

The microstructure of macrodefect-free cement with different polymer contents and the effect on water stability

C. S. POON, G. W. GROVES

Department of Metallurgy and Science of Materials, Oxford University, Parks Road, Oxford OX1 3PH, UK

The effect of different polymer contents on the microstructure of ordinary Portland cement-based macrodefect-free cement was studied by high voltage transmission electron microscopy. The microstructure, especially the morphology and composition of the gel matrix, of material with a low polymer content was significantly different from that of material with a high polymer content. The former consisted mainly of gelatinous material with some microcrystallites and with some porosity. The latter consisted of mainly pure non-porous polymer gel with little metallic content. Although the dry strength of the material with high polymer content was higher than that of the lower polymer content material, the former was extremely unstable after immersing in water. This was attributed to the difference in microstructure of the polymer gel as revealed by electron microscopy.

1. Introduction

High-strength cement pastes formulated from ordinary Portland cement and water-soluble polymers have been developed recently [1-3]. Strength values of the order of 50 to 80 MPa are normally achieved, depending on the initially forming and curing conditions. This is nearly an order of magnitude higher than that of normal hydrated cement. The high strength is generally attributed to the lack of large pores and the reduction in porosity resulting from the special method used during paste formation [4, 5]. Therefore the cement system is sometimes called "macrodefect-free" (MDF) cement.

However, this polymer-modified cement material has been demonstrated to be water-sensitive and large reductions in strength and expansion can be produced by water ingress [6]. This paper aims to provide an understanding of the weakening mechanism by studying the microstructures of materials with different polymer contents and water-sensitivity characteristics.

2. Experimental procedure

The MDF cement being studied was formulated from ordinary Portland cement (OPC) with a high molecular weight (> 20 000) polyacrylamide as the binding polymer. Some samples were prepared by replacing 30% of the OPC by pulverized fly-ash (PFA). The chemical compositions of OPC and PFA are given in Table I. The samples were prepared with different amounts of polymer. The method and procedure used for preparing the MDF paste has been given elsewhere [7] and the compositions and curing conditions of each sample are given in Table II.

Flexural strength was determined by three-point bending with an Instron machine and the dimensional stability under water was measured by immersion in a 20°C water bath. Wet strength and expansion

measurements were determined at 1 and 7 days after immersion. The porosities of the samples were assessed by the methanol replacement method.

The degree of hydration of some of the OPC pastes was determined by solid-state nuclear magnetic resonance (NMR) [8]. This method is adopted because of the presence of water-containing polymer in the hardened paste, and the normal drying method to determine bound water as an indication of hydration is not suitable. The degrees of hydration of the PFA-containing pastes were not determined because of the presence of a large amount of iron compound ($\approx 7\%$) in the fly-ash, making NMR measurement impossible.

The microstructure of the samples was studied by a high-voltage electron microscope (HVEM) at 1000 kV. An argon ion-beam thinning technique was used to prepare thin sections for HVEM examinations.

3. Results

3.1. Flexural strength, porosity and degree of hydration

Flexural strength results (average of three) of the dry samples are given in Table II. Generally the strength values increase with polymer content. Hydration in a 40°C water bath increased the strength values of the OPC paste but did not affect the PFA-replaced material. Replacement of OPC by PFA at the 30% level did not affect the strength of the product at small hydration.

Porosity measurement results as determined by methanol replacement are also given in Table II, and the results show that all samples have a similar porosity of about 26%.

The degree of hydration as determined by solid-state NMR is 12% for Sample 1, 20% for Sample 2, and 5% for Sample 4.

TABLE I Oxide contents of OPC and PFA

Component	Oxide content (%)	
	OPC	PFA
SiO ₂	19.9	48.7
Al ₂ O ₃	5.5	32.3
Fe ₂ O ₃	3.7	7.8
CaO	65.0	3.2
MgO	1.1	1.3
SO ₃	2.7	0.48
Na ₂ O	0.16	1.1
K ₂ O	0.54	2.8
LOI*	1.3	1.9

*Loss on ignition.

3.2. Water stability

Table III gives the strength and expansion data of the samples after 1 and 7 days immersion in 20°C water. The data show that most of the lower polymer-content samples (i.e. 4 and 6 g) gave similar expansion values after 1 and 7 days (0.3%), but the samples (both OPC and OPC-PFA) containing 8 g polymer underwent substantial expansion after 1 day immersion (2%).

The flexural strengths of all the samples were decreased after water immersion, but the most substantial decrease was observed with the samples with high polymer content. There was a gradual recovery of strength after 7 days immersion. For Sample 1 the strength value recovered to 45 MPa after 14 days immersion.

3.3. Microstructure

The HVEM micrographs of Sample 1 (OPC, 6 g polymer, 1 day hydration) are shown in Fig. 1. The microstructure is consistent with that observed by Sinclair and Groves [7]. The anhydrous grain is surrounded by a gel matrix of polymer and cement hydrates. There is no fibrous C-S-H as observed in normal hydrated OPC paste [9]. This has been attributed to the lack of space for its growth. Selected-area diffraction (SAD) analysis in the gel gave largely diffuse ring patterns, but there were also spots scattered in some regions indicating the presence of microcrystalline structure. The identity of these microcrystalline materials cannot be determined from the scattering pattern. In the same sample there are also areas with distinctive lamellar arrays of crystals in the matrix. The SAD pattern was

TABLE II Formulation, strength and porosity data

Sample No.	Content (g)			Curing method*	Strength (MPa)	Porosity (%) [†]
	OPC	PFA	Polymer			
1	100	—	6	1	47	24
2	100	—	6	2	72	26
3 [‡]	100	—	8	1	—	—
4	100	—	8	2	85	28
5	70	30	4	1	36	26
6	70	30	6	1	50	28
7	70	30	8	1	80	30
8	70	30	6	2	50	30

*(1) 6 h in oven at 80°C; (2) 3 days in 40°C water bath + 6 h in oven at 80°C.

[†] Assuming a density of 2.2.

[‡] Sample split when being cut with diamond saw.

TABLE III Expansion and strength data after 1 and 7 days water immersion

Sample No.	Expansion (%)		Strength (MPa)		
	1 day	7 days	0 day	1 day	7 days
1	0.39	0.43	47	15	32
2	0.27	0.28	72	26	37
4	1.7	1.9	85	20	18
5	0.16	0.23	36	23	30
6	0.21	0.27	50	18	24
7	2.0	2.4	80	Plastic	

identified to be calcium hydroxide. This finding is consistent with the results of former microstructure studies [7, 10].

Fig. 2 shows the microstructure of Sample 2 which was essentially the same as Sample 1 but was hydrated for 3 days in a 40°C water bath. The anhydrous material has been further hydrated, as indicated by the area at the top left-hand corner which suffered most beam damage. This shows the inner product of tricalcium silicate hydration. The crystal at the bottom of the micrograph revealed the twinning morphology of the anhydrous grain which is characteristic of dicalcium silicate grains [11]. Little hydration has taken place in this grain. The SAD pattern from the gel in the centre of the micrograph gave a diffuse ring pattern but it also contained some strong Bragg reflection spots. Lamellar calcium hydroxide crystals were more evident in this sample and are shown in Fig. 3.

Fig. 4 shows the microstructure of Sample 4 (OPC, 8 g polymer, 3 days hydration); very little hydration is evident in this sample. The gel is largely made up of low-porosity material which gave only a diffuse ring diffraction pattern.

The microstructure of the PFA-substituted MDF pastes is shown in Figs 5 and 6. Fig. 5 represents the microstructure of Sample 6 (OPC-PFA, 6 g polymer, 1 day hydration) with spherical PFA particles embedded in a gel matrix. The surface morphology of the PFA particles was unmodified. There are also small gaps between some of the PFA particles and the gel matrix. The SAD pattern from the gel matrix revealed amorphous diffuse rings and spots of microcrystallinity.

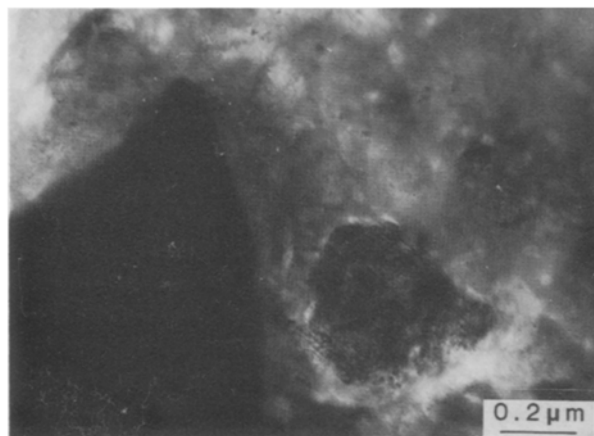


Figure 1 Micrograph of Sample 1 (OPC, 6% polymer, 1 day hydration) showing anhydrous grain and polymer matrix with microcrystallites.

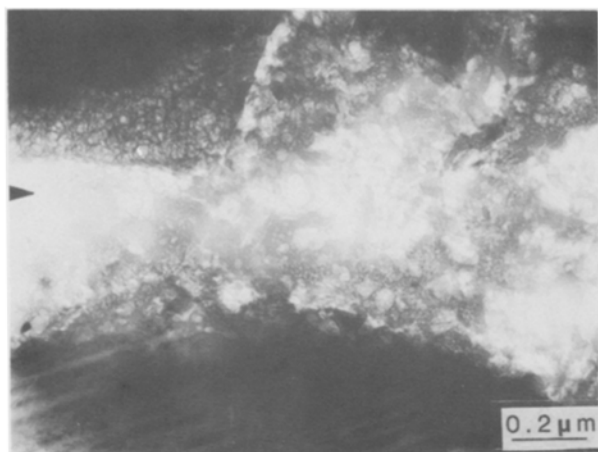


Figure 2 Micrograph of Sample 2 (OPC, 6% polymer, 3 days hydration) showing hydration products suffering beam damage (top), polymer gel with microcrystallites and twinned dicalcium silicate particle (bottom).

Fig. 6 is a micrograph of Sample 7 (OPC-PFA, 8 g polymer, 1 day hydration). The most significant difference between Sample 7 and Sample 6 is the presence of large areas of apparently non-porous gel next to the anhydrous grains (Fig. 6). X-ray microanalysis on this gel produced very low count rates for metals. There are also areas in the same sample showing the presence of some small crystals. Microanalysis gave high count rates for calcium and sulphur approximately in the ratio of 1 : 1, indicating a possible CaSO_4 composition. The SAD pattern also confirmed that these crystals are hydrated calcium sulphate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

4. Discussion

The discussion of the above results can be divided into two sections.

4.1. The influence of polymer content and degree of hydration on dry strength

The results showed that the dry strength of the MDF cement generally increases with polymer content. Porosity data, however, showed that all the samples have almost similar amounts of porosity as determined by methanol replacement. Eden and Bailey [12] attri-

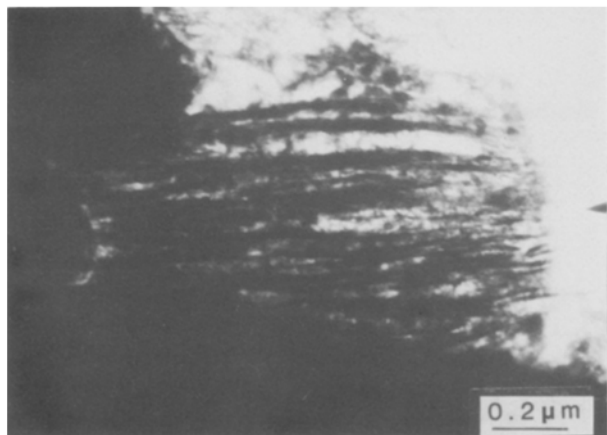


Figure 3 Micrograph of Sample 2 showing lamellae of calcium hydroxide crystals.

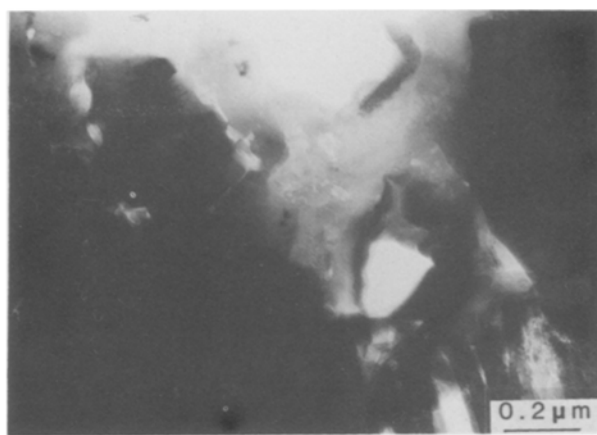


Figure 4 Micrograph of Sample 4 (OPC, 8% polymer, 3 days hydration) showing largely anhydrous cement grain with non-porous polymer gel.

buted this to the increase in shear strength terms in their fibril pull-out model for cement strength:

$$\sigma_y = \pi d l T_s N \quad (1)$$

where σ_y = tensile strength, d = diameter of fibre, l = length of fibre, T_s = shear strength and N = number of fibres per unit area.

They claimed that an increase in polymer content will simply increase T_s and thus the tensile strength. But microstructural evidence has disproved this model as there are no fibrils observed in this low water/cement ratio, high-strength cement paste. However, the present HVEM study revealed that an increase in polymer content in the MDF formulation resulted in a change in morphology of the polymer/C-S-H gel. The microstructural study of the high polymer content pastes showed the presence of a large part of non-porous pure amorphous gel areas. These areas are in close contact with the anhydrous grains, leaving little cracks or porosity. In low-porosity cement systems, it has been suggested that when the pore size is less than $100 \mu\text{m}$ the anhydrous grains and other particles in the cementitious matrix may become critical flaws [5]. Therefore, the increase in strength in a high-polymer MDF system may be due to a reduction in critical flaw size by the formation of this continuous amorphous material around cement grains.

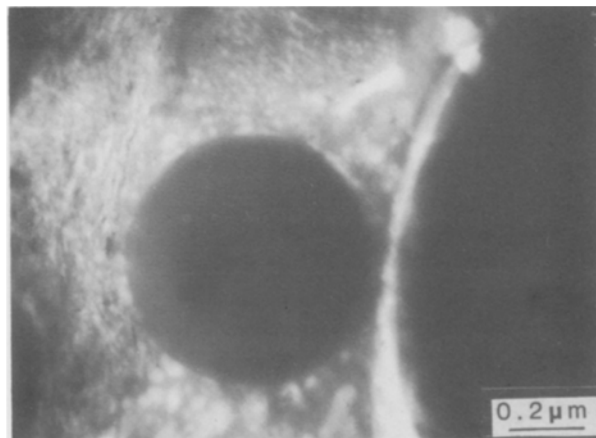


Figure 5 Micrograph of Sample 6 (OPC-PFA, 6% polymer, 1 day hydration) showing PFA particles embedded in the polymer matrix.

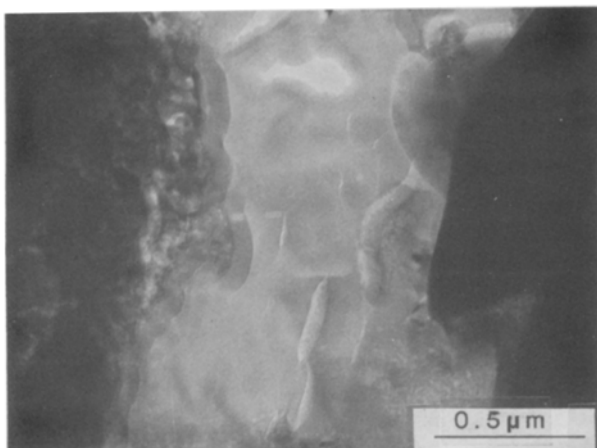


Figure 6 Micrograph of Sample 7 (OPC-PFA, 8% polymer, 1 day hydration) showing non-porous gel covering the anhydrous grain.

The chemical composition and formation mechanisms of the usual gel matrix in low polymer content MDF cement have been discussed by Rodger *et al.* [13]. They postulated that the carbonyl group of the polyacrylic acid was replaced by the metallic ions in the cement matrix, and setting and hardening resulted from the crosslinking of the polyacrylate chains by the cations. The microcrystallites detected by SAD in the present study may be the reaction products between the polymer and the dissolved ions. There may also be some crystalline cement hydration products incorporated in the gel matrix.

From the HVEM study, this gel morphology is altered by using a high polymer content. Beside the usual gel morphology, there are also some apparently non-porous pure amorphous gel areas. The degree of hydration as determined by NMR study is also lowered by adding more polymer. From calorimetry, the polyacrylic acid is known to retard the hydration of cement. The exact mechanism of retardation is not known but it would be anticipated that both the dissolved ion content and rate of hydration product formation will be lowered as a result of retardation. The excess polymer was therefore unable to react with metallic ions, resulting in a pure amorphous gel. The cement paste was able to be hardened only by dehydration due to loss of water.

This postulate can be further substantiated by the microstructural evidence from the samples with 30% PFA replacement. In the sample with low polymer content, a normal gel matrix was formed. For the high polymer content sample a large part of the gel was of non-porous amorphous type. Furthermore, microcrystalline gypsum was detected in the sample with high polymer content. When PFA reacts with water the surface layer of sulphate ions and some calcium ions are quickly released into solution [14]. When the sample is dried, gypsum crystals are precipitated and can be detected by electron microscopy and X-ray diffraction. However, when the PFA is placed into an OPC system, the dissolved sulphate ions will be utilized quickly by tricalcium aluminate to form ettringite or monosulphate. This was the situation in the low polymer content PFA sample, and the dissolved sulphate was incorporated into the hydrated gel by the hydration

of tricalcium aluminate. In the sample with high polymer content, the hydration of cement was retarded and the released sulphate ion was not utilized and was observed in the microstructure.

4.2. The influence of gel composition on water stability

The expansion and wet strength data (Table III) indicated that the samples with high polymer content underwent substantial expansion and strength loss after water immersion. The effects of water on the lower polymer content samples were less harmful. From the microstructural studies they can be attributed to the different quantity, and especially composition, of the gel formed. It is suggested that in the low polymer content samples, the gel is stabilized by the presence of metallic ions which crosslinked the polymer chain and formed certain crystalline products. The observed behaviour, that the initially lost strength can be recovered by prolonged immersion up to 14 or 21 days, is probably due to the loss in stiffness of the gel which is compensated for by the hydration of cement and further stabilization of the gel by metallic ion crosslinking.

In the gel with high polymer content the initial substantial expansion and reduction in strength is due to the instability of the unstabilized gel. Prolonged immersion may recover part of the strength but the material is permanently weakened by the excessive initial expansion.

Acknowledgements

The authors wish to thank the British Technology Group for financial support and S. A. Rodger for assistance in NMR measurement.

References

1. J. D. BIRCHALL, A. J. HOWARD and K. KENDALL, *Nature* **289** (1981) 388.
2. Imperial Chemical Industries Ltd, European Patent No. 0021 682 (1981).
3. J. D. BIRCHALL, *Phil. Trans. R. Soc.* **A310** (1983) 31.
4. K. KENDALL, A. J. HOWARD and J. D. BIRCHALL, *ibid.* **A310** (1983) 139.
5. N. McN. ALFORD, G. W. GROVES and D. D. DOUBLE, *Cem. Concr. Res.* **12** (1982) 349.
6. C. M. CANNON and G. W. GROVES, *J. Mater. Sci.* **21** (1986) 4009.
7. W. SINCLAIR and G. W. GROVES, *ibid.* **20** (1985) 2846.
8. N. J. CLAYDEN, C. M. DOBSON, G. W. GROVES, C. J. HAYES and S. A. RODGER, *Proc. Br. Ceram. Soc.* **35** (1984) 55.
9. D. D. DOUBLE, A. HELLAWELL and J. PENNY, *Proc. R. Soc.* **A359** (1978) 435.
10. G. W. GROVES, *Cem. Concr. Res.* **11** (1981) 713.
11. F. P. GLASSER, in "Cement Production and Use", edited by J. Skalny (Engineering Production, New York, 1979) p. 31.
12. N. B. EDEN and J. E. BAILEY, *J. Mater. Sci.* **19** (1984) 2677.
13. S. A. RODGER, S. A. BROOKS, W. SINCLAIR, G. W. GROVES and D. D. DOUBLE, *ibid.* **20** (1985) 2853.
14. C. S. POON, PhD thesis, Imperial College London (1985).

Received 1 May
and accepted 20 July 1987