High strength cement pastes
Part 1 *Microstructures*

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The microstructures of high strength cements containing polymer (sometimes known as MDF cements) has been examined. They are basically composed of either clinker or clinker plus hydration products embedded in an amorphous polymeric matrix. Cement pastes based on ordinary Portland cement (OPC) contain the usual hydrates but lack the pronounced fibrillar morphology of hydrate gel often observed in conventional pastes. In contrast, pastes based on the high alumina cement Secar 71 did not contain the normal cyrstalline hydrate phases. Energy dispersive microanalysis of the polymeric phase in Secar 71 material revealed the presence of calcium and aluminium while calcium-rich interstitial material was found in OPC pastes. These results indicate that the organic component plays a more active role than that of an inert rheological aid. The effect of prolonged reaction with hot water is to cause the formation of crystalline hydrate products in Secar 71 paste with a permanent loss in strength of the order of 50%. OPC based pastes appear to be less affected by a similar treatment.

1. Introduction

Materials based on cements but having unusually high strength in bending were first reported in 1981 by Birchall *et al.* [1, 2]. Because their relatively high strength was proposed to be due primarily to the absence of large flaws they are sometimes termed macro-defect-free (MDF) cement pastes. In the case of pastes based on high alumina cements such as the Lafarge product "Secar 71" strengths in bending as high as 150 MPa can be achieved. The technique of making such pastes has been described by Birchall *et al.* [1–3]; in outline it is to form a dough by high-shear mixing of cement, water and an appropriate water-soluble polymer. The dough can then be shaped by pressing, rolling etc. A suitable polymer for Secar 71 has been found to be poly(vinyl alcohol/acetate) such as the commercial product "Gohsenol" while polyacrylamide is successfully used with ordinary Portland cement (OPC), forming a paste with a strength in bending of the order of half that of a paste based on high alumina cement. Such strengths are still about an order of magnitude

higher than those of normal pastes, cast in the normal way. The fracture toughness of MDF pastes is also greater than that of normal pastes although values of critical stress intensity factor are no greater than those for a typical ceramic.

The improved mechanical properties of such pastes have been reported to arise mainly from the absence of macropores with low overall porosity also making a contribution in the case of high alumina cement based pastes [3, 4]. According to Birchall [3] the polymer assists in the packing of the particles of the paste in two main stages, firstly by acting as an interparticle lubricant allowing adjustment of the particles to closer packing during mixing the components of the paste and secondly by drawing the particles closer together as the polymer dehydrates after the forming operation.

In this paper the microstructures of high strength pastes are examined, using TEM observations of ion-beam thinned sections of pastes together with optical microscopy and X-ray diffraction, and compared with more conventional

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pastes. The influences of the special features of the microsturcture on mechanical properties are discussed. Microanalysis of pastes has also been carried out in the TEM, and the results have implications for the reaction occurring during the setting of the pastes, which are further studied by other techniques in a subsequent paper.

The stability of microstructure and strength of pastes under extreme conditions of heat and moisture is of interest and the effect of treatment with water at 80° C has been studied.

2. Experimental details

High strength cements were obtained from ICI or prepared by the method outlined in Birchall et al. [1-3]. Typically, 10 g of powdered polymer was added to 100 g Secar 71 and stirred. To this powder, 12 ml water was added and the resulting paste was thoroughly mixed and sheared in a twin-mill roller device. After an initial 12 h hardening and drying under modereate pressure the Secar 71 cement was finally transferred to a low temperature furnace at 80° C for a short period of time (~ 4 h). Preparation of OPC based cements followed a similar procedure. However, they were not heated after setting but instead cured at high humidity for one week.

The resulting cement samples were examined using the standard techniques of X-ray diffraction (XRD) and transmission electron microscopy (TEM). X-ray powder diffraction patterns of ground material were obtained on a Philips powder diffractometer using $CuK\alpha$ radiation with a graphite monochromator between sample and counter. Electron microscopy studies were carried out on a high voltage electron microscope (HVEM) at 10^6 V in bright field and diffraction modes. TEM specimens were prepared by the conventional ion-milling technique which preserved the spatial arrangement of phases within the cement paste. Chemical analyses of this material were obtained using a JEOL 100C fitted with an energy dispersive X-ray detector. The microscope was operated in the STEM mode at 100 keV and the thinned sample, clamped in a graphite holder, was tilted at 35° towards the lithium-drifted silicon detector. Calcium aluminate ($CaAl_2O_4$) grains within the Secar 71 pastes and wollastonite ($CaSiO_3$) were used as standards for
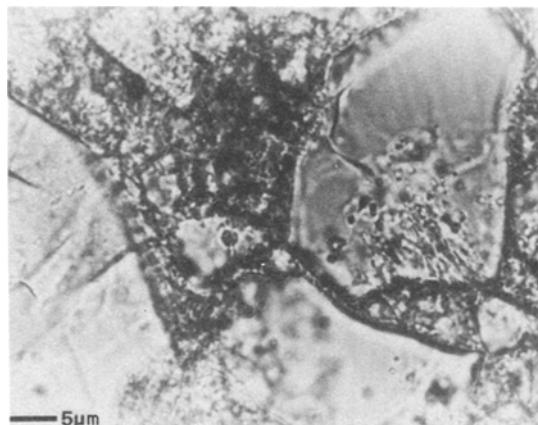

Figure 1 Optical transmission photo-micrograph of high strength Secar 71 cement.

determining empirical scaling factors (k) (Cliff and Lorimer [5]) for both pairs of elements. Twenty-six analyses from a number of different CA* grains gave a k_{CA} scaling factor of 0.90, range 0.98 to 0.81 and standard deviation of 0.05. From a single crystal of wollastonite (CS) 47 analyses were obtained which gave a k_{CaSi} value of 1.14, range 1.23 to 1.06 and standard deviation of 0.05. Flexural strengths were measured using an Instron tensometer (centre-point loading) at a crosshead speed of $0.5\,mm\,sec^{-1}$.

3. Results
3.1. Microstructures

One of the most striking features of Secar 71 and OPC based high strength material when viewed through an optical microscope is the lack of defects such as air bubbles, cracks etc, which normally occur in cement pastes cast at higher water/solid ratios [1-4]. An optical photo-micrograph of a Secar 71 based high strength cement (Fig. 1) displays large grains of CA and CA_2 surrounded by a fine scale matrix. At the higher magnifications available in TEM, the microstructure of these finer grained areas (Fig. 2) is found to be composed of very small crystals, typically less than 1 μm in size, embedded within a low contrast medium. The small crystalline phases have been identified by electron diffraction and qualitative energy dispersive analysis as α-alumina (Al_2O_3) and β-alumina ($Na_2Al_{22}O_{34}$) occurring with CA and CA_2. The sodium aluminate phase has also been detected in XRD traces of Secar 71

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*Conventional cement chemistry notation is used within this paper. Thus C = CaO, A = Al_2O_3, S = SiO_2, H = H_2O.
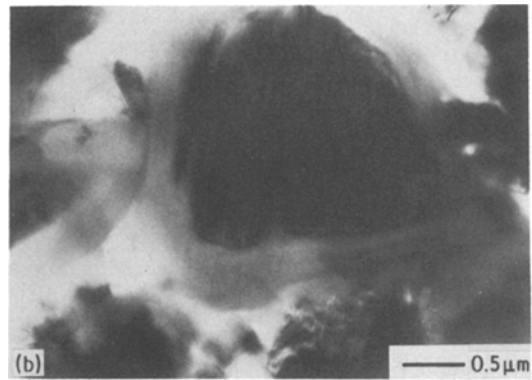
Figure 2 HVTEM micrographs of Secar 71 based high strength cement.

powder by the presence of a weak peak at 1.13 nm. (A complete diffraction pattern of $Na_2Al_{22}O_{34}$ includes many lines at smaller spacings, though these have intenisties of less than half that of the 1.13 nm peak and would not be observable for the concentration present in Secar 71.)

Selected-area diffraction patterns of the low contrast interstitial material gave only a broad powder ring typical of amorphous material. This was confirmed during tilting experiments where the contrast of these areas remained unchanged. The polymeric material must reside in these areas. Normal cyrstalline hydration products of CA and CA_2, i.e. C_2AH_8 and CAH_{10}, were not found by either XRD or TEM in these high strength specimens. When thin areas of the amorphous phase were analysed in the analytical electron microscope small quantities of calcium and aluminium were detected in a variable ratio ranging from $CA_{1.2}$ to CA_2. Count rates arising from these regions were usually low at around 100 to 150 counts sec^{-1}. Eighteen analyses from the polymer matrix gave a mean C/A ratio of 0.61, i.e. $CA_{1.64}$, range 0.49 to 0.80 and standard deviation of 0.30.

No obvious large pores or other defects were observed in TEM specimens of Secar 71 pastes

and this is reflected in high flex strength values of 130 to 150 MPa. An extremely fine porosity is present in the interstitial low contrast material on a scale of less than 0.01 μm, shown in Fig. 2. These observations confirm the conclusions of Kendall et al. [4] which suggest that Secar 71 based material is a special form of macro-defect-free cement characterized by an extremely low porosity.

Pastes formed with OPC and polyacrylamide achieve their strength over a period of time reaching a maximum at around 28 days (Fig. 3). Final flexural strengths typically ranged from 50 to 80 MPa. These values are an order of magnitude greater than for conventionally made cement but about 50% lower than for the aluminous material mentioned above. The microstructure of these pastes has been reported by Alford et al. [6] and Groves [7]. These studies suggest that the structures of MDF cement pastes and conventional pastes of very low water content are very similar; both materials contained microcrystalline CH and amorphous regions surrounding clinker grains. However, some differences are apparent between MDF pastes and OPC or C_3S pastes made with a more usual water content, e.g. water : cement ratio = 0.5. Fibrous outgrowths, so characteristic of such conventional pastes are absent. Such fibrous outgrowths are often visible on their fracture surfaces but they are not seen on fracture surfaces of MDF paste, an example of which is shown in Fig. 4. Further, semiquantitative powder XRD shows that the amounts of crystalline hydration product (CH, AFt) are relatively low in MDF pastes.
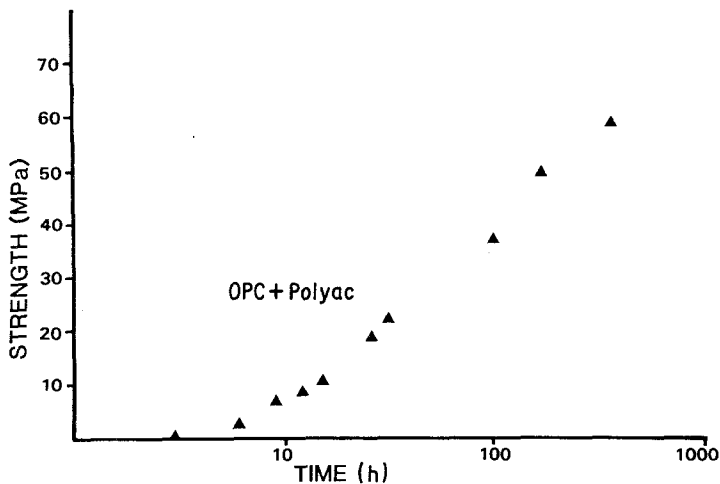
Energy dispersive microanalysis in the TEM was

Figure 3 Graph showing the development of strength plotted against time for an OPC/polyacrylamide paste.

also undertaken on thin areas of MDF OPC pastes. The analysis is complicated because of the intimate mixture of hydration products, CH, AFt and CSH, with the polymeric matrix. The crystalline hydrates and clinker phases can be avoided by carefully selecting areas which do not generate diffraction spots but the identification and separation of CSH from polymer is rather more difficult as both give an amorphous ring pattern. Several analyses were therefore obtained on areas which did not display diffraction spots nor were close to clinker crystals. It was hoped that by examining regions away from crystalline phases the CSH gel surrounding alite would not interfere with the chemical analysis of polymeric material. The results of four analyses show a range of C/S ratios of 4.86 to 3.38, mean of 4.26 and standard deviation 0.80. Also identified in these spectra were small amounts of sulphur from dissolved gypsum and aluminium.
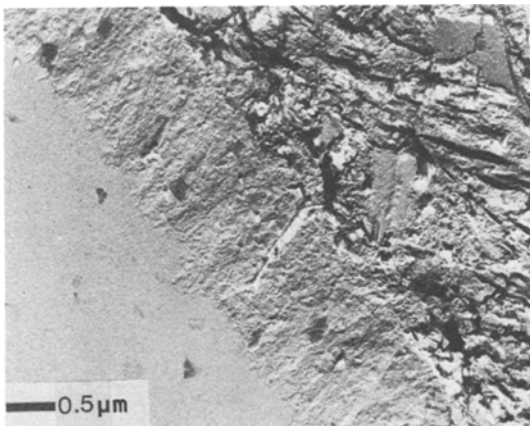

Figure 4 Replica of fracture surface of an OPC based MDF cement paste.

3.2. The effect of hot water on the strength and constitution of high strength cements

Small beams of high strength Secar 71 cement containing 7% polymer and suitable for three-point bend tests, were placed in water or just above water (surfaces wet) at 80° C. After 3 days hot water treatment the flex strength had decreased by about 40% (Table I, 2). Several of the treated samples were allowed to dry and again tested for flexural strength and modulus. The values obtained show that these properties were not regained (Table I, 3).

Powder XRD revealed that hot water treatment leads to the formation of the stable hydrates C_3AH_6 and AH_3. X-ray traces of slices taken from various depths of a rectangular beam suggest that the formation of C_3AH_6 is controlled by the rate of water diffusion since the quantity of this crystalline hydrate decreases with distance from the surface (Fig. 5). Scanning electron microscopy of fracture surfaces of the treated material did not display the large euhedral grains of C_3AH_6 characteristic of the conversion reaction in high alumina cement pastes of conventional type; nor were such grains evident in TEM observations. Sections taken from near the surface of a hot water treated Secar based paste did, however, show evidence of extensive further hydration of the cement in TEM observations. Fig. 6 shows an extensive area of microcrystalline material, giving a diffraction pattern identifying it as AlO(OH). It is probable that this has resulted from the partial dehydration of gibbsite during specimen preparation and therefore has arisen from hydration product. Such regions were never observed in the original untreated pastes.

TABLE I Effect of hot water on high strength cements

Sample		Exp. Conditions	Flex strength (MPa)	Modulus (GPa)
Secar 71 + 7% PVA/Ac:	1.	Control	133(4)	32(3)
	2.	Hot water treatment	52(3)	23(4)
	3.	As above + drying 2 h at 80° C	59(6)	20(5)
OPC + 4% PAcrylamide:	4.	13d strength; control	49(5)	19.0(0.6)
	5.	15d + hot water treatment	49(4)	20.8(1.6)
	6.	21d strength; control	56(6)	21.0(0.8)
	7.	18d + hot water treatment	56(3)	19.8(1.1)
	8.	32d strength; control	56(1)	21.1(0.5)

High strength OPC based pastes were also subjected to a wet environment at 80°C for 3 days. As these pastes do not develop their ultimate strength rapidly, the hot water treatment was repeated at prescribed time intervals up to 32 days from initial mixing. The results (Table I, 4 to 8) show that, unlike Secar 71 cements, OPC material when redried maintains its flexural strength and modulus. Furthermore, the time-dependent strengthening process of high strength OPC appears to be little affected.

4. Discussion
TEM results presented in this paper show that the microstructures of the two MDF cements, Secar 71 and OPC, are essentially composed of either clinker or clinker and hydrate grains embedded in a continuous amorphous polymeric matrix. OPC high strength pastes contain the normal hydration products CH and AFt, whereas high alumina Secar 71 based cement is unusual in that it does not display any crystalline hydrate phases. There is no

evidence in either type of paste of grains being joined by interlocking fibrils similar to the CSH fibrils often seen in conventional pastes of relatively high water : cement ratio. There is, therefore, no support for the model recently proposed by Eden and Bailey [8] whereby the strength of MDF pastes was controlled by the shear resistance of the polymer-fibril interface of CSH fibrils as they were pulled apart from an original interlocking structure. Fracture surfaces of MDF pastes do not show protruding fibrils as would be required by this model (Fig. 4).

Although both Secar 71 and OPC MDF pastes are processed in a similar manner the high alumina cements typically yield much higher flex strength values by a factor of 2 or 3. A comparison of the microstrcuture of the two cement types may provide some insight into the underlying cause of the differences in their flex strengths. Fig. 7 shows a typical TEM micrograph of an area of high strength OPC paste. It can be seen that the material between the large clinker grains, which is
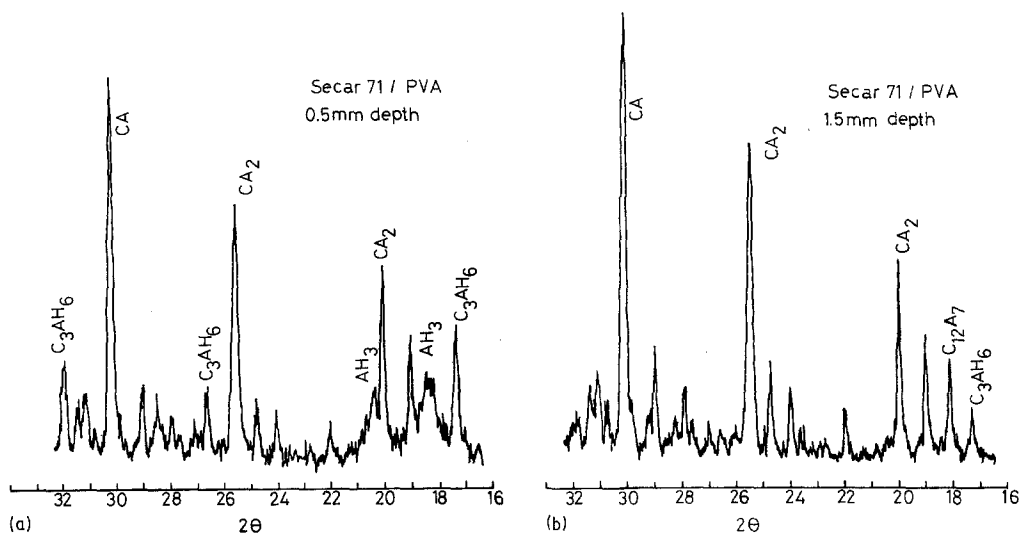

Figure 5 X-ray powder diffraction tracers from Secar based paste treated in water at 80° C for 3 days.
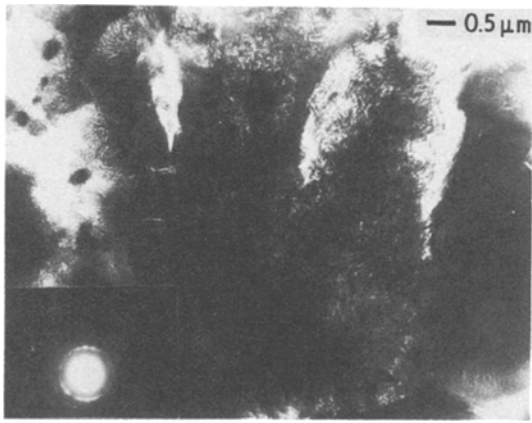
Figure 6 HVEM micrograph of near-surface region of Secar based paste after 3 days in water at 70° C.

Figure 7 HVTEM micrograph of OPC based high strength cement.

composed of polymer gel and hydration products, exhibits a coarse porosity on a scale of 0.1 μm. Furthermore, the amount of porous material is clearly much greater in OPC based MDF than in Secar 71 based MDF. Therefore, in both scale and amount the porosity in OPC based material exceeds that in the alumina cement based material. For cement pastes with a given flaw distribution, increasing porosity reduces the strength as shown by Kendall et al. [4].

The polymeric material added to the cements to allow the fabrication of MDF material must reside in the amorphous regions seen in TEM. However, microanalysis shows that all amorphous material in Secar 71 pastes contains both calcium and aluminium and is aluminium rich while in OPC pastes interstitial amorphous material is very rich in calcium. These results suggest that the polymer additive reacts with the cement rather than existing as an entirely inert lubricant.

An important question regarding the durability of high strength cement pastes is their stability in water both at room and elevated temperatures. Of particular interest is the reaction of high alumina Secar cement pastes in hot, wet conditions. Under these conditions it is well known that conventional high alumina cements lose nearly all strength due to the "conversion" of the metastable hexagonal hydrates to the stable cubic hydrate C_3AH_6.

If hardened MDF paste is immersed in cold water for long periods then it will suffer a reduction in strength but this strength can be regained if the ceme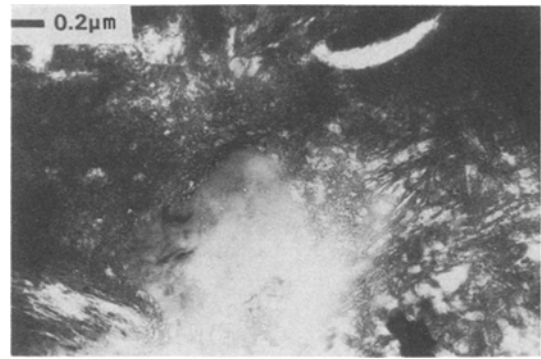nt is dried [9]. The softening is possibly due to the absorption of water by the polymer. A similar pheonmena has been reported to occur when certain dental ionic-polymers are subjected to an aqueous environment [10].

When the Secar 71 product is placed in water at high temperature, e.g. 80° C, the reduction in strength is irreversible, see Table I and X-ray analysis reveals the formation of C_3AH_6 and AH_3. This is concentrated initially on the surface of the cement but penetrates further into the material at longer time intervals presumably as the surface becomes more porous due to the formation of the cubic hydrate and so allows access of water further into the material.

It should be emphasized that the loss of strength of Secar based MDF pastes cannot be attributed to the conversion reaction of a conventional high alumina cement paste since the hexagonal hydrates CAH_{10} and C_2AH_8 are not initially present. Furthermore, the loss in strength is less catastrophic than that due to conversion, the residual strength being still of the same order as that of an OPC based MDF paste. The loss in strength may be attributable to direct reaction of CA and CA_2 grains to form C_3AH_6 and gibbsite, the substantial volume of hydration product so formed introducing porosity. It may be significant that the proportion of hydration product seen in the microstructure of hot water treated Secar pastes near the surface appears similar to that normally present in OPC based pastes.

Acknowledgements

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