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The mineralogy and microstructure of three composite cements with high replacement levels

J. Hill, J.H. Sharp *

Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

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Abstract

The hydration products of three high replacement, composite cement pastes, i.e. Portland cement mixed with 75% and 90% ground, granulated blast furnace slag (BFS) and 75% pulverised fuel ash (PFA), are reported and compared with those from a 100% ordinary Portland cement (OPC) paste. The samples were cured in air under the same temperature and humidity conditions and tested at various times for up to six months. The hydration products were identified by means of X-ray diffraction (XRD) and their microstructure by scanning electron microscopy (SEM). Although the observed hydration products were mostly as expected, due to the high replacement levels, the degree to which these phases was present was unusual. In particular the calcium hydroxide initially formed in the BFS-cement systems was totally consumed within six months, indicating the important pozzolanic behaviour of BFS at such high replacement levels. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Blast furnace slag; Composite cements; Portland cement; Pulverised fuel ash; Scanning electron microscopy; X-ray diffraction

1. Introduction

Composite cements based on the partial replacement of Portland cement by waste materials have become commonplace, because they offer cost reduction, energy saving, and arguably superior products. The replacement materials fall into two principal groups, pozzolanic materials, such as pulverised fuel ash (PFA), rice husk ash, volcanic ash and silica fume, and latent hydraulic materials, notably ground, granulated blast furnace slag (BFS). In both groups, the replacement materials participate in the hydraulic reactions, contributing significantly to the composition and microstructure of the hydrated product.

Pozzolanic materials are rich in SiO_2 and usually have a low CaO content. They react with lime, $Ca(OH)_2$, produced during the early hydration of alite, Ca_3SiO_5, in Portland cement, and water to form C–S–H gel, which contributes to the strength of the cement paste. Because they are low in CaO, the amount of portlandite in the hydrated cement paste is reduced, with potential benefits in terms of reduced carbonation and improved durability.

Latent hydraulic materials have a chemical composition intermediate between that of a pozzolanic material and Portland cement. They act as a hydraulic cement when mixed with water in the presence of a suitable activator. BFS typically has a CaO content of about 40% and can be activated by alkalis, such as the portlandite formed from the hydration of alite. The principal product of the reaction is C–S–H gel, but its composition may be modified, along with C–A–$\overline{S}$–H products and a hydrotalcite-like phase of approximate composition, $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$, which is formed from the MgO content of BFS, typically 5–9%.

Under optimum conditions, which include effective blending of the components, these composite cements can have excellent properties, including high ultimate strength, low heat of hydration, low permeability and good durability in a wide range of media. As such, cements containing up to about 35% PFA and up to about 65% BFS are now well established in the construction industry and fully characterised in the scientific literature [1–3]. Composite cements with higher levels of replacement are less fully documented, but may have advantages in specific applications, for example when

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* Corresponding author. Tel.: +44-114-222-5504; fax: +44-114-222-5943.

E-mail address: j.h.sharp@sheffield.ac.uk (J.H. Sharp).

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very low heat evolution is required as in the encapsulation of radioactive waste.

The aim of the present work was to investigate the chemical composition and microstructure of composite cements incorporating 75% PFA, and 75% and 90% BFS. Data obtained using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to study the hydration products of these three composite cements are compared with similar data from a control sample, based on the same Portland cement paste that was used to make the blended materials.

2. Experimental

2.1. Cement systems

Four cement systems were used for this work. These were 100% ordinary Portland cement (OPC) (included as a reference material), 3:1 BFS:OPC, 9:1 BFS:OPC and 3:1 PFA:OPC. The OPC and BFS were supplied by Castle Cement and the PFA by Pozzolanic Lytag. All the powders were prepared to comply with the specification of British Nuclear Fuels plc, essentially to the appropriate British Standard but with modified physical and chemical limitations. The chemical analyses for the OPC and BFS are shown in Table 1. A Bogue analysis indicates a potential phase composition of C_3S, 53.2%; C_2S, 20.1%; C_3A, 8.3%; C_4AF, 9.4%; suggesting a normal Portland cement. There was no chemical analysis supplied for the PFA, therefore, it is only possible to quote the calcium oxide content which was 1.9%. However, an analysis [4] of a typical UK fly ash is shown in Table 2.

An XRD trace of the PFA indicated the presence of small amounts of crystalline quartz and mullite, while that of the BFS indicated the presence of gehlenite, $Ca_2Al_2SiO_7$. Both samples displayed amorphous humps indicating the presence of large amounts of glass.

Table 1
Chemical analyses for OPC and BFS

	OPC	BFS
CaO	64.1	41.4
SiO_2	21.0	32.9
Al_2O_3	5.1	13.5
Fe_2O_3	3.1	0.8
MgO	2.5	8.3
SO_3	2.2	–
K_2O	0.7	0.4
Na_2O	0.3	0.2
Chloride	0.03	0.03
Insolubles	0.3	–
Loss on ignition	0.6	0.5
Free Lime	0.8	–
Sulphide	–	0.9

Table 2
Composition of a typical UK fly ash

Component	Percentage
SiO_2	51.0
Al_2O_3	25.6
Fe_2O_3	9.6
CaO	1.7
MgO	1.6
K_2O	3.8
SO_3	0.7
C	2.8

2.2. Casting and curing

Cements were prepared in 500 g batches with a *w*:*s* ratio of 0.35. However, this does not equate to a constant water:cement (*w*:*c*) ratio of 0.35 for the composite cement systems because of the different amount of OPC present in each. Table 3 shows the *w*:*c* and *w*:*s* ratios for all four cement systems.

Powders (500 ± 0.1 g) were weighed and, where necessary, thoroughly mixed. Distilled water (175 ± 0.1 g) was weighed and the cement powder gradually added to the water. Once all the powder had been added the cement was mixed manually for approximately 3 min. The paste was then poured into PTFE moulds creating 100 mm × 10 mm × 10 mm prisms.

The samples were cured at 23 ± 2°C and 86 ± 2% relative humidity. This was achieved by placing the sample in an environmental cabinet in the laboratory and using a saturated solution of potassium sulfate, K_2SO_4, to control the humidity. The freshly cast samples were placed in the cabinet for 24 h and were then demoulded. The samples were returned to the cabinet and left until they were required for analysis. When removed from the cabinet the samples were quenched in acetone and then stored in acetone to prevent further hydration.

Table 3
w:*c* ratios for the composite cements studied

Cement system	*w*:*s*	*w*:*c*
100% OPC	0.35	0.35
3:1 BFS:OPC	0.35	1.4
9:1 BFS:OPC	0.35	3.5
3:1 PFA:OPC	0.35	1.4

3. Characterisation

3.1. X-ray diffraction

A cement prism was crushed in a percussion mortar and then placed in an agate mortar. An excess of acetone was added (to stop further hydration of the cement and to aid grinding) and the cement was ground by hand to a fine powder of <63 μm. The powder was packed into back-filled sample holders (to minimise preferred orientation) for use in the X-ray diffractometer.

A Philips 1710 X-ray diffractometer using monochromatic CuKα radiation operating at a voltage of 50 kV and current of 30 mA was used. A scanning speed of $2°2\theta/$ min and a step size of 0.02° were used to examine the samples in the range of $5–55°2\theta$.

3.2. Scanning electron microscopy

A cement prism was cut into cubes of approximately 10 mm square, one side of which was ground flat. The samples were then placed in a vacuum desiccator for a minimum of three days. After this time, the sample was cold resin mounted and then ground and polished. The samples were polished manually using diamond paste from 6 through to 0.5 μm. The finished samples were carbon-coated under vacuum to render them conducting for use in the microscope. A JEOL JSM 6400 scanning electron microscope equipped with Link X-ray analytical facilities for quantitative analysis was used. Backscattered electron imaging was used throughout.

4. Results and discussion

4.1. X-Ray diffraction

The development with time of the four cement systems, as indicated by XRD, is shown in Figs. 1–4. They show the X-ray patterns obtained after 3, 28, 90 and 180 days curing, except in the case of the 9:1 BFS:OPC. The products from this system were noticeably weaker than from the other systems, hence the earliest data available are after 7 days.

The XRD patterns indicating the hydration of the control cement (100% OPC) are shown in Fig. 1. The expected crystalline hydration products are clearly evident. Calcium hydroxide was formed in appreciable amounts after only 3 days, and remained as a good crystalline reaction product throughout the period of investigation, although some calcium carbonate was also formed (main peak at $29.4°2\theta$). The relative amounts of calcium hydroxide and calcium carbonate in these XRD patterns can be attributed to carbonation of calcium hydroxide, that occurred due to the samples being cured in air. The amount of unhydrated C_3S decreased with increasing time, as expected. Small, but definite, peaks could be attributed to ettringite, which persisted throughout the period of investigation. No other phases were identified in the XRD patterns.

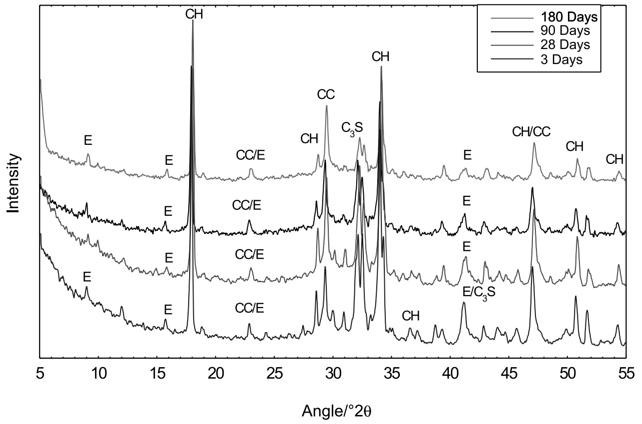

Fig. 1. XRD pattern of the OPC. CH, calcium hydroxide ($Ca(OH)_2$); CC, calcium carbonate ($CaCO_3$); E, ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$); G, gehlenite ($Ca_2Al_2SiO_7$); Q, quartz ($SiO_2$); M, mullite ($3Al_2O_3.2SiO_2$); C_3S, tricalcium silicate (Ca_3SiO_5).

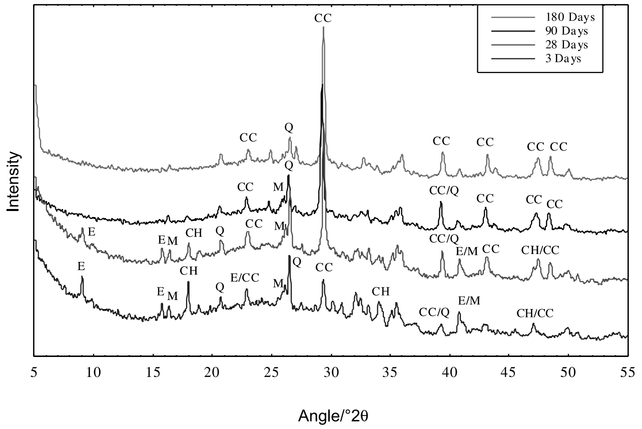

Fig. 2. XRD pattern of the 3:1 PFA:OPC. CH, calcium hydroxide ($Ca(OH)_2$); CC, calcium carbonate ($CaCO_3$); E, ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$); G, gehlenite ($Ca_2Al_2SiO_7$); Q, quartz ($SiO_2$); M, mullite ($3Al_2O_3.2SiO_2$); C_3S, tricalcium silicate (Ca_3SiO_5).

There is a marked difference in the XRD patterns of the 3:1 PFA:OPC composite cement shown in Fig. 2. Calcium hydroxide was formed initially, but in smaller amounts than in the control system, and the amount present decreased with increasing time until the peaks disappeared (between 90 and 180 days). The amount of calcium carbonate present increased substantially after 28 days, and remained high throughout the period of investigation. Ettringite was present after 3 and 28 days

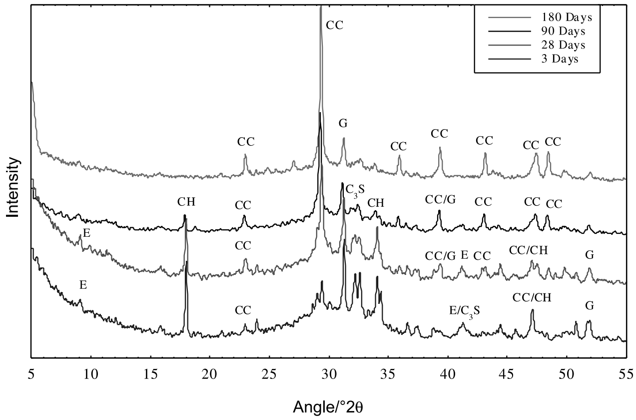

Fig. 3. XRD pattern of the 3:1 BFS:OPC. CH, calcium hydroxide ($Ca(OH)_2$); CC, calcium carbonate ($CaCO_3$); E, ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$); G, gehlenite ($Ca_2Al_2SiO_7$); Q, quartz ($SiO_2$); M, mullite ($3Al_2O_3.2SiO_2$); C_3S, tricalcium silicate (Ca_3SiO_5).

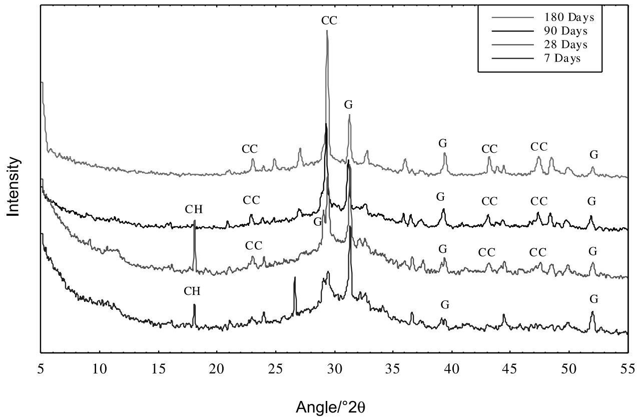

Fig. 4. XRD pattern of the 9:1 BFS:OPC. CH, calcium hydroxide ($Ca(OH)_2$); CC, calcium carbonate ($CaCO_3$); E, ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$); G, gehlenite ($Ca_2Al_2SiO_7$); Q, quartz ($SiO_2$); M, mullite ($3Al_2O_3.2SiO_2$); C_3S, tricalcium silicate (Ca_3SiO_5).

curing, but neither AFt nor AFm phases were evident after 90 and 180 days. The Bogue analysis indicated that the Portland cement contained about 8.3% C_3A, which is reduced to about 2% on dilution with 75% PFA. Hence the peaks attributable to any AFm phase are likely to be very weak, especially if it is poorly crystalline, and perhaps in the form of a solid solution containing both sulfate and carbonate ions. Small amounts of quartz and mullite which were present in the PFA are also evident in the XRD traces shown in Fig. 2. Interestingly, they decreased in intensity with increased curing time.

The X-ray traces for the two slag cements (3:1 and 9:1 BFS:OPC, respectively) are shown in Figs. 3 and 4. The two systems had very similar hydration products, as would be expected. The phases identified were: gehlenite (G), calcium carbonate (CC), calcium hydroxide (CH), ettringite (E) and some unreacted C_3S. Gehlenite was present in the anhydrous slag, therefore, it would be expected that there would be more in the 9:1 BFS:OPC than in the 3:1 BFS:OPC and that, in both systems, the amount present would remain constant or decrease as hydration proceeded. It can be seen to have decreased in both systems, especially in the 3:1 system. The amount of calcium hydroxide present in the slag systems can be seen to vary between the 3:1 and 9:1 BFS:OPC cements. In the 3:1 BFS:OPC system, a substantial amount of calcium hydroxide formed after 3 days, which subsequently decreased up to 90 days hydration, after which time there was no evidence for the presence of calcium hydroxide. In the 9:1 BFS:OPC system (Fig. 4), a small amount of calcium hydroxide had formed after 7 days, which increased between 7 and 28 days hydration. There was, however, no evidence of this phase after 90 days hydration, and its absence was confirmed after 180 days hydration. The amount of calcium carbonate present in both slag systems increased markedly with increasing time. Unreacted alite was more prominent in the 3:1 BFS:OPC system than in the 9:1 system, and decreased with time. No evidence was observed for the formation of a hydrotalcite-like phase, hydrogarnet or stratlingite.

An alternative way of presenting the same data is shown in Figs. 5 and 6. The differences between the four cement systems can be seen after 28 days curing in Fig. 5 (note that the OPC trace is now on top because of the intensity of the CH peaks), and after 180 days curing in Fig. 6. The major difference shown in Fig. 5 is in the amount of calcium hydroxide present. Not surprisingly, the neat OPC system had produced much more CH than the composite cement systems, principally because it contained substantially more Portland cement, and therefore alite, than the other cements, especially the 9:1 BFS:OPC cement that had only 10% Portland cement

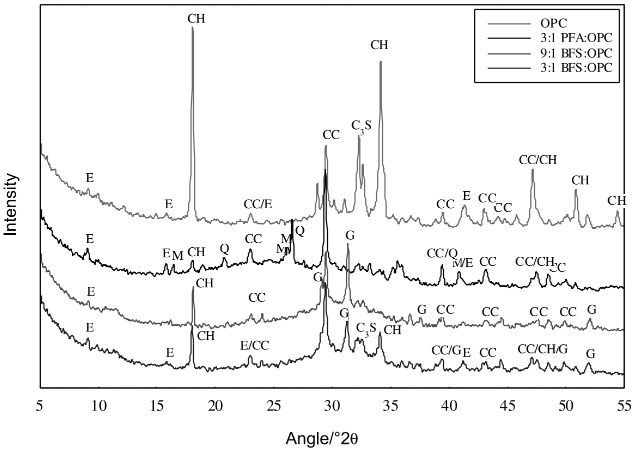

Fig. 5. XRD patterns of the four cements after 28 days hydration.

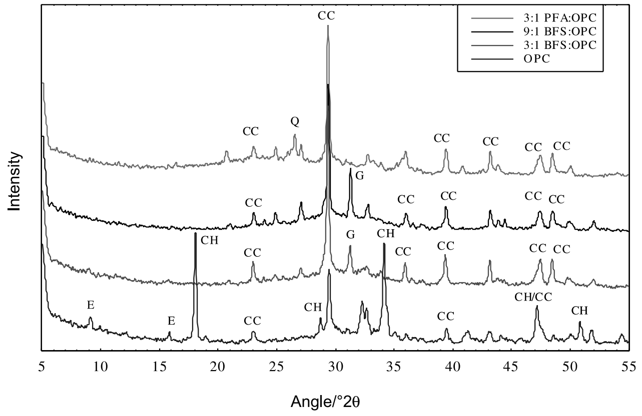

Fig. 6. XRD patterns of the four cements after 180 days hydration.

present. Calcium carbonate was formed in all systems, especially in the 3:1 PFA:OPC cement. Ettringite is apparent in all four cements, while unreacted alite is most noticeable in the neat OPC cement paste. Peaks due to gehlenite, and to mullite and quartz, are evident in the slag and PFA-containing systems, respectively, but not in the other systems.

The XRD patterns of the four cements after curing for 180 days are somewhat simpler, as shown in Fig. 6. Calcium hydroxide is now observed only in the neat OPC cement paste, having disappeared in the composite cements by a combination of carbonation and the pozzolanic reaction (discussed below). All the cements contain calcium carbonate, with especially strong peaks evident in the slag-containing cements. Ettringite was present in the OPC paste, but was not detected in the composite cements. Peaks due to gehlenite and quartz from the original replacement materials are still evident.

4.2. Scanning electron microscopy

Scanning electron micrographs are presented as backscattered electron images (BEI) in Figs. 7, 8, 10 and 11. All samples had been hydrated for 90 days, with the exception of the OPC paste, which is shown in Fig. 7 after 180 days. This sample was selected because the details of the micrograph obtained were clearer, but there were no significant differences between the microstructures observed after 90 and 180 days curing. The relatively low magnification SEM shown in Fig. 7 indicates a comparatively dense microstructure, typical of a sound Portland cement paste. Some anhydrous particles are surrounded by rims of inner hydration products (IP), while outer hydration products (OP) have also been formed.

The microstructure of the composite cement based on 3:1 PFA:OPC, shown in Fig. 8, is dominated by the PFA particles which are spherical (such as that marked A). These hollow spheres are known as cenospheres. Local concentrations of hydrating cement (B) indicated the continuing presence of anhydrous material, but with hydration products forming a rim around the outside. Outer hydration products have started to act as a matrix binding together the PFA cenospheres, but the microstructure is much more porous than that shown in Fig. 7. The EDS trace shown in Fig. 9 shows that the PFA grain contains silicon, aluminium, potassium and iron, with lesser amounts of calcium and titanium. Micrographs of fly ash cements showing similar observations to those reported above have been published [5–8].

Back-scattered electron images of the BFS:OPC composite cements are shown in Figs. 10 and 11, after hydration for 90 days. The angular grains of BFS stand

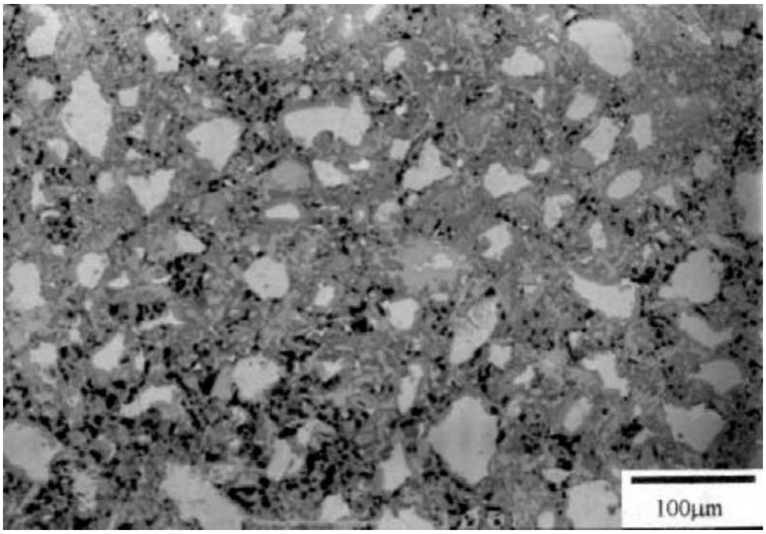

Fig. 7. Backscattered electron image of the OPC hydrated for 90 days.

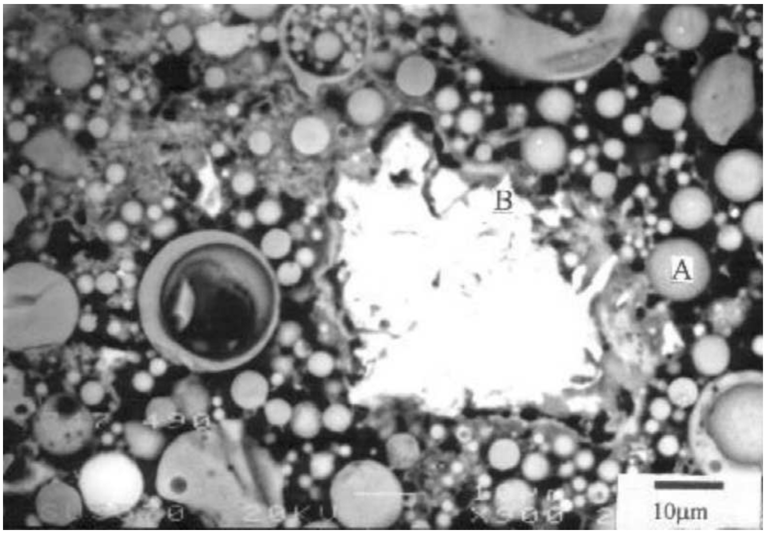

Fig. 8. Backscattered electron image of the of the 3:1 PFA:OPC cement hydrated for 90 days.

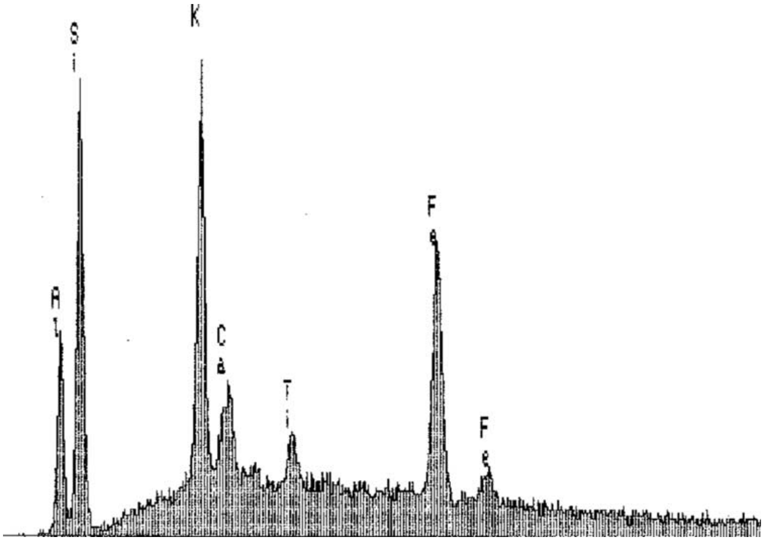

Fig. 9. EDS trace of a PFA particle.

out in stark contrast to the spherical grains of PFA shown in Fig. 8. In the 3:1 composite cement, it can be seen from Fig. 10 that a thin rim had formed around some of the slag grains, while the cement fraction had hydrated (e.g. region A). As in the PFA-containing system, the hydrated cement gel was building up a matrix between the slag particles, hence reducing the porosity. The micrograph of the 9:1 BFS:OPC composite cement is shown in Fig. 11 at the same magnification as in Fig. 10 to allow direct comparison. Although at first glance the microstructures may appear similar because they are dominated by the angular slag grains, there are notable differences. The 9:1 system (Fig. 11) contains more slag grains of larger size, whereas the grains in the 3:1 system seem to have been more extensively broken down. The cement hydration products seemed to be quite localised in the 9:1 system, leading to the very porous microstructure observed in Fig. 11. The slag grains did not show any rims, but instead many of them were surrounded by a gap. In some respects, this microstructure is reminiscent of that reported recently by Escalante-Garcia and Sharp [9] in a BFS–OPC composite cement paste with 60% replacement cured at 10°C. This microstructure was notably different from that developed in the same cement paste hydrated at 30°C and 60°C, when extensive rims of hydration products were observed around the anhydrous slag grains.

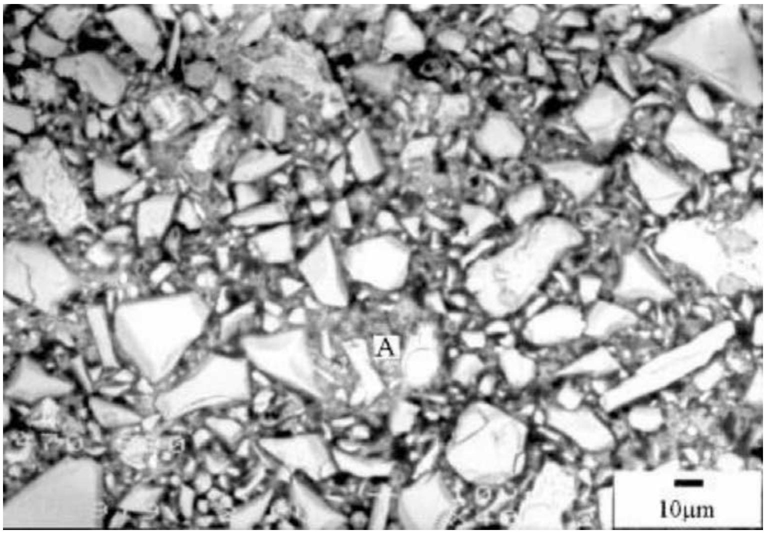

Fig. 10. Backscattered electron image of the 3:1 BFS:OPC cement hydrated for 90 days.

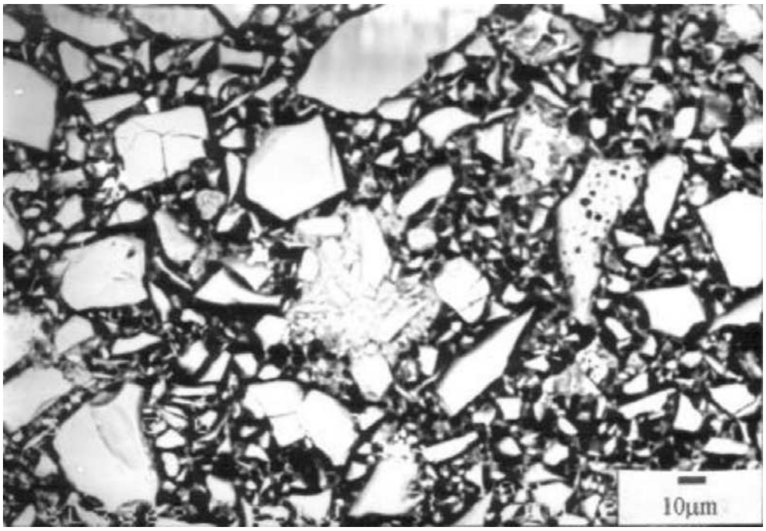

Fig. 11. Backscattered electron image of the 9:1 BFS:OPC cement hydrated for 90 days.

5. Further discussion

Significant differences have been observed in both the mineralogy and microstructure of the four cements, although the two BFS-containing composite cements were similar in most respects, which is hardly surprising since they both contained very high levels of replacement material, 75% and 90%. A detailed account of these differences has been given above, but the most significant of these, the relative amounts of calcium hydroxide formed, is worthy of further discussion.

The control cement behaved as would have been predicted from the literature. Substantial amounts of calcium hydroxide were formed initially and remained throughout the period of investigation. Some of the calcium hydroxide was converted into calcium carbonate through atmospheric carbonation, because the sample was air cured. Similarly, the PFA:OPC composite cement behaved as expected for a composite cement containing a pozzolanic replacement material. Some calcium hydroxide was formed initially, but it was never present in anything like the amount formed in the neat OPC paste after only 3 days curing. This calcium hydroxide was rapidly consumed by the combined effects of the pozzolanic reaction and carbonation, until only a trace of it remained after 90 days and it was below the level observable by XRD after 180 days.

Blast furnace slag is generally regarded as a very different replacement material from PFA, because it is a latent hydraulic material whereas PFA is pozzolanic. This means that in the presence of an alkali activator, such as calcium hydroxide formed during the hydration of alite in OPC, the slag grains themselves hydrate to form additional C–S–H gel. The calcium content of BFS is, however, less than that in the C–S–H gel commonly formed in hydrated Portland cement pastes, so that at the high replacement levels used in the present study, it too acts as a pozzolanic material. This is clearly evident from the XRD traces shown in Figs. 3 and 4 for the 3:1 and 9:1 BFS:OPC composite cement pastes, respectively. In the 3:1 paste, the calcium hydroxide formed after 3 days was gradually consumed, until no trace of it remained after 180 days. Qualitatively its behaviour was, therefore, very similar to that of the 3:1 PFA:OPC paste, but quantitatively more calcium hydroxide was formed in the BFS system, indicating that the PFA was a stronger pozzolanic material. In both these 3:1 systems, the increasing extent of the pozzolanic reaction with increasing time resulted in a denser microstructure, although not as dense as that observed in the control system. The occurrence of a pozzolanic reaction with slag replacement has been documented previously [10–13].

The amount of calcium hydroxide formed initially in the 9:1 BFS:OPC composite cement paste was less than that formed in the 3:1 cement paste, because it contained appreciably less OPC (10% compared with 25%). After 28 days, however, the magnitude of the strongest calcium hydroxide XRD peak at $18.1°2\theta$ in the 9:1 cement paste was comparable with that in the 3:1 cement paste, although the second peak at $34.1°2\theta$, which is less vulnerable to preferred orientation, was much weaker. This calcium hydroxide was then rapidly consumed, so much so that none was observed after hydration for either 90 or 180 days. The pozzolanic reaction and carbonation probably both contributed. The end result may have been that the alkali activation was so much reduced that little slag hydration occurred, hence the lack of visible rims around the slag particles in Fig. 11. The gaps around the particles may be due to the removal of calcium ions to participate in the pozzolanic reaction, although this is at present a speculative suggestion.

6. Conclusions

This study has demonstrated that sound cement pastes, with potential application as useful grouts, can be obtained from cementitious systems including 75% and even 90% replacement of OPC by BFS and PFA. Although the compressive strength is much reduced, in applications where this is unimportant, other properties may be advantageous, e.g. low heat evolution and low level of CH. The 9:1 BFS:OPC cement paste was the weakest of those investigated, and took longer to set than the other pastes. It had a high level of porosity, as was evident from the scanning electron micrographs (e.g. Fig. 11).

The hydration products formed in the four systems studied were as expected, although they differed in magnitude. Calcium hydroxide was formed initially in all systems, but in the presence of large amounts of PFA and BFS, it did not become such a major reaction product as in the OPC system (Fig. 5), and had disappeared from all three composite cement systems after hydration for 180 days (Fig. 6). Hence, at such high replacement levels, BFS acts as a pozzolanic material as well as PFA. The disappearance of calcium hydroxide from the three composite cements was in the sequence: 3:1 PFA:OPC sooner than 9:1 BFS:OPC, sooner than 3:1 BFS:OPC, which correlates with the lime content of these systems.

Acknowledgements

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