275	3	15	(0.7)	2.0
25	CF	0.275	3	15	0.5	
26	>300#	0.300	3	15	0.5	
27	300-350#	0.375	3	15	0.5	
28	<350#	0.375	3	15	0.5	
29	<350#	0.375	5	15	0.5	
30	<350#	0.375	37	15	0.5	
31	<350#	0.375	27	15	0.5	
32	<350#	0.375	12	15	0.5	
33	<350#	0.375	16	15	0.5	
34	<350#	0.375	15	15	0.5	

Table 9.1

The following particle size distribution was thus obtained:

$> 53 \mu\text{m}$ (+300#)	22.9%
$45 - 53 \mu\text{m}$ (300 - 350#)	26.1%
$< 45 \mu\text{m}$ (-350#)	61.0%

Water/cement ratios for these cement fractions were selected to give a paste of a workable consistency in each case for pull-out tests (runs 26, 27 and 28).

Pull-out tests were discontinued at run 34 as the Instron tester was no longer available.

9.2.2 Results

Table 9.2 shows the individual results from each run in order of testing. Rank correlation calculations (see Table 9.3) show that in none of the runs is this order associated with a trend in pull-out stress at a significance level of more than 20%, and there is no overall correlation.

Figure 9.2 shows the four main types of load-extension pull-out curves obtained on the Instron chart recorder. The "ideal" pull-out curve (type i) shows a steady increase of fibre stress up to pull-out, after which a lower interfacial stress was observed, presumably due to frictional forces. This frictional bond stress is important as it represents the value of τ which should be used in the work-to-fracture calculations (see Section 5.1.2), and occasionally it appears

Individual values of pull-out stress (II)

Run No.	No. of samples	τ values	Ratio breakages: pull-outs
16	6	>4.67 >3.77 5.89 1.55 >5.56 6.90	3:3
17	5	>4.29 >4.52 >6.11 >6.32 2.62	4:1
18	5	1.11 >0.68 1.46 0.96 >1.25	2:3
19	8	2.25 2.33 3.29 0.15 1.57 4.84 >3.41 2.36	1:7
20	2	1.74 1.12	0:2
21	5	>3.50 4.00 2.69 3.08 3.73	1:4
22	6	0.49 0.41 0.75 0.32 >2.87 >0.82	2:4
23	12	2.47 >3.71 >2.13 >3.72 >0.94 >2.06 >2.24 4.58 >3.68 >1.37 1.32 >2.40	9:3
24	12	0.18 >1.33 3.29 >1.89 >2.07 >0.92 >1.55 >1.64 >1.89 >1.99 0.44 0.59	8:4
25	12	>3.11 2.06 2.24 1.96 4.37 3.88 >6.21 3.75 2.62 3.04 >7.83 1.68	3:9
26	12	>4.48 >3.51 1.91 >4.36 4.93 2.05 3.47 >5.94 >3.68 4.74 2.95 3.43	5:7
27	12	5.33 >3.47 4.23 2.88 >6.90 >13.03 >4.02 >4.53 >6.24 6.24 8.02 4.84	6:6
28	11	2.32 0.29 >8.61 0.31 2.97 >2.90 >1.39 1.64 2.28 2.14 1.06	3:8
29	12	12.06 3.14 4.26 5.14 3.62 0.79 3.03 >7.96 5.30 3.16 1.21 8.09	1:11
30	10	6.25 >8.68 >7.98 3.32 >2.68 >4.67 6.86 5.05 >3.71 >5.11	6:4
31	10	>5.61 >3.39 2.69 2.41 2.08 >3.58 4.47 2.28 2.95 4.30	3:7
32	11	>20.61 3.23 2.17 >3.55 2.23 1.19 >4.96 >2.35 >5.23 >3.67 >3.21	7:4
33	12	>8.25 >6.62 >6.51 >16.45 >4.26 >2.66 10.77 2.70 >4.02 8.90 >18.05 >4.05	9:3
34	11	>6.10 >8.45 10.25 >4.65 1.25 >10.61 >4.95 3.20 >6.62 >3.76 >4.34	8:3
<hr/> 174			<hr/> 81:93

Table 9.2

Correlation between measured pull-out parameters (II)

Run No.	Rank corrln. of τ vs. testing order	Product-moment coefft. of correlation	
		P vs. $d.\theta$	τ vs. P
16	+0.49	+0.02	+0.55
17	+0.00	+0.77	+0.95
18	+0.00	+0.88	-0.14
19	+0.09	-0.03	+0.95
20	-	-	-
21	-0.10	+0.90	+0.22
22	+0.54	+0.41	+1.00
23	-0.25	+0.01	+0.73
24	-0.18	+0.41	+0.88
25	+0.14	+0.08	+0.91
26	-0.06	+0.39	+0.85
27	+0.39	+0.10	+0.72
28	-0.16	-0.12	+0.47
29	-0.08	-0.30	+0.81
30	-0.35	+0.45	+0.42
31	-0.07	+0.35	+0.65
32	+0.02	-0.44	+0.88
33	-0.06	-0.20	+0.88
34	-0.42	+0.21	+0.89

Table 9.3

Typical load-extension curves from Instron tester

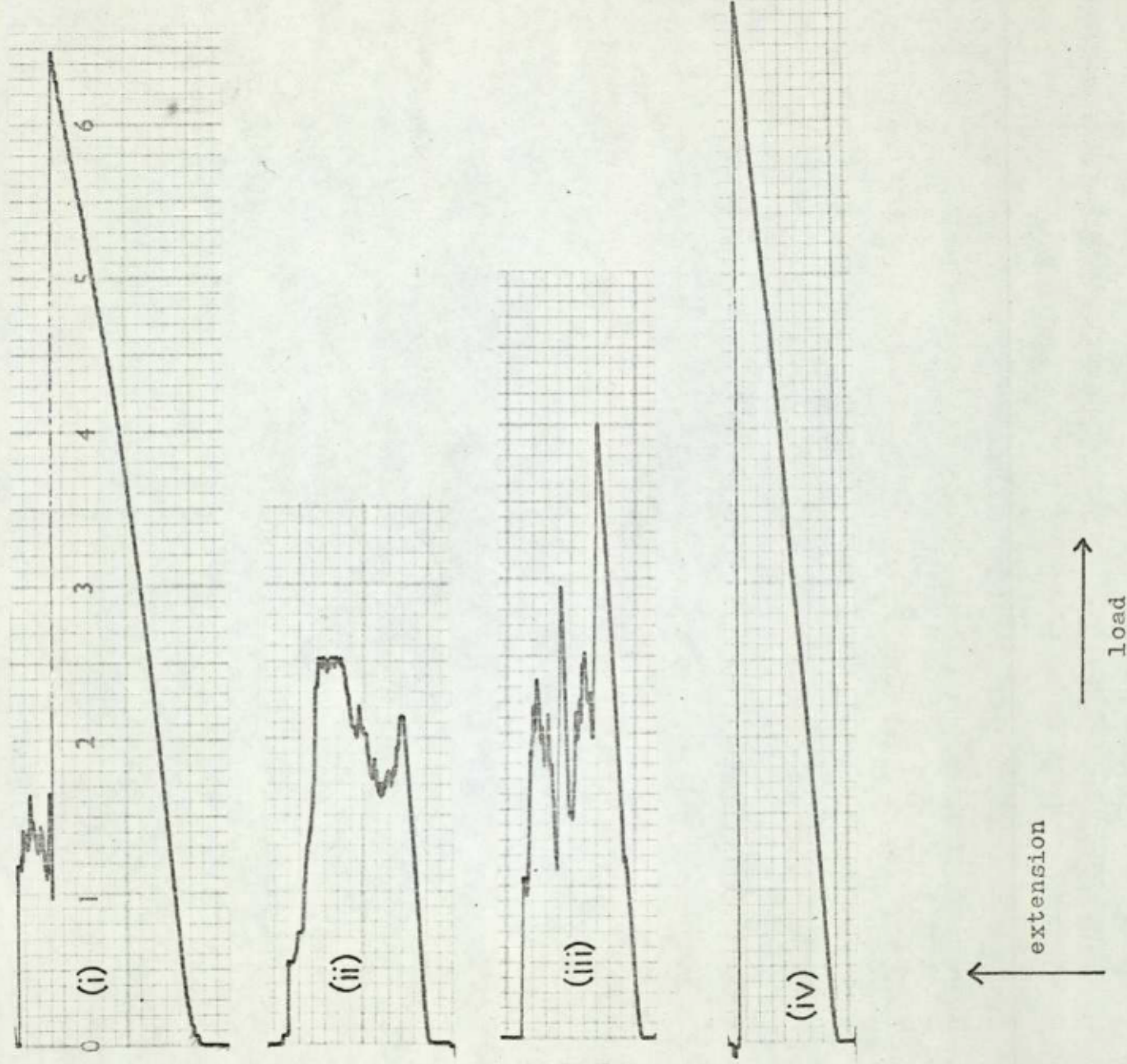


Figure 9.2

to be greater than the initial pull-out stress (curve ii) or too erratic to be assigned a value (curve iii). Type iv represents breakage of the fibre before pull-out, and as before, values of τ calculated from the maximum stress observed are included in the results (and are indicated by ">") to avoid bias towards lower values of τ . The frequency of fibre breakage increased with τ as expected, and this problem is discussed further in Section 9.3.1.

Following the arguments presented in Section 7.3.1, the median was again selected as the best measure of the "central tendency" of each run. Again, the rank correlation between mean and median for runs 16 to 34 is extremely high (Spearman's coefficient = +0.95), so that computations based on the mean (which is more amenable to statistical treatment than the median) may be used.

Statistical parameters for each run are listed in Table 9.4 (cf. Table 7.4), and it is apparent from the high coefficients of variation that these results are no more reliable than the previous set, despite a considerable improvement in experimental technique. This problem can be resolved into two parts: premature fibre breakage, and possible variation of stress in the pull-out system used. Both are discussed in the following section.

Statistical parameters (II): values of τ

Run No.	No. of samples	Mean (MNm ⁻²)	Coefft. of variation (%)	Lowest value	Median (MNm ⁻²)	Highest value
16	6	4.72	40	1.55	5.11	6.90
17	5	4.77	32	2.62	4.52	6.32
18	5	1.09	27	0.68	1.11	1.45
19	8	2.52	55	0.15	2.34	4.84
20	2	1.43	31	1.12	1.43	1.74
21	5	3.40	15	2.69	3.50	3.73
22	6	0.94	102	0.32	0.62	2.87
23	12	2.55	44	0.94	2.32	4.58
24	12	1.48	58	0.18	1.59	3.29
25	12	3.56	52	1.68	3.08	7.83
26	12	3.79	31	1.91	3.60	5.94
27	12	5.81	47	2.88	5.09	13.03
28	11	2.36	96	0.29	2.14	8.61
29	12	4.81	67	0.79	3.94	12.06
30	10	5.43	37	2.68	5.08	8.68
31	10	3.38	34	2.08	3.17	5.61
32	11	4.76	113	1.19	3.23	20.61
33	12	7.77	66	2.66	6.56	18.05
34	11	5.83	50	1.25	4.95	10.61

Table 9.4

9.3 FACTORS AFFECTING THE DISPERSION OF PULL-OUT STRENGTH VALUES

9.3.1 Premature fibre breakage

The distribution of ">" values in the pull-out strengths listed in Table 9.2 indicates that fibre breakage is more liable to occur at high τ values, as expected. Now in order for the fibre not to break before pull-out

$$\sigma_f^u \cdot \frac{\pi d^2}{4} > \pi d \varnothing \cdot \tau \quad (9.1)$$

$$\text{or} \quad \frac{\sigma_f^u \cdot d}{4 \varnothing} > \tau \quad (9.2)$$

Thus the critical parameter for the fibres which should be maximised for pull-out tests is $\sigma_f^u \cdot d$.

Median values of σ_f^u and $\sigma_f^u \cdot d$ were derived from pull-out runs 16 to 34 either directly from observed fibre breakages or by inference from the stress in the fibre at pull-out, these values being included in the calculations for similar reasons as for pull-out values. Although the strength of fibres will depend to some extent on how long they have been immersed in hydrating cement, it is still valid to consider all runs together in this case, as fibre diameters were randomly distributed through the runs.

σ_f^u and $\sigma_f^u \cdot d$ are plotted against fibre diameter in Figures 9.3 and 9.4 respectively. The σ_f^u/d distribution compares with that obtained typically for commercial fibres (see Figure 3.2(a)), whereas the $\sigma_f^u \cdot d/d$ distribution does not show a fall-off with

Fibre strength vs. diameter

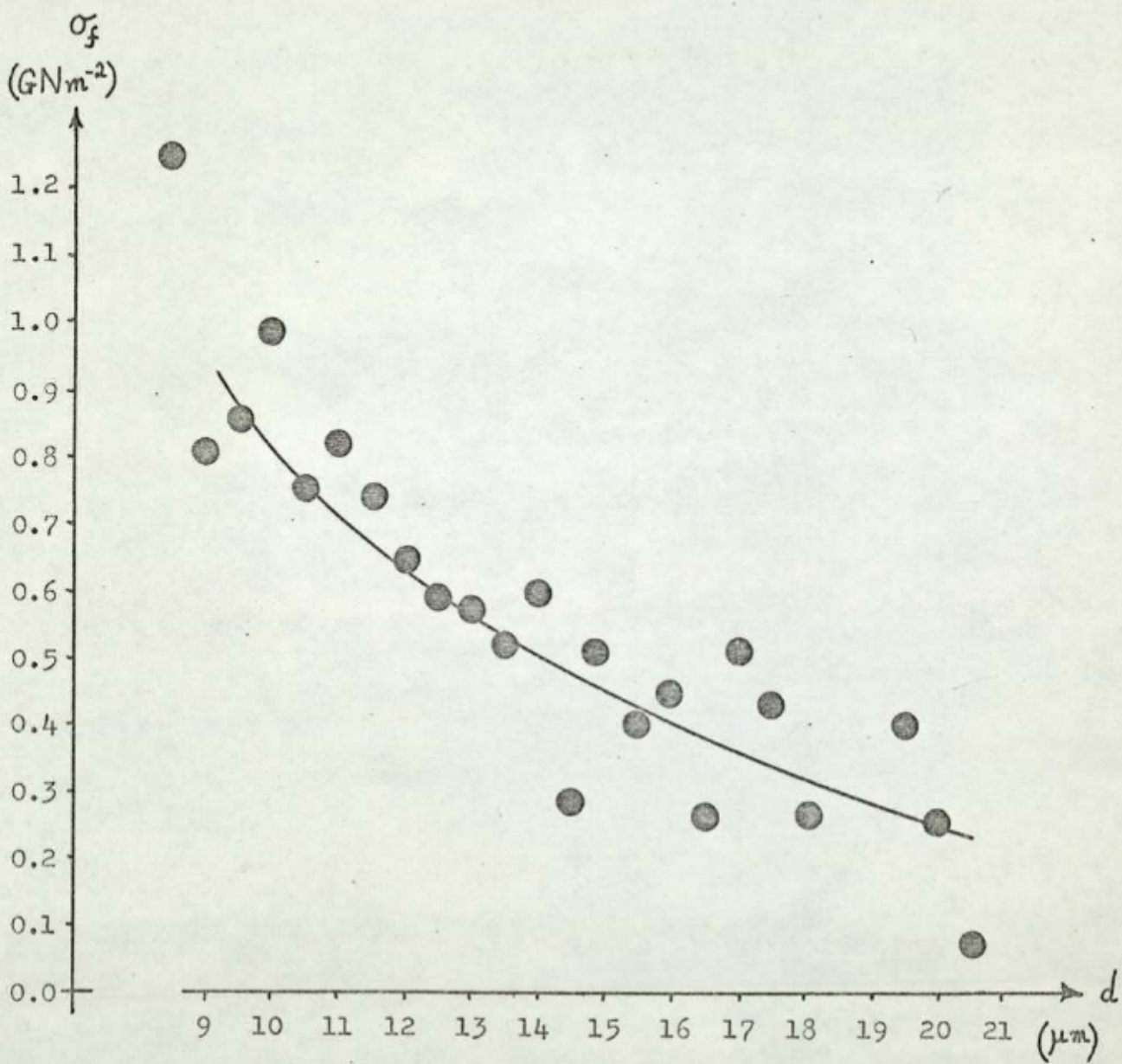


Figure 9.3

Fibre (strength x diameter) vs. diameter

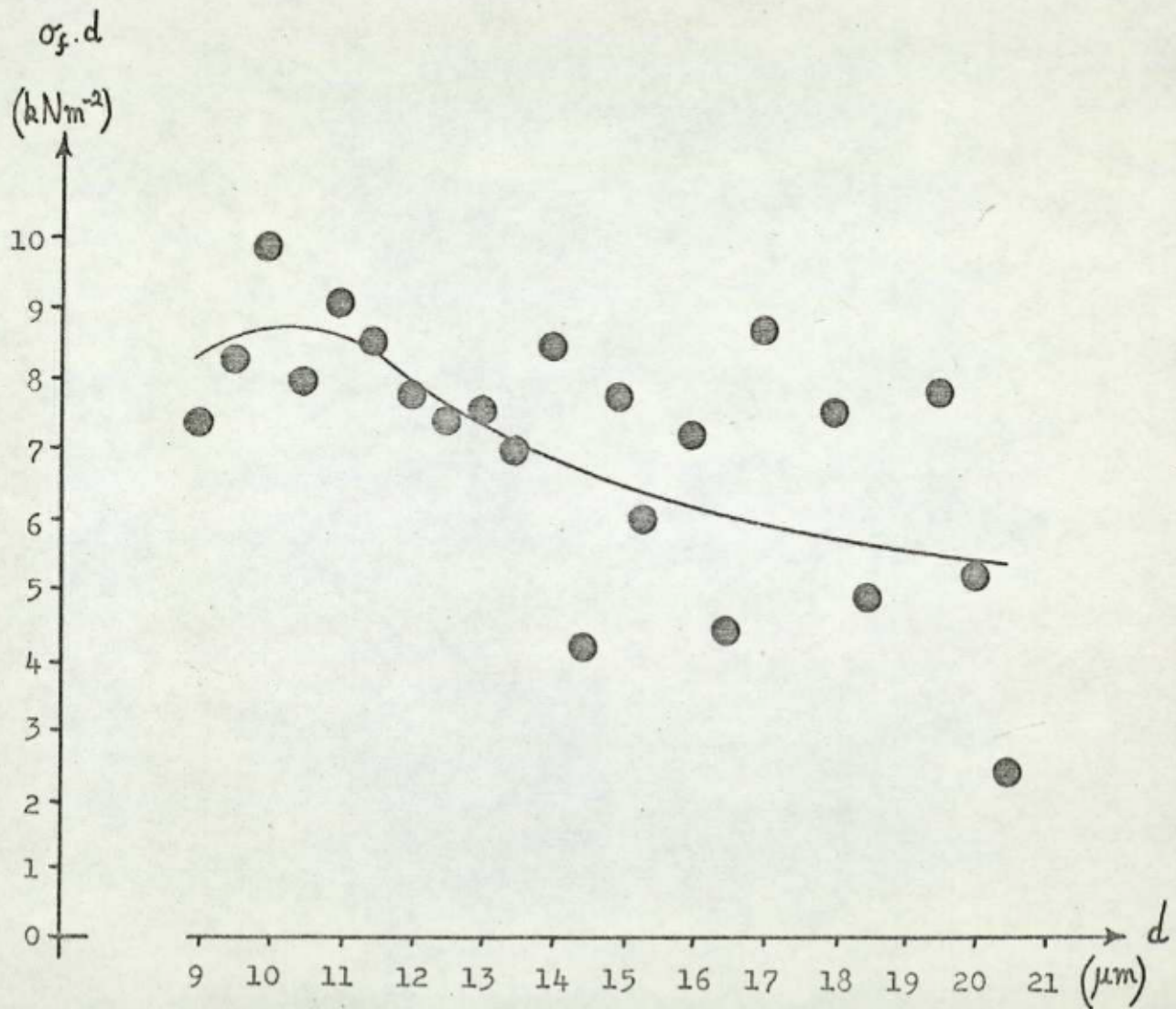


Figure 9.4

increasing diameter to the same extent. In fact, reference to Figure 9.5 shows that the value of $\sigma_f^* d$ reaches a shallow maximum near the most frequently observed fibre diameter, suggesting that for this fibre, diameters were about optimal for use in single fibre pull-out tests.

There thus seems to be little hope of increasing the experimental value of the parameter $\frac{\sigma_f^* d}{\phi}$ in glass fibre / cement systems and thereby avoiding fibre breakage, and for this reason (among others), alternative methods of measuring interfacial strength will be considered in the final chapter.

9.3.2 Distribution of shear stress along the interfacial bond

As with the preliminary runs, the product-moment correlation coefficients were generally higher between τ and P than between P and $d \cdot \phi$ (see Table 9.3), suggesting that the critical condition of bond failure is inadequately described by the simple averaging of Equation 7.1. We should therefore investigate how the shear stress varies through the thickness of the disc in a pull-out specimen.

Many studies, both theoretical and experimental, have been made on the stresses at the end of a fibre embedded in a matrix (Broutman 1969). The agreement between shear-lag type calculations (Rosen et al. 1964, Cox 1952) and finite-element (Carrara & McGarry 1963) and photoelastic (Allinson

Distribution of fibre diameters in runs 16 - 34

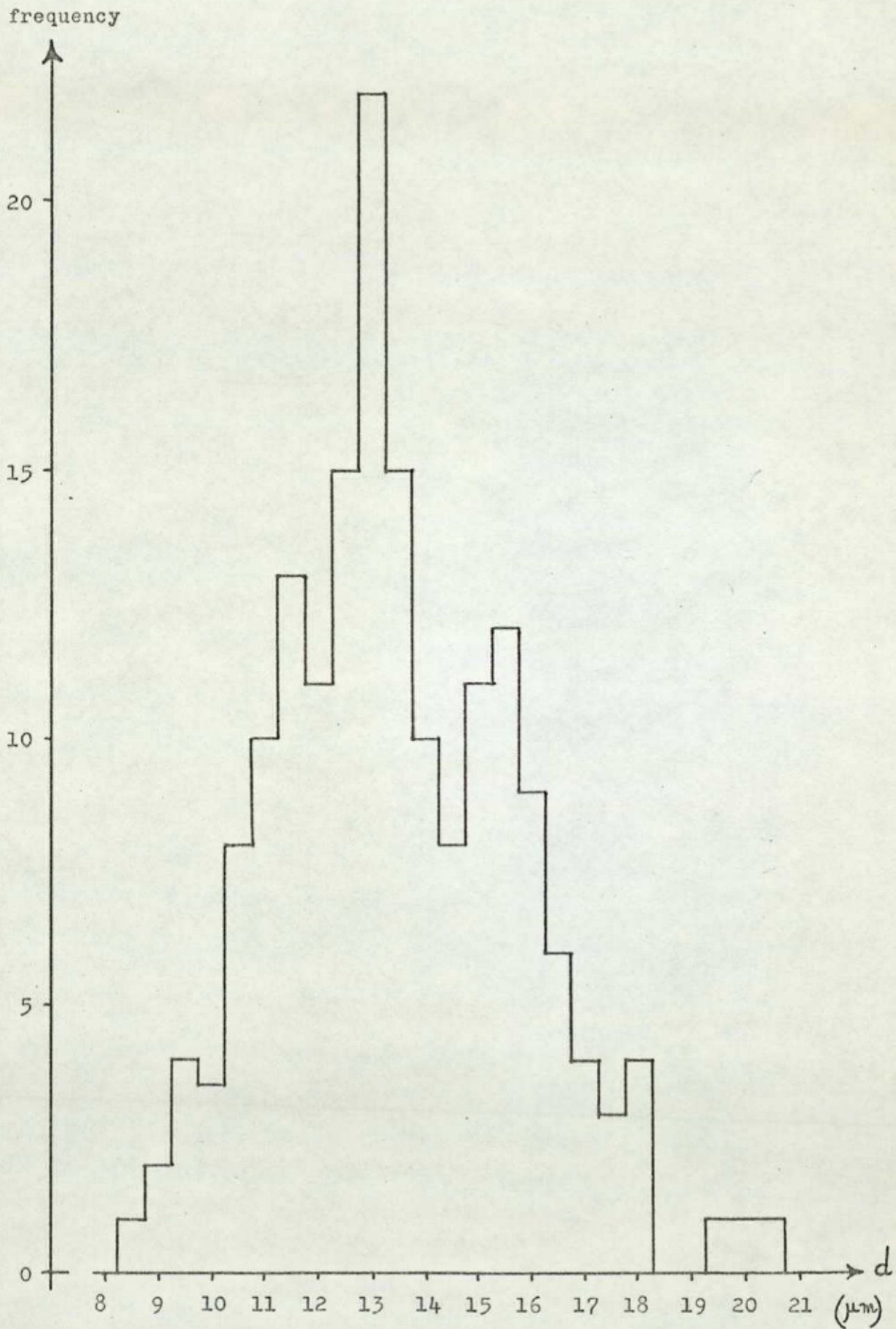


Figure 9.5

& Holloway 1967, Owen 1969) analyses is reasonably good, although the results depend somewhat on the geometry of the fibre end. Figure 9.6 shows how the interfacial stress may be expected to vary along a fibre being pulled from a matrix disc of thickness ϑ with a force P . We are interested in the maximum value of interfacial stress, $\tau^{\max}$, which is not simply twice the average bond strength τ for this more sophisticated view of stress distribution.

The longitudinal stress distribution between a fibre sustaining a load P and a surrounding cylindrical matrix in conditions of elasticity and perfect bonding has been worked out by Cox(1952) and others (e.g. Dow 1963) who found the solution to be of the form

$$P = A \sinh \beta x + B \cosh \beta x \quad (9.3)$$

where A and B are constants of integration, β depends on the dimensions and elastic constants of the model, and x is the distance from the end of the fibre.

Consideration of the cylindrical stress distribution in the matrix element of diameter D around the fibre gives

$$\beta^2 = \frac{8G_i}{E_f \cdot d^2 \cdot \ln(\frac{\vartheta}{d})} \quad (9.4)$$

where G_i is the shear modulus of the interface. For the case where a fibre is pulled by a force P from a matrix disc of thickness ϑ the boundary conditions are

Distribution of interfacial stress along embedded fibre

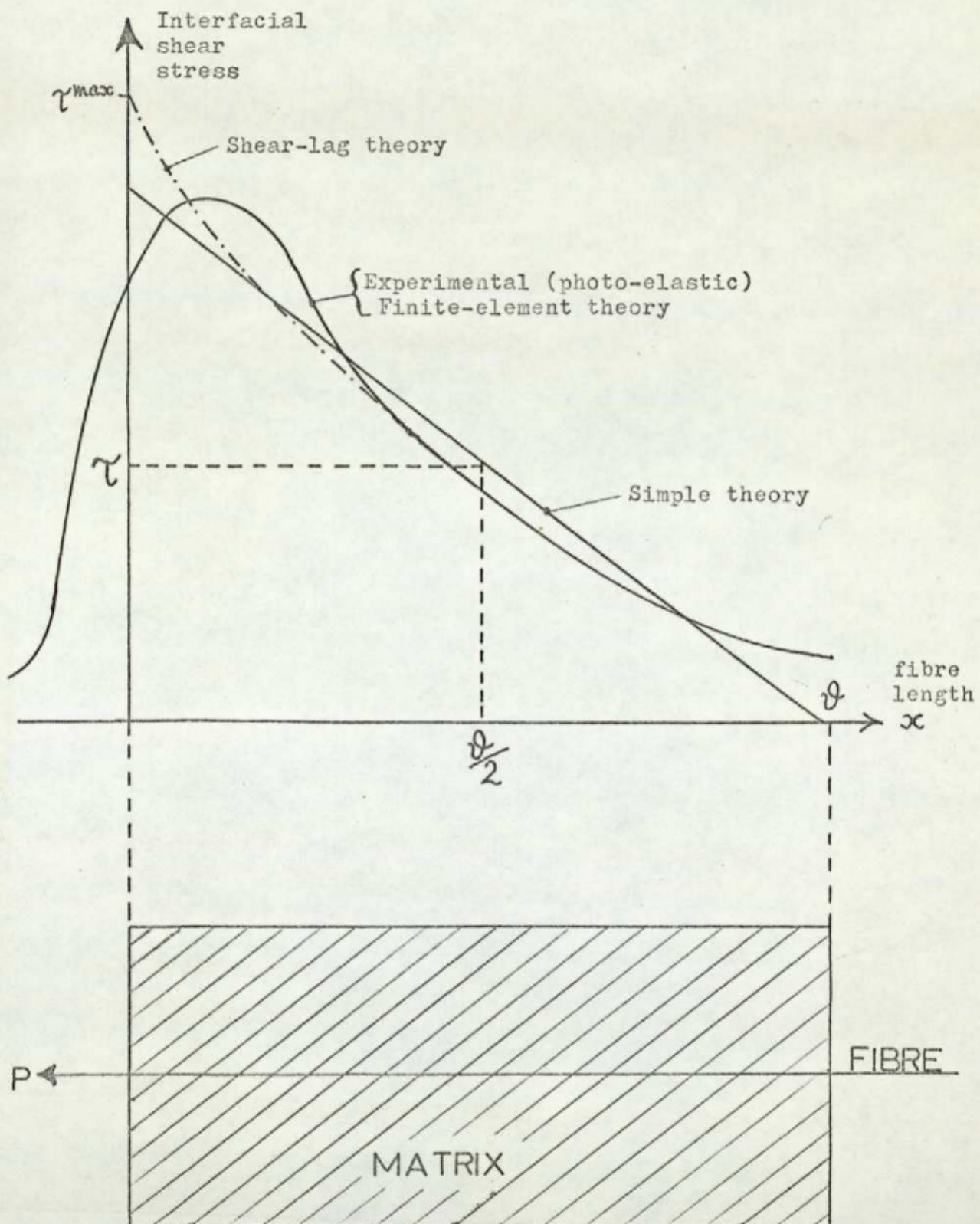


Figure 9.6

$$P = \tau \cdot \pi d \vartheta \text{ at } x = 0$$

$$P = 0 \quad \text{at } x = \vartheta. \quad (\text{Greszczuk 1969})$$

$$\text{So we have} \quad \tau \cdot \pi d \vartheta = B \quad (9.5)$$

$$\text{and} \quad 0 = A \sinh \beta \vartheta + B \cosh \beta \vartheta \quad (9.6)$$

$$\text{whence} \quad P = \tau \cdot \pi d \vartheta (\cosh \beta x - \coth \beta \vartheta \cdot \sinh \beta x). \quad (9.7)$$

$$\text{But} \quad \tau = \frac{1}{\pi d} \cdot \frac{dP}{dx} \quad (\text{by definition}) \quad (9.8)$$

$$= \tau \cdot \beta \vartheta (\sinh \beta x - \coth \beta \vartheta \cdot \cosh \beta x) \quad (9.9)$$

and τ reaches its greatest value, $\tau^{\max}$, at $x = 0$.

$$\text{Hence} \quad \tau^{\max} = \tau(\beta \vartheta) \coth \beta \vartheta. \quad (9.10)$$

$$\text{Defining} \quad \alpha = \beta \cdot d = \sqrt{\frac{8G_i}{E_f \ln(\frac{\vartheta}{d})}} \equiv \sqrt{\frac{G_i}{E_f}} \cdot \left(\frac{8}{\ln(\frac{\vartheta}{d})}\right)^{\frac{1}{2}} \quad (9.11)$$

$$\text{we have} \quad \tau^{\max} = \tau \left(\frac{\alpha \vartheta}{d}\right) \coth \left(\frac{\alpha \vartheta}{d}\right). \quad (9.12)$$

Both photoelastic (Carrara & McGarry 1968, Tyson & Davies 1964) and theoretical (Amirbyat & Hearle 1969) have shown that the shear stress in the matrix at the fibre ends is distributed approximately inversely with the radial distance from the fibre, so we would expect at a distance 20 diameters from the fibre surface that it would have dropped to 5% of its value there. (In fact, misestimation of D by an order of magnitude either way would make little difference to the value of α .) Table 9.5 gives estimates of $\tau^{\max}/\tau$ for typical pull-out systems, where $D = 20d$ and values for

Estimates of $\tau^{\max}/\tau$ in typical pull-out systems

System	G_i (GNm ⁻²)	E_f (GNm ⁻²)	$\sqrt{\frac{G_i}{E_f}}$	$\sqrt{\frac{8}{\ln(\frac{D}{d})}}$	α	ϑ (mm)	d (mm)	$\alpha \frac{\vartheta}{d}$	$\frac{\tau^{\max}}{\tau}$ ($\propto \frac{G_i}{d} \cdot \cot \alpha \frac{E_f}{d}$)
Glass fibre/cement	17	75	0.5	1.1	0.5	0.5	0.013	20	20
Glass rod/cement	17	75	0.5	2.1	1.1	0.5	1	0.5	1.1
Glass fibre/resin	1.3	75	0.13	1.1	0.14	1	0.013	11	11
Glass rod/resin	1.3	75	0.13	2.1	0.27	1	1	0.27	1.0

Table 9.5

G_i (usually not known) are taken as the shear modulus of the bulk matrix, G_m , from Table 1.2. It is apparent that the effect of stress concentration is most significant for glass fibre / cement systems, and since $\coth x \approx 1$ for $x \gg 3$, we may estimate $\tau^{\max}$ as

$$\tau^{\max} \simeq 0.5 \frac{d}{d} \cdot \tau \cong 0.1 \sigma_f^u \quad (9.13)$$

i.e. the maximum stress in the system is a function only of the stress in the fibre at pull-out, and does not depend on the thickness of the cement disc.

Whereas our measured pull-out strengths are similar in magnitude to those obtained by de Vekey & Majumdar (1970) in glass rod / cement systems (little or no stress concentration), values of $\tau^{\max}$ are typically over an order of magnitude greater.

If $\tau^{\max}$ were the interfacial stress which is critical for bond failure rather than τ , we would expect the dispersion in $\tau^{\max}$ measurements to be less than that for τ . Comparison of coefficients of variation for $\tau^{\max}$ (Table 9.6) with those for τ (Table 9.4) shows that, with one or two exceptions, there is little advantage in accuracy to be gained by choosing $\tau^{\max}$ rather than τ as the criterion for pull-out strength.

9.3.3 Specimen size effects

One of the chief disadvantages encountered in the single

Statistical parameters (II): values of $\tau^{\max}$

Run No.	No. of samples	Mean (MNm ⁻²)	Coefft. of variation (%)	Median (MNm ⁻²)
16	6	48	40	51
17	5	77	21	79
18	5	15	58	12
19	8	44	76	34
20	2	27	58	27
21	5	94	23	91
22	6	23	135	12
23	12	79	48	64
24	12	56	62	52
25	12	49	36	45
26	12	48	35	56
27	12	69	43	59
28	11	37	69	34
29	12	50	45	51
30	10	82	33	78
31	10	63	33	58
32	11	61	66	60
33	12	81	59	71
34	11	92	41	90

Table 9.6

fibre pull-out tests has been shown to be unreliability, and since cement hydrate size seems to be of similar magnitude to glass fibre diameter (see Figures 7.1 to 7.5), there is a possibility that non-uniformity of the fibre-cement bond may contribute to this.

An attempt to increase the uniformity of the bond by using a fine fraction of cement powder was nevertheless unsuccessful, as the coefficients of variation for runs 28 to 34 show (Table 9.4), perhaps because finer particles tend to hydrate faster than coarse (see Section 5.2.2). Furthermore, a possible increase in σ_m ^(and hence τ) with small particle size (Bache 1970) was not observed either (runs 26 to 28).

Much attention has been devoted to the statistical aspects of specimen size in fracture observations (Saibel 1969), and Sabnis & Aroni (1969) have demonstrated in concrete systems strength distributions of the type proposed by Weibull (1951). Tucker (1945) has further shown that whether his own "summation theory" or Weibull's "weakest link theory" is used, then the coefficient of variation is approximately inversely proportional to fracture area. Thus glass rod (as opposed to fibre) / cement disc pull-out specimens should not only give a more uniform stress distribution over the interface but should also increase the reproducibility of pull-out tests on a purely statistical basis.

9.4 INTERPRETATION OF RESULTS

Having investigated several possible ways of improving the accuracy of our results without success, we are forced to conclude that our experimental method allows no better than qualitative results to be obtained for pull-out strengths. For instance, Figure 9.7 shows how τ and τ^{max} vary with time of hydration: the central value in each case is the median, with the 90% confidence limit of the mean ($t_{10}^{n-1} \cdot \frac{\text{std. deviation}}{\sqrt{n}}$) superimposed as a vertical line in order to give a rough estimate of the dispersion in each value. It would be very unwise to attach much quantitative significance to this graph, except to note a general increase in τ after the first few days of hydration. The reason for the low value of bond strength at 27 days is not known: but it worth bearing in mind that the dispersion in τ is great enough for the values at 15 and 16 days to be considered statistically "equal" at a 25% confidence level.

To summarise, the only firm conclusion we may draw from these results is that, as expected, the bond strength between our home-produced glass fibre with no surface treatment is much higher than that between commercial sized fibre and cement (cf. for example runs 16 and 12 or 13). Despite a considerably improved experimental technique, coefficients of variation were no lower than for the preliminary experiments described in Chapter 7, and the only study of the variation of τ which we were able to carry out (vs. hydration time) gave

Variation of τ and $\tau^{\max}$ with hydration time

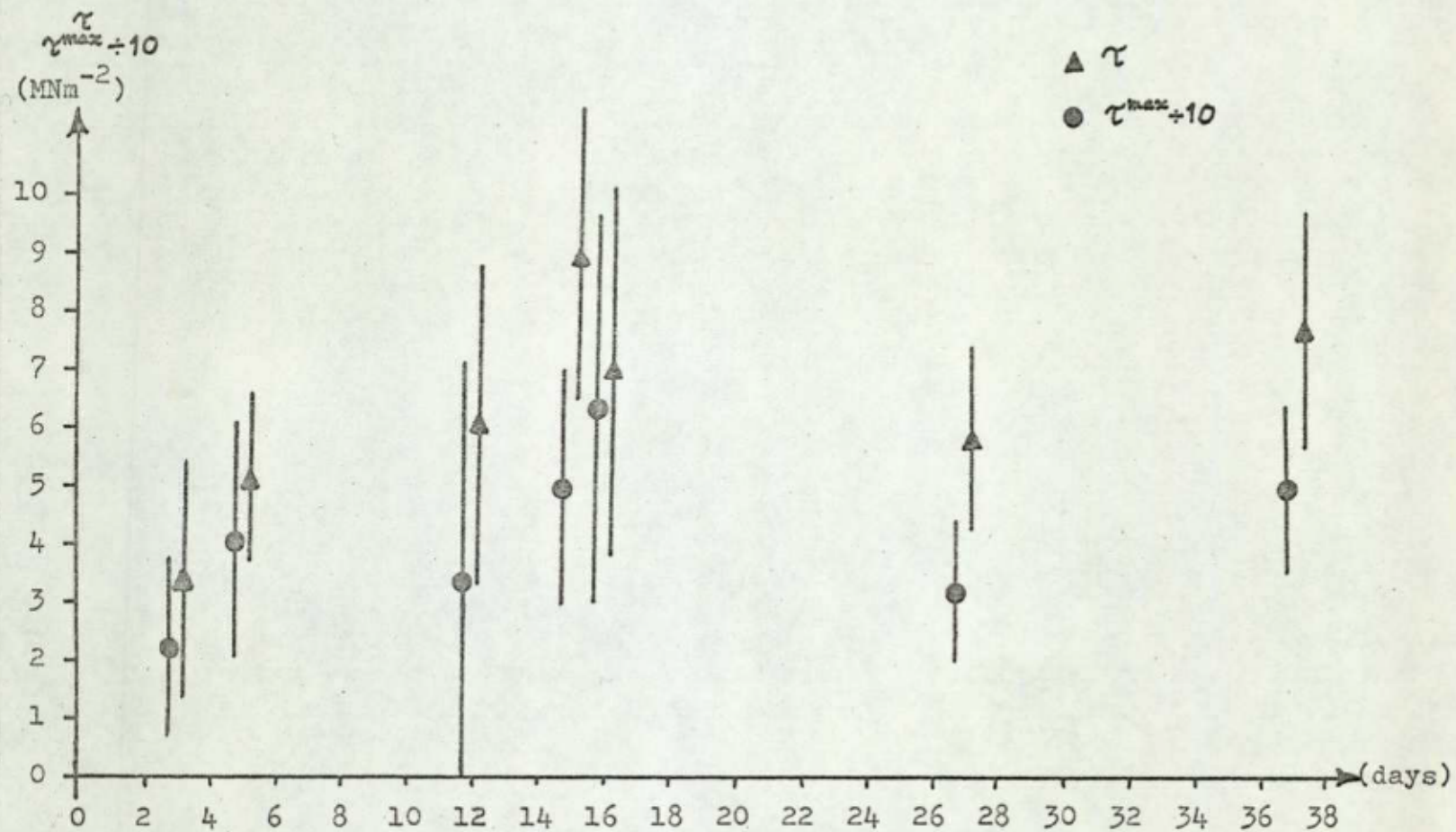


Figure 9.7

inconclusive results. Either radical changes must be made to the single fibre pulling technique, or else alternative methods of determining interfacial bond strength must be investigated.

CHAPTER TEN: CONCLUSIONS AND SCOPE FOR FURTHER STUDY

10.1 MEASUREMENT OF GLASS FIBRE / CEMENT BOND STRENGTH

10.1.1 Improvement of fibre pulling method

Experimental work described in the previous chapter has revealed disadvantages inherent in a fibre-pulling system: high dispersion in the results, premature fibre failure, unreliability of small fibre/cement contact area, and uneven stress distribution at the interface. It seems unlikely that these problems could be overcome in order to make use of the advantages of using this type of system: a small specimen requiring simple testing apparatus and taking up little space during curing even in large numbers. There is, however, some difficulty in relating single fibre pull-out tests to the situation in an actual composite. Although for an ideal composite it is possible to calculate how adjacent fibres affect the stress distribution round a single fibre (Owen 1969, Greszczuk 1969), cement paste may not penetrate into some bundles of fibres.

Reference to Figure 9.4 shows that for a cement disc thickness of 0.5 mm, $\frac{(\sigma_f d)^{\max}}{\phi} \approx 5 \text{ MNm}^{-2}$, so that a 4-fold increase in fibre strength would be necessary to keep breakage within acceptable limits at pull-out stresses of 20 MNm^{-2} (see Equation 9.2). No proven methods exist which will give this

order of increase. Ryabov & Fedoseev (1970) have suggested that the thinner the fibre and the further from equilibrium the cooled glass fibre is, the greater will be its strength, thus favouring a high drawing rate. But as even this cannot increase σ_f^u enough, it seems we must turn to techniques other than fibre-pulling for determining glass/cement bond strengths.

10.1.4.2 Alternative methods of measuring interfacial shear stress

The interfacial bond is so high in GRP systems that it is rarely possible to measure bond strength by single fibre pull-out methods as the fibre fails before the bond unless this has been considerably weakened by, for instance, boiling the specimen in water (Norman et al. 1964). However, the pulling of glass rods (ca. 1 mm diameter) from resin blocks is a well-established technique for measuring τ , and bond strengths of up to 25 MNm^{-2} have been recorded by this method (Broutman 1969). Although these rods are weaker than glass fibres, they are less likely to fail before pull-out as the parameter $\sigma_f^u d$ is at least an order of magnitude higher (see Section 9.3.1). Furthermore, rod-disc systems are fairly similar geometrically to actual composites, especially where resin shrinkage due to curing is concerned, and failure initiation is reasonably realistic. de Vekey & Majumdar (1968, 1970) have used this method to measure bond strength in GRC systems with results very similar in magnitude to our own,

but with greater reproducibility and lower dispersion (coefficient of variation generally around 20%). Nevertheless, they admit to some uncertainty in correlating their results with the situation in cement reinforced with multi-filament glass fibre strands.

Broutman (1969) describes how completely embedded single fibre specimens have been used to study debonding in GRP systems: with trapezoidal specimens the interface fails in shear when axially loaded in compression, but if a curved neck shape is used, tensile failure occurs. Progressive bond failure or fibre fracture can be observed visually as the load is applied, but unfortunately this type of study is not suitable to opaque cements.

Flat plate specimens consisting of cement sandwiched between two glass plates have the advantage that they are easy to prepare, and that bond failure may be easily observed and failure mode characterised. But the large interfacial area would necessitate fairly heavy duty testing apparatus, and it would be quite difficult to relate results to a fibre reinforced cement.

Pashchenko et al. (1965) have measured the force necessary to peel glass mat strips from cement blocks and have compared different glass and cement compositions. The results of this type of test can be expressed only in units of force per strip width, and so are of little use in relation to other composite parameters.

Perhaps the most promising test method is that of measuring the interlaminar shear of multiple fibre reinforced specimens, since results are directly applicable to composites. Various specimen geometries may be used (Goan & Prosen 1969), but a 3-point test on short beams (about 5:1 span:thickness ratio - Harris et al. 1971) offers further advantages: by varying the rate and mode of the test procedure, tensile, flexural or impact strengths may be carried out on the same shape of specimen. The interfacial shear strength τ_i should be related to the composite interlaminar (τ_c) and matrix (τ_m) shear strengths by

$$\tau_c = y \tau_i + (1-y) \tau_m \quad (10.1)$$

where y , the proportion of the fracture area occupied by the fibre/matrix interface is given by

$$y = \frac{1}{\sqrt{\frac{\alpha}{V_f}} + (1 - \frac{2}{\alpha})} \quad (10.2)$$

The constant α is equal to $1/\pi$ for square packing, or $\frac{2}{\sqrt{3}}\pi$ for hexagonal packing of the fibre array, and microscopic examination of the fracture interface has confirmed experimental values of y to be very near theoretical - at least in GRP systems (Hancock & Cuthbertson 1970).

The interlaminar shear method therefore offers a fairly simple and very realistic way of determining bond strength on small portions of specimens which may be used for further tests or checked for reproducibility. Further advantages include an inherent averaging process and the production of a large fracture surface for microscopic examination.

10.1.3 Factors affecting the interfacial bond

Apart from the necessity to vary composition of the composite components in order to optimise composite properties, and to provide values of γ for theoretical predictions, we may summarise other good reasons for the study of parameters affecting γ that have been discussed above. Variation of water/cement ratio, hydration time and cement composition should enable the significance of theories of Fermi levels in adhesion to be tested (see Section 5.2.2): in particular, it seems worth investigating means of reducing the crystal size of cement hydrates.

The interlaminar shear type of tests described above would be ideal for solving problems concerned with the instability of the fibre/cement interface and for testing the alkali resistance of glass fibres (see Section 6.2.3), since petrographic characterisation of the fracture surface, possibly using a more crystalline matrix than HAC (such as Secar 250), could be related directly to bond strength or fracture toughness values.

There is considerable scope for the correlation of chemical and mechanical data on interfacial properties, although some caution should be exercised in the application of results from work in aqueous solutions to cement hydrate systems on account of the comparative restriction in ionic mobility. In addition, it would be well worth examining the practicability of the coupling agents suggested in Section 5.3.2.

10.2 IMPROVEMENTS TO GRC COMPOSITES

The main aim of attempting to calculate the strength of a composite from its constituent parameters is to enable the mechanical properties of a particular design of composite to be predicted with a reasonable degree of accuracy. We have seen that there is considerable scope for adjustment of composite behaviour by such methods as the use of ductile fibres in addition to glass reinforcement. (to promote toughness) or the adding of sand or other modifiers to the matrix, and it should be possible to provide some theoretical basis for these improvements.

It is clear from theoretical calculations of composite tensile strength and fracture energy presented in Chapters 4 and 5 that it is essential to make our own measurements of component and composite parameters in order to ensure reliability. In particular, the properties of the cement matrix (density, porosity, strength, elasticity) depend on water/cement ratio and on curing conditions, and it is an oversimplification to use only one value of each property for all calculations: cements are much more complex in structure and behaviour than the matrices in GRP composites. Similarly, the value of σ_f^u used for fibres in the composite must depend not only on the curing conditions, but also on the distribution of individual fibre strengths: this problem has been discussed in Section 3.1.3. Measurement of τ by the interlaminar shear type of test outlined above would naturally give values of

bond strength as affected by partial bonding, pores etc. in the composite, and which could therefore be used directly in calculations.

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APPENDIX ONE: NOMENCLATURE

Abbreviations

ARC	-	Asbestos reinforced cement
CRP	-	Carbon fibre reinforced plastic
GRC	-	Glass fibre reinforced cement
GRG	-	Glass fibre reinforced gypsum
GRP	-	Glass fibre reinforced plastic
HAC	-	High alumina cement
OPC	-	Ordinary portland cement

Subscripts (refer in general to one particular phase)

c	-	denotes property of composite
f	-	fibre
i	-	interface
m	-	matrix
p	-	pores
1,2	-	phase 1, 2

Superscripts (refer in general to modification of the property)

e	-	denotes value of property at the elastic limit
c _r	-	at cracking stress
f _{f,m}	-	at failure of fibres, matrix
u	-	- ultimate value
y	-	at yield point

Roman type

a	-	fibre packing constant
c	-	critical crack length (Griffith)
d	-	fibre diameter

D	-	diameter of matrix element in fibre stress distribution calculations
E	-	elastic (Young's) modulus
F	-	fracture energy
F^d	-	energy of fibre debonding
F^p	-	work of fibre pull-out
F^s	-	energy of simple plane fracture
F^x	-	work of fibre pull-out (integrated)
$F_{\alpha}^{m,n}$	-	variance ratio between two means with m and n degrees of freedom
G	-	shear modulus
I	-	impact strength
ℓ	-	fibre length
M_m	-	molarity of aqueous phase species liberated by hydrating cement
N	-	fibre drawing speed
P	-	fibre / matrix pull-out load
R	-	Spearman's coefficient of rank correlation
s	-	average spacing between fibres
t_{α}^m	-	Student's t value with m degrees of freedom at a confidence level of α (%)
u	-	fracture displacement
V	-	volume fraction
V_{ϕ}	-	critical fibre volume fraction
W	-	weight fraction
x	-	longitudinal distance from fibre end
y	-	proportion of fracture area occupied by fibre / matrix interface

Greek type

α	-	fibre stress distribution parameter (Eqn. 9.2)
β	-	" " " " (Eqn. 9.9)
α^f	-	failure strain
γ	-	surface energy
ϵ	-	tensile strain
η	-	efficiency of reinforcement
θ	-	(angle) fibre orientation w.r.t. specified axis

δ	-	thickness of matrix disc in pull-out test
$\lambda/2$	-	stress transfer length of fibre
λ^*	-	critical length of fibre
μ	-	refractive index
ν	-	Poisson's ratio
ρ	-	density
σ	-	tensile strength
$\bar{\sigma}_f$	-	mean fibre stress
τ	-	single fibre pull-out stress
τ^{max}	-	maximum value of interfacial stress
τ_i	-	interfacial shear stress
ϕ	-	flexural strength
ω	-	composite stress transformation coefficient

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