

Cement in the Context of New Materials for an Energy-Expensive Future [and Discussion]

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Cement in the context of new materials for an energy-expensive future

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[Plate 1]

Hydraulic cements are energy-cheap relative to other common materials, are manufactured on a large scale and, when mixed with water, form readily mouldable pastes that harden at low temperature. In a technological sense, such pastes can be regarded as inorganic 'plastics', but the types of article that can usually be fabricated from the cements has been restricted by the low tensile strength and fracture toughness of hardened cement pastes. Poor mechanical properties are not inherent in inorganic solids formed under mild conditions; mineral structures of biological origin can display relatively high strength and useful toughness as a result of microstructural features determined by biopolymers. Recent studies have shown that the low tensile properties of cement paste result from the presence of macroscopic pores. The elimination of such defects by the use of polymeric rheology modifiers gives unreinforced cement pastes a flexural strength of 150 MPa or more. Such novel materials should considerably extend the range of uses for hydraulic cements.

Introduction

The hydraulic cements (Portland cement, its variants and the calcium aluminate cements, etc.) are of interest, not only because of their familiar use in construction, but because they may form the basis of novel materials for a future in which energy is expensive and hence materials of high energy content are costly. Table 1 sets out the common materials of fabrication in order of total energy content per unit volume relative to ordinary Portland cement. o.p.c. is a useful standard because it is made on a huge scale (109 t/year) and is essentially a processed chemical, despite which it remains attractively cheap in energy terms (Duckworth 1982).

The low energy content of cement-based materials relative to plastics and metals is not their only attraction. The growth in technology in the 1950s and 1960s created a considerable interest in inorganic polymers because of their potential incombustibility and inertness. Although the term 'inorganic polymer' was initially used to define a macromolecule (usually linear) not having a backbone of carbon atoms (Currel & Frazer 1969), the term has been used to cover such substances as diamond, graphite and silica (Holliday 1970) and even cement (Cherkinski 1965). The search for the non-carbon backbone polymer has not generated many industrial products (other than the silicones) and yet the target of easily manipulated inorganic materials is becoming increasingly relevant as incombustibility is demanded (Ray 1978).

The rapid growth in the use of synthetic organic polymers was due in part to the relative ease and speed by which they could be shaped into final articles. From this view point, the hydraulic cements are also attractive; when mixed with water, cements form mobile pastes that can readily be moulded or cast, with setting taking place at ordinary temperature. Unfortunately, the set material has a number of mechanical deficiences when compared to the usual materials of fabrication. Figure 1 compares the Young modulus, flexural strength and fracture



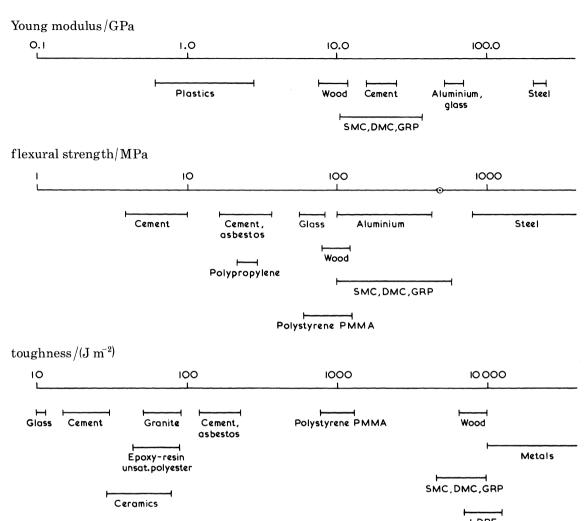


FIGURE 1. A comparison of the physical properties of common materials.

Table 1. Total energy content of materials per unit volume relative to Portland cement

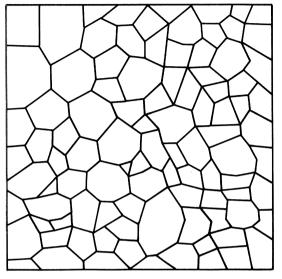
material	total energy (volume basis)
Portland cement	1.0
flat glass	3.0
PVC	3.8
LDPE	4.2
HDPE	4.4
polystyrene	6.0
steel	19.2
stainless steel	28.8
aluminium	31.8
zinc	34.8

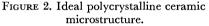
toughness for a variety of common materials from which the poor tensile performance and low fracture toughness of unreinforced cement products are obvious.

Thus, although hydraulic cement paste is, in a technological sense, an inorganic 'plastic' in allowing facile moulding and fabrication, the poor mechanical performance of the unreinforced

hardened material has precluded its penetration into uses presently dominated by the metals and synthetic polymers. However, recent studies have shown that these deficiences are not fundamental and considerable advances have been made in the manipulation and performance of cements (Birchall et al. 1981 a, 1982 a).

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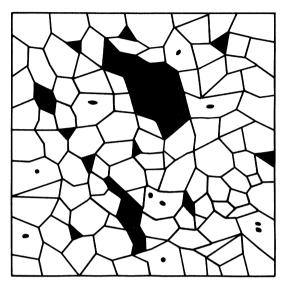


Figure 3. Porous polycrystalline ceramic microstructure.

Approaches to the problem

Ceramics

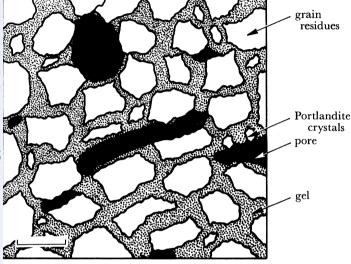
Once the problem has been formulated in terms, not of improving conventional cement products as such (although this may be a consequence of any new approach) but in terms of using hydraulic cements as raw materials from which advanced materials can be made, it becomes essential to seek new approaches in apparently unrelated areas of science. The areas that have proved to be of value are ceramics and biogenic inorganic materials. The anhydrous cements (the calcium silicates and the calcium aluminates) are themselves ceramics with bond energies of the order of 0.4 MJ mol⁻¹. Figure 2 shows an ideal conventional ceramic microstructure.

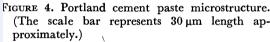
The ceramist will aim for a dense, non-porous structure in which there are no grain or phase boundary defects and in which the grain size is small; strength will rise as grain size is reduced (Petch 1953) and fall as the Griffith (1920) crack size increases. Figure 3 shows a ceramic microstructure that would give a weak material. Maximum density and minimum porosity – those features essential for strength – are attained by careful sintering at high temperature.

For the hydraulic cements, union between grains is attained by reactions with water that produce hydrated solid phases in the form of colloidal gel-like material, which itself has a high surface area (10²-10³ m² g⁻¹) (Diamond 1976). An excess of water is needed for the suspension to be sufficiently mobile for casting, and this excess water is lost by evaporation. This, together with the facts that the cement particles are poorly dispersed and are extensively flocculated (and hence pack inefficiently) and that air is occluded in the suspension, results in macroscopic porosity. The *overall* porosity of the hardened material will normally be in the range 25–35% (by volume) and will comprise pore sizes from a few nanometres (gel pores) to a few millimetres. Figure 4 is an illustration of the microstructure of a Portland cement paste.

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Although there have been many attempts to relate the strength of hardened cement paste to total porosity volume, it has been shown (Birchall et al. 1981 b) that the major determinant of strength is the size of the macropores resulting from poor particle packing and air occlusion. The topic is treated in greater detail by Kendall et al. in this Seminar. One feature that distinguishes cement paste from ceramics is the wide range of pore sizes present in cement, and confusion has resulted from the fact that although gel pores contribute vastly to overall porosity, a small number of large pores largely determine strength. In the presence of large pores, the microchemistry and morphology of the gel phase can have only a minor influence on tensile strength (Kendall et al. this Seminar; Birchall et al. 1981 b; Alford 1981; Alford et al. 1982).





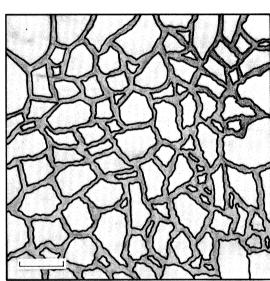


FIGURE 5. Ideal hydraulic cement paste microstructure. (The scale bar represents 20 μm length approximately.)

The ceramist would presumably argue that an ideal cement paste structure should be that shown in figure 5, with the anhydrous grains packed as closely as possible, no macroscopic defects and with a minimum of the intergrain hydrate gel within which, at least initially, are chemical bonds lower in strength by one order of magnitude than those in the grains.

It has long been known that the strength (both tensile and compressive) of cement paste rises as the ratio of water to cement (w/c ratio) is reduced (Feret 1897) but, of course, there is a practical limit to this in that a water-cement mixture becomes unworkable at low w/c ratios. The flocculated nature of cement particles does not permit fluid suspensions unless they are dilute. To an extent, this can be overcome by the addition of dispersing agents to the water, usually organic polyanions such as the products of condensing sulphonated napthalene or melamine with formaldehyde. These, by adsorption on the particles, promote dispersion and allow a workable fluidity to be retained at lower water contents (Malhotra et al. 1978).

However, such methods do not result in sufficient improvements in tensile strength to make cement solids suitable to replace the more conventional materials of fabrication and, indeed, 20 MPa would be a high flexural strength for a material so derived. Much macroscopic porosity remains as a result of air entrainment and defective particle packing. Figure 1 suggests that a target flexural strength of at least 100 MPa should be the aim if cement products are to compete with conventional materials.



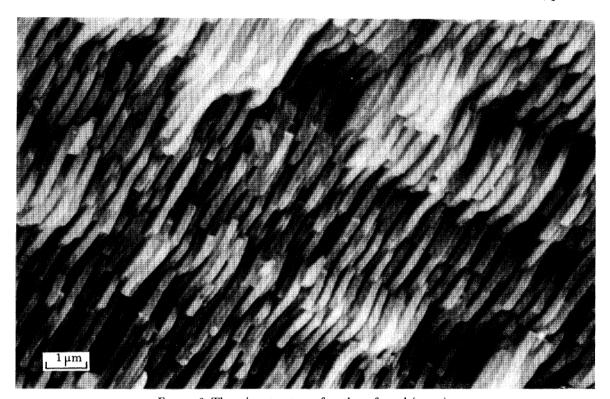


FIGURE 6. The microstructure of mother-of-pearl (nacre).

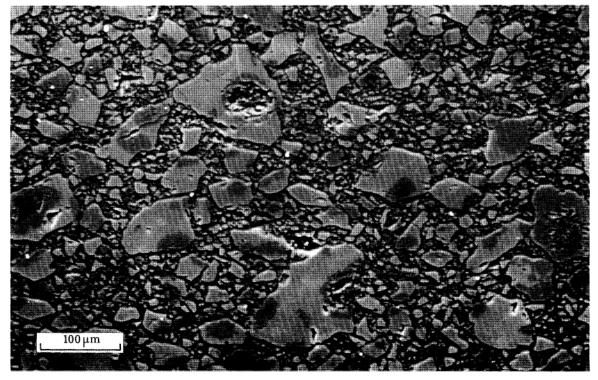


FIGURE 9. The microstructure of MDF (calcium aluminate) cement.

Biogenic inorganic materials

A study of inorganic materials of biological origin (such as skeletal structures) shows that inorganic materials formed in an aqueous system at low temperature need not be poor mechanically (Wainwright et al. 1976). Mother-of-pearl (nacre), which is 99% (by mass) CaCO₃, can have a flexural strength in excess of 100 MPa, say tenfold that of cement paste (Currey 1977). The microstructure of nacre is shown in figure 6, plate 1.

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The crystallites are flat plates of aragonitic CaCO₃ (0.2–0.3 µm thick) arranged in layers with a tenuous interlayer of protein. Nacre has a fracture toughness comparable to that of poly-(methylmethacrylate) and this possibly results from separation of the brittle platelets as a crack advances through the matrix. The material shows marked, though not extensive, plastic deformation before fracture (maximum strain 0.018), presumably caused by plastic deformation of the organic matrix. The organic matrix in inorganic biogenic materials controls the nucleation, growth and morphology of the inorganic crystallites and ultimately, the macroscopic morphology of the structure (Nakahara & Bevelander 1971), although only a small proportion of organic matrix is necessary for this; organic matrix in excess of this can have an important mechanical role (Wainwright *et al.* 1976). The effect on nucleation is probably brought about by groups on the biopolymer which bind specific ions and promote heterogeneous nucleation at predetermined sites (Hughes 1981).

A UNIFIED APPROACH TO STRONG SOLIDS FROM HYDRAULIC CEMENT

If it is accepted that the ideal structure for a strong cement paste is as illustrated in figure 5, how might such a structure be made? The problem is to attain maximum particle packing, a minimum total porosity volume and the elimination of macroscopic voids. One recent approach has been to disperse the cement grains at low w/c ratio by the use of relatively high levels of a dispersing agent, such as a sulphonated naphthalene formaldehyde condensate, and to densify the intergrain hydrate gel by the addition of fine silica (average diameter 0.1 μ m) (Bache 1981; Hjorth this symposium).

The compressive strength of concretes made from such materials is well over 100 MPa and, when made with strong (in compression) aggregates (e.g. calcined bauxite), can exceed 250 MPa. Tensile failure is brittle, the failure stress being about one tenth the compressive strength.

The optimum packing of particles in an aqueous phase requires more than an initial dispersion of the particles. As a suspension becomes concentrated, particles come into contact and bridge, and interparticle friction is such that an adjustment to optimum packing by sliding cannot readily occur, even under pressure (Gray 1968).

Recent work has shown that both dispersion and particle lubrication can be achieved by the use of water-soluble organic polymers – such as hydroxypropylmethylcellulose, hydrolysed poly(vinylacetate) – in a cement/water mixture (Birchall *et al.* 1981 *a.*, 1982 *a*). A typical composition of such a mixture would be 100 parts (by mass) cement, 7 parts (by mass) polymer and 10 parts (by mass) water. The polymer-water composition alone is, of course, a stiff gel. Such a composition, on high shear mixing, forms a readily deformable dough in which there is some occluded air and in which the volume fraction of cement particles is about 0.6 (the volume fraction for dense random packing of uniform spheres is 0.63). The dough can be processed by conventional plastic techology – press-moulded, extruded, calendered, etc.

Figure 7 shows a sheet of dough that has emerged from a roller mill; the 'plastic-like'

consistency of the material is obvious. Once formed into the desired shape, the object becomes hard as a result of the normal inorganic hydration reactions which, of course, may be accelerated by heat. Figure 8 illustrates the role of the polymer in the formation of a plastic cement dough.

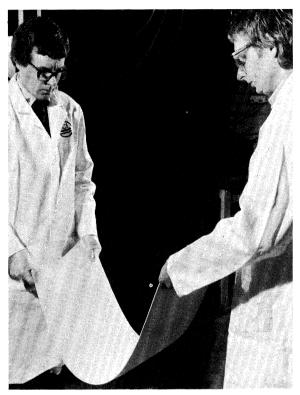


FIGURE 7. Roller-milled sheet of MDF cement dough illustrating 'plastic-like' quality.

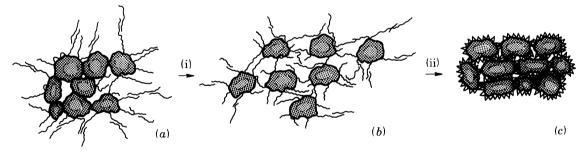


FIGURE 8. The role of the polymer in the formation of MDF cement doughs.

(i) Shear; (ii) hydration of particles, dehydration of polymer.

It appears to be essential that segments of the polymer are capable of strong attachment (figure 8a) to the cement particles with trains of polymer extending into the aqueous phase and there entangling. It is found that intense shear mixing can be applied to such a material without cavitation and with the result that flocculated particles are torn apart (figure 8b). The adsorbed hydrated polymer acts as an effective interparticle lubricant, allowing sliding adjustment of the particles to close packing. The polymer remains at the interfaces between the packed particles and becomes intergrated with the inorganic hydration products (figure 8c).

This technique is the basis of the high flexural strength o.p.c. pastes first reported in 1981

(Birchall et al. 1981 b). The aqueous chemistry of the cement and the nature of the polymer will obviously influence the rheological behaviour of the cement-polymer-water system. The polymer must, for example, be compatible with the high pH of cement aqueous phase and must not be prematurely precipitated by reaction with dissolved species derived from the cement, for example carboxylated polymers precipitating as a result of the formation of calcium salts. One specific example of a very effective system is calcium aluminate cement – poly(vinyl alcohol/acetate) – water. There is strong interaction between cement particles and polymer, and the dough formed by high shear mixing consists of packed particles (ca. 0.6 volume fraction) interconnected by entangled hydrated polymer chains. Gentle pressure on such a dough (less than 5 MPa) compresses occluded air bubbles and raises the particle volume fraction to about 0.7 (the volume fraction for hexagonal close packing of uniform spheres is 0.74).

If modest temperature is applied to the dough with pressure maintained, the hydration of the cement is accelerated, the deformability of the dough markedly decreases and air pockets are not reformed on release of the pressure. There is then a post-forming volume contraction (ca. 10%), which raises the particle volume fraction, calculated from the original volumetric composition and measured porosity, to about 0.80. This appears to result from the contraction of the extended polymer chains that interconnect the particles as the polymer dehydrates, polymer dehydration being caused by the hydration of the inorganic cement. The inorganic hydration products increase still further the volume fraction of inorganic solid so that the final porosity volume fraction is 0.01 or less. The contraction of a polymer on dehydration can result in massive forces on solids to which the polymer is attached. The contraction of a gelatine film on glass is sufficient to tear pieces from the glass surface and this technique was used some years ago to make ornamental 'frosted' glass (Smith 1925; Gulati & Hagy 1982). The final hardened cement has a flexural strength of 150 MPa or more and the Young modulus is in the range 40-50 GPa; these properties reflect the absence of macroscopic voids and the low total porosity volume (Kendall et al. this Seminar). That the major role of the added polymer is as an aid to the reduction of porosity is illustrated by the fact that identical cement-polymer-water compositions can be manipulated to give both high and low strength products, only if the manipulation is such that macropores are removed is high strength achieved. Under this circumstance, it is significant that the addition of a low modulus polymer increases the modulus of the composite. The absence of macropores in high strength material is illustrated in figure 9, plate 1.

In the final densified material, the polymer resides at the interface between the close-packed cement grains and cannot be easily leached out, indicating firm binding to the hydrated material present at the interface. The initial adsorption of loops of polymer onto the particle surface may be due to 'water bridges' between the water molecules of the hydration shell surrounding cations and polar groups on the polymer (Parfitt & Greenland 1970), but it seems likely that such relatively weak bonds are replaced by strong bonds as hydration products are precipitated.

The space available for the growth of hydration products is restricted in the case of close-packed, low porosity, MDF cement and this appears to influence the morphology of hydration products. Indeed, it has been suggested that the morphology of hydration products is dependent on the space available for growth (Birchall et al. 1978). In macro-defect-free o.p.c. pastes, for example, there is evidence that much of the calcium hydroxide is present in microcrystalline form, the platelets being ca. 10 nm thick (Groves 1981). It has been suggested that large crystals of calcium hydroxide may act as flaws in the paste (Dalgleish et al. 1980). The absence of large

crystals in the gel phase of MDF paste may contribute to the observed high tensile strength of such materials.

It will be seen that the approach to high strength cement products described above combines lessons taken from ceramic science and the science of biogenic inorganic materials – particle packing and porosity removal, and the control of microstructure by polymeric material respectively.

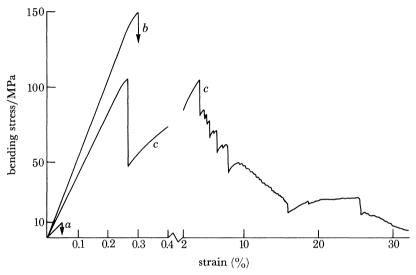


FIGURE 10. A comparison, for the three-point bend configuration, of normal cement paste, (a) an MDF calcium aluminate cement (b) and the latter reinforced with 9% (by volume) Kevlar fibre (4.5% (by volume) in the direction of maximum stress) (c).

APPLICATIONS

The values of the Young modulus, flexural strength and fracture toughness obtained for the best unreinforced MDF materials (50 GPa, 150 MPa and 1 kJ m⁻² respectively) can be put into context by reference to figure 1. These properties are allied to processing and fabrication technology extensively used in the plastics industry. The levels of toughness achieved in the unreinforced material allow it to be machined easily. Fibre-reinforced materials have been prepared, for which fracture toughness approaches 10⁵ J m⁻² (N. McN. Alford, personal communication). These advances are dramatically illustrated in figure 10 in which stress–strain plots (three-point bend test configuration) are compared for conventional cement paste, an MDF calcium aluminate cement and the latter reinforced with 9 % (by volume) Kevlar fibre.

Just as an organic polymer may be used alone or combined with a particulate filler, MDF paste may be filled with particulate material such as sand, silicon carbide, alumina, metal powders, etc. thereby altering secondary properties such as hardness, abrasion resistance, thermal and electrical conductivity and so on. The materials may be pigmented with organic or inorganic pigments, painted or metallized. Not surprisingly, in view of the low porosity, the rate of water penetration into MDF cements can be lower than that observed for conventional pastes by several orders of magnitude.

This technology is clearly capable of still further development as fundamental understanding increases and as experience is gained of the performance in service of these materials. Experi-

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mentally, various forms such as pipe, rod, T-section, sheet and complex shapes have been fabricated by extrusion, press moulding, calendering, and machining, and these are receiving exhaustive performance testing. There is every indication that cement-based materials will, in the not too distant future, be used in some applications at present dominated by plastics, metals and ceramics used at low temperature (Birchall et al. 1982b, c).

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Discussion

- K. I. Majid (Department of Civil and Structural Engineering, University College, Cardiff, U.K.).
 - (1) Can Professor Birchall give more details about the polymer used?
 - (2) Can we buy it and mix our own cement to produce our own paste?
- (3) Can MDF cement be used in the construction industry as ordinary cement is used in reinforced concrete structures? I am interested in its use in this field and would like to know the reasons why it cannot be used in the construction of structures and also whether we can work together in this field to ensure that it is introduced into the construction industry.
- J. D. BIRCHALL. Details of the preparation of MDF cements are given in European Patents no. 0021682 and no. 0055035 and, of course, the details revealed therein could be repeated in your laboratory, bearing in mind the proprietary interests.

It is too early to say what the future of MDF cement is in the construction industry. The process requires very much more quality control than I believe to be possible on site. There is, however, considerable interest in the use of MDF sheet as cladding or permanent shuttering, where the high strength and low permeability of the material may be an advantage.

- B. W. Staynes (*Department of Civil Engineering*, *Brighton Polytechnic*, *U.K.*). When the MDF dough is being produced, air must be entrained unless deliberate steps are taken to eliminate it. Is it necessary to prepare MDF dough under vacuum?
- J. D. BIRCHALL. It is not essential to prepare MDF dough under vacuum. Air can be removed by compression of the dough.
- A. A. Rahman (Aberdeen University, U.K.). Professor Birchall has discussed the low (less than 1 %) porosity of the MDF material. What is the level of permeability of this material for different gases and vapours? Is the residual porosity in the form of connected networks or has Professor Birchall any evidence of isolated extremely small pores or voids? Has he any information about the pore size distribution of the residual porosity?
- J. D. BIRCHALL. The oxygen permeability of a typical MDF cement is four orders of magnitude less than that of a conventional paste and the rate of water penetration six orders of magnitude less than ordinary paste. There is as yet little information about the nature of the residual porosity available.
- N. J. Dave (University of Salford, U.K.). Professor Birchall has already mentioned that his MDF cement is not most suitable for site mixing, perhaps he could tell us whether it is suitable for various building and construction products (factory made) like boards, sheets, tiles, etc. or whether he envisages the use of MDF cement for some special applications. In brief, he could perhaps comment on the field of application of MDF cement. Has he done tests on creep and fatigue behaviour of MDF cement products? What will be the cost of MDF cement products?
- J. D. BIRCHALL. There is much interest World-wide in the potential of MDF cement in the form of sheet, tile, board, etc. Such forms have been produced and are undergoing the standard tests for such building products. I cannot give a brief reply on the question of costs relative to products made from o.p.c. because the final product cost is critically dependent on scale of manufacture and the nature (geometry, etc.) of the product.

An extensive program to study creep and fatigue is underway.

H. F. W. Taylor (*University of Aberdeen*, *Scotland*, *U.K.*). In MDF cement, a substantial proportion of the cement is presumably not reacting and acts as a micro-aggregate. It is a relatively expensive micro-aggregate. Would it be possible to replace the cement in part by some cheaper material, for example a waste material such as fly ash?

In a related question, to what extent is the glue between the unreacted cement particles provided by the cement hydration products, and to what extent is it provided by the water-soluble organic polymer?

J. D. BIRCHALL. We have shown it to be possible to dilute MDF by the addition of fillers such as sand and fly ash to reduce the cost. Equally, it is possible to fill with rather more exotic materials such as alumina, silicon carbide, etc. to alter secondary properties such as hardness, abrasion resistance, etc.

The nature of the bonding between cement grains can be varied depending on the exact process condition but in general we regard the glue to be an intimate combination of organic polymer and inorganic hydration products.

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- F. Tamàs (University of Veszprem, Department of Silicate Chemistry, Hungary). What is the role of plastics when preparing MDF cement? Is it only a lubricating agent? Could it be replaced by inorganic 'lubricants', montmorillonite, for example?
- J. D. BIRCHALL. The polymer acts as a dispersant by transmitting shear to aggregates so that they are broken down. It then lubricates individual particles to allow adjustment to close packing. We have not found colloidal inorganic suspensions capable of this.
- A. J. MAJUMDAR (Building Research Station, Watford, U.K.). Could Professor Birchall comment about the ease or difficulty of incorporating fibres in the MDF cement?
- J. D. BIRCHALL. It is difficult to incorporate a significant volume fraction of short fibre into MDF dough without a loss of the rheological characteristics that permit facile moulding. However, we have developed methods for the production of layer laminates and these processes are cheap and effective.
- A. CHAMPION (EI du Pont Experimental Station, Wilmington DE 19809, U.S.A.). In fibre reinforced. MDF cement, what degree of fibre to matrix bonding was achieved? Was there significant fibre pullout? Would there be a benefit in increasing fibre to matrix bonding?
- J. D. BIRCHALL. The shear stress between Kevlar fibre tows and the MDF cement matrix measured in pull-out was found to be between 4 and 6 MPa. Pull-out measurements on a single filament have not been done.

We observed significant fibre pull-out. Increasing the fibre to matrix bond would probably improve the stress at first crack. However, our aim has been to improve toughness and for this purpose there may be little to be gained from increased bonding.

Della M. Roy (Materials Research Laboratory, The Pennsylvania State University, Pennsylvania 16802, U.S.A.). First, I should like to comment on the water sensitivity of the MDF cements. In our earlier work on compacted and warm pressed cement (completely inorganic) having similar strengths and very low porosities we found no problem with water sensitivity but, in fact, an increase in strength with time upon water immersion. Does Professor Birchall know if the water sensitivity is in any way related to the organic polymer?

Second, it appears that Professor Birchall has achieved some measure of success with incorporation of filler in the MDF cements. What was the particle size of the silicon carbide particles shown in his one microstructural slide?

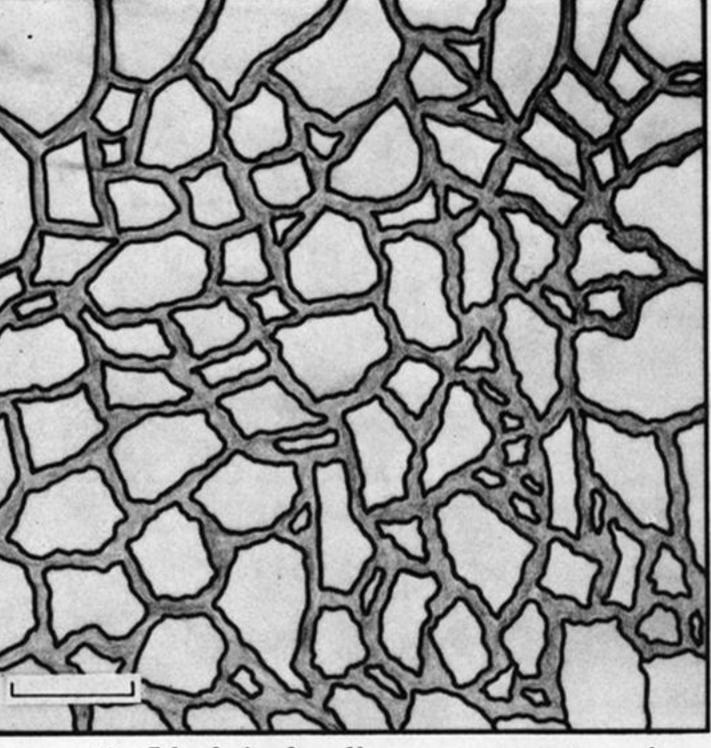
J. D. BIRCHALL. We find that the water sensitivity (fall in modulus and strength on immersion in water, reversed on drying) is related to the proportion of interparticle bonding that is inorganic as against that via the organic polymer. This can be varied and as inorganic bonding becomes predominant, the sensitivity to water decreases as illustrated by the behaviour of the compact.

The median size of the silicon carbide filler was 30 µm.

J. Bensted (Blue Circle Technical Research Division, Greenhithe, U.K.) The low degree of hydration of the cement in these materials creates a potential unsoundness problem if hydration continues. How durable are these materials in a wet environment?

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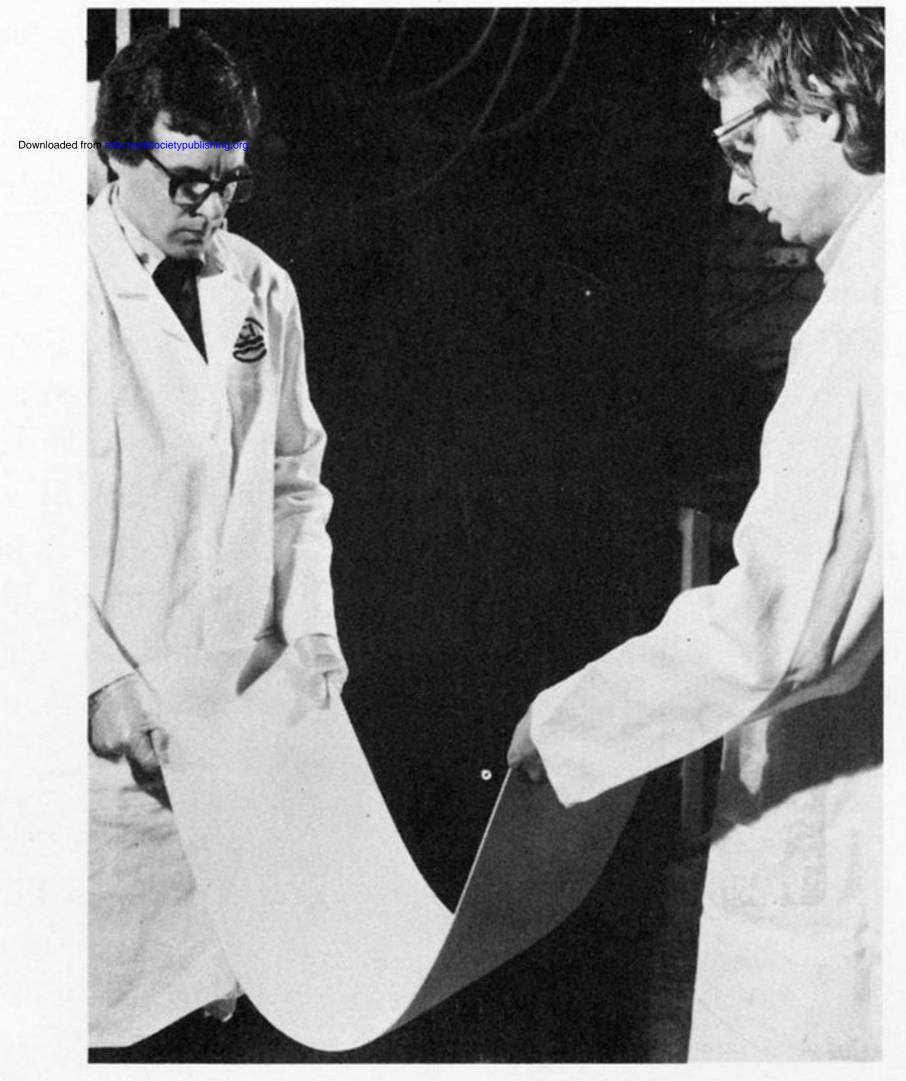
J. D. Birchall. Extensive studies are being made, at present, into durability and the effect of exposure to water. Two aspects are being considered: first, the effect of weathering (both natural and accelerated) and second, the effect of prolonged immersion. The compact nature of the material is such that the rate of penetration of water is some 106 times lower than for normal cement pastes, so that in outside exposure the material never becomes saturated. Samples exposed for over 12 months have shown only slight reduction in properties. Total immersion can result in a fall in both modulus and flexural strength, which is reversible on drying and with modulus creeping higher than the original dry value as wet-dry cycling is continued. In recently prepared materials, these changes on immersion in water have been stabilized. Obviously, much more work will be needed to be done on long-term durability. It should be emphasized that considerable modification and improvement to MDF cements seems possible as experience and knowledge grow.



GURE 5. Ideal hydraulic cement paste microstructure. (The scale bar represents 20 μm length approximately.)

FIGURE 6. The microstructure of mother-of-pearl (nacre).

FIGURE 9. The microstructure of MDF (calcium aluminate) cement.



'IGURE 7. Roller-milled sheet of MDF cement dough illustrating 'plastic-like' quality.