Pergamon

Cement and Concrete Research 32 (2002) 1813–1821

CEMENT AND CONCRETE RESEARCH

Sorptivity and strength of air-cured and water-cured PC–PFA–MK concrete and the influence of binder composition on carbonation depth

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Received 29 June 2001; accepted 20 May 2002

Abstract

The paper reports the influence of the composition of Portland cement–pulverised fuel ash–metakaolin (PC–PFA–MK) binders on sorptivity and strength development of PC–PFA–MK concrete cured both in air and in water and on carbonation depth, and relates this to measured changes in sorptivity of the concrete. Concrete mixtures covering four different total cement replacement levels (10%, 20%, 30% and 40%) for PC–PFA–MK concrete with various MK/PFA proportions, water and air cured for up to 18 months, were investigated. The change in compressive strength and sorptivity with age at all cement replacement levels under both water and air curing are compared with those of the control PC concrete. The results presented in this paper form part of an investigation into the optimisation of a ternary blended cementitious system based on ordinary PC, PFA and MK for the development of high-performance concrete.

Keywords: Sorptivity; Compressive strength; Metakaolin; Fly ash; Curing

1. Introduction

Bai et al. [1] have demonstrated that judicious use of Portland cement–pulverised fuel ash–metakaolin (PC–PFA–MK) blends in concrete enables a much reduced PC requirement whilst still maintaining or enhancing strength in the medium to long term. MK is known to increase pore refinement [2] and enhance strength [1] at relatively early ages, and its incorporation in concrete containing PFA might therefore be expected to produce a marked reduction in sorptivity or capillary water suction, in addition to enhancing strength. A relationship between strength and sorptivity has been demonstrated by Gopolan [3] for fly ash concrete. Gopolan reported that for concrete of a particular composition cured under given conditions, strength varies in a linear manner with sorptivity. Minimising sorptivity is important in order to reduce the ingress of chloride-containing or sulphate-containing water into concrete, which can cause serious damage [4].

Condensed silica fume (CSF), an ultrafine, highly active pozzolan similar to MK, has been shown, under normal curing environments, to both increase strength and reduce sorptivity. At early ages (1 day) Durekovic [5] observed a marked decrease in capillary water suction with increase in CSF content for water-cured PC–CSF pastes. In contrast, some pozzolans have the opposite effect on sorptivity. For example, Sabir et al. [6] found that in water-cured mortar in which the PC was partially replaced by ground clay brick (GB), the sorptivity increased with increase in GB content. However, at long curing periods, sorptivity values tended to approach or drop below that of the control PC mortar. Curing environment has a significant influence on sorptivity development. For example, Gopalan [3] reported that the sorptivity of air-cured PFA concrete, cured for 28, 90 and 180 days, increases with increase in PFA content, but if the concrete is ‘fog’ cured, the sorptivity tends to decrease with increase in PFA content. Kelham [7] also demonstrated, for PC, PC–PFA and PC–GGBS concrete, that replacement of PC with 25% PFA or with 60% GGBS produces substantially lower sorptivity relative to the PC control concrete in water-cured samples but higher sorptivity relative to the control concrete in air-cured samples. In addition, water-cured samples give

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PII: S0008-8846(02)00872-4

Table 1
Composition of PC, PFA and MK

Oxide	PC (%)[a]	PFA (%)[b]	MK (%)[c]
SiO_2	21.0	49.8	52.1
Al_2O_3	4.63	26.4	41.0
Fe_2O_3	2.26	9.3	4.32
CaO	65.6	1.4	0.07
MgO	1.18	1.4	0.19
SO_3	–	0.8	–
Na_2O	0.16	1.5	0.26
K_2O	0.78	3.5	0.63
TiO_2	–	1.0	0.81
Cl	0.01	0.01	–
LOI	0.99	4.9	0.6

[a] Data supplied by Rugby Cement.
[b] Data supplied by Ash Resources.
[c] Data supplied by Imerys (formerly ECC International).

generally lower sorptivity than equivalent concrete that has been air cured.

Sorptivity is also strongly influenced by sample location within the concrete. Khatib and Mangat [8] have shown that sorptivity values determined on concrete taken from the top surface of a concrete cube can be several times greater than those for concrete taken from the bottom surface of the cube. The concrete cubes were air cured at different temperatures and relative humidities. In addition, carbonation influences sorptivity. Dias [9] observed that air-cured concrete, over a 4-year period, undergoes an increase in weight and a reduction in sorptivity as a result of carbonation of the surface zone. Also, the greater the initial (6 months) sorptivity, the greater is the reduction in sorptivity (at 4 years) due to carbonation. Equivalent water-cured concrete does not show any drop in sorptivity from carbonation, although sorptivity does decrease with time as a result of continued hydration. Carbonation is itself also modified by partial cement replacement. Papadakis [10] has demonstrated, for mortars containing various amounts of fly ash and silica fume as partial cement replacements, that carbonation depth increases with increase in pozzolan content. The more rapid carbonation of mortars made with blended cements is accounted for by the reduced total amount of CaO in the system available for carbonation.

In addition to the factors described above that influence sorptivity, sample preparation also has a significant effect on sorptivity [4]. Thus, conditioning samples in a standard manner prior to testing is essential in order to obtain consistent and meaningful results. The effect of conditioning samples using the common method of oven drying at 105 °C [3,7,8] can cause microcracking, will remove any internal moisture gradient (typical of normal concrete in the field) and will result in artificially high sorptivity values, which will be further enhanced by any microcracking [4]. Hence, other workers [6,11] have used a more 'gentle' method of conditioning by drying to constant weight at 40 °C, which gives lower sorptivity values.

The current paper reports the influence of the composition of PC–PFA–MK binders on the strength development of PC–PFA–MK concrete cured both in air and in water and on carbonation, and relates this to measured changes in sorptivity of the concrete.

2. Experimental details

2.1. Materials and mixtures

PC complying with BS 12 [12] was used throughout the investigation. Ash Resources supplied the PFA, and the MK was supplied by Imerys (formerly ECC International). The compositions of the three binder constituents are given in Table 1. Natural sea dredged sand of grading M-F complying with BS 882 [13] was used throughout the investigation. The coarse aggregates employed were 10 and 20 mm crushed limestone.

Eleven mixes, with a binder (PC–PFA–MK) content of 390 kg/m^3, water-to-binder (w/b) ratio of 0.5 and a wide range of MK–PFA combinations, were investigated. In addition to PC only (control) mixtures, total cement replacement levels (MK and PFA) of 10%, 20%, 30% and 40% by mass were employed. From cost-effectiveness considerations, the proportion of MK did not exceed that of PFA, other than for the lowest cement replacement level (10%). Workabilities were in the range 35–130 mm. The compositions of the binder components and mixture details for the concretes in this study are given in Table 2.

2.2. Specimen preparation and curing

The sampling was carried out in accordance with BS 1881-108 [14]. Each 100-mm cube mould was filled with concrete, vibrated to give good compaction and covered with cling film for 24 h to preserve the initial moisture condition of the sample. The samples were demoulded and

Table 2
Mix proportions, w/b = 0.5

Percentage			Mix proportions, kg/m^3					
PC	PFA	MK	PC	PFA	MK	Sand	10-mm Aggregate	20-mm Aggregate
100	0	0	390.00	0.00	0.00	755.0	335.6	783.0
90	10	0	351.00	39.00	0.00	750.3	333.5	778.1
	7.5	2.5	351.00	29.25	9.75	750.6	333.6	778.3
	5	5	351.00	19.50	19.50	750.9	333.7	778.6
	2.5	7.5	351.00	9.75	29.25	751.1	333.8	778.9
80	15	5	312.00	58.50	19.50	746.1	331.6	773.7
70	30	0	273.00	117.00	0.00	740.8	329.2	768.2
	27.5	2.5	273.00	107.25	9.75	741.1	329.4	768.5
	25	5	273.00	97.50	19.50	741.4	329.5	768.8
	22.5	7.5	273.00	87.75	29.25	741.6	329.6	769.1
60	30	10	234.00	117.00	39.00	737.2	327.6	764.4

Mass of water = 195 kg/m^3.

cured under two curing environments either water curing (up to 18 months at 20 ± 2 °C) or air curing (1-day water curing followed by air curing for up to 18 months at ambient temperature of 20 ± 2 °C and 55 ± 5% relative humidity). Note that time zero is taken from demoulding. The cubes used for producing sorptivity test specimens were coated with Poxtar F on four adjacent faces including the top trowelled face, leaving two opposite uncoated side faces exposed to either water or air. The sorptivity specimens comprised 75mm-diameter × 30mm-thick discs dry-cut from the surface portions of cylindrical cores, obtained from coring along the line joining the centres of the two uncoated surfaces of the concrete cubes (see Fig. 1). One specimen was used from each core, and the rest of the core was discarded. The concrete discs were dried to constant weight in a drying cabinet containing silica gel with a controlled constant temperature of 40 ± 2 °C. The total drying times of the various specimens varied with the composition of the concrete and its curing history and ranged between 25 and 30 days. This sample drying method was chosen as it is considered to minimise any modification to the capillary pore structure that would be caused by a higher temperature and more rapid drying.

2.3. Test procedures

Strength and sorptivity tests were carried out at each of the water and air curing times of 28 days, 2, 4, 10 and 18 months. The compressive strength values were determined from the average of three cube tests carried out in accordance with BS 1881-116 [15].

The sorptivity test method adopted (see Fig. 2) was, with minor modifications (i.e. for easier horizontal alignment of the specimens the rigid copper wire support was replaced by a brass chain), the same as that developed in Ref. [6]. The test allows automatic monitoring of the water uptake experienced by the concrete disc specimen when its lower surface is in contact with water in a reservoir. The light aluminium holder has a 75-mm-diameter central hole, facilitating contact of the concrete disc test surface with the water, and a computer automatically records weight gain by the test specimen at specified intervals (every minute in the current work). Because of small initial surface tension and buoyancy effects, the relationship between cumulative water absorption i (g/mm^2) and the square root of exposure time ($t^{0.5}$) shows deviation from linearity during the first few minutes. Also, after long periods, the curves again deviate from linearity as the specimens approach saturation. Thus, for the i versus $t^{0.5}$ curves, only the section of the curves for the exposure period from 9 to 36 min, where the curves were consistently linear, was used for the calculation of sorptivity (see Fig. 3).

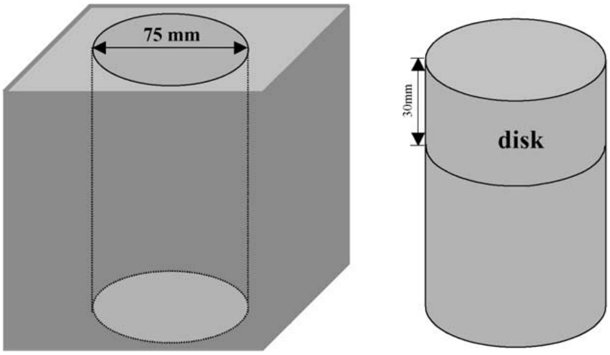

Fig. 1. Sample discs for sorptivity measurement.

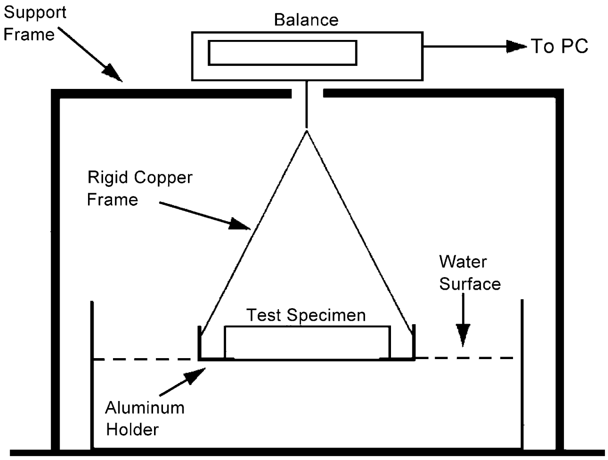

Fig. 2. Sorptivity test apparatus [6].

Cube specimens for carbonation measurement were initially air cured in the same manner as the air-cured sorptivity specimens. However, after 12 months, it was apparent that carbonation levels were extremely small for all the concretes. Therefore, the cubes were transferred to a 'carbonation chamber' where they were exposed to a CO_2 rich atmosphere (96% air–4% CO_2) at 20 °C and 65% relative humidity (controlled by an NaCl/water mixture). The cubes spent a further 6 months in the latter environment prior to the carbonation depth being measured in accordance with RILEM recommendations [16].

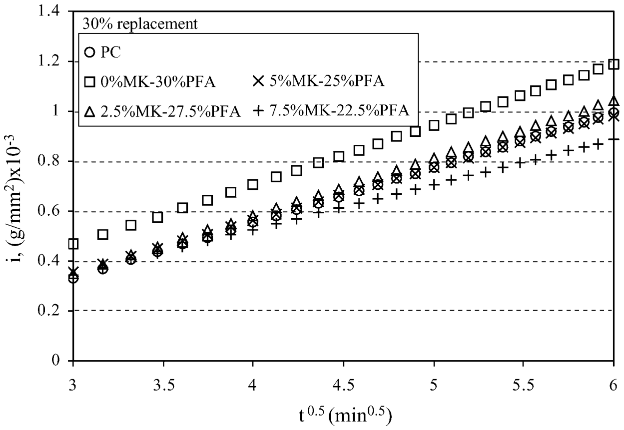

Fig. 3. Typical plots of i versus $t^{0.5}$ for PC-PFA-MK concrete at 28 days.

3. Results and discussion

Fig. 4 shows the change in compressive strength with age at four different total cement replacement levels (10, 20, 30 and 40%) for PC–PFA–MK concrete with various MK/PFA proportions, water cured for up to 18 months. In each case, strengths are compared with the control PC concrete and the equivalent PC–PFA concrete. MK enhances substantially the early (28 days) strength, whereas PFA retards early strength. The degree of early strength enhancement (due to MK) or retardation (due to PFA) is in direct relation to the amount of MK of PFA present. At long curing periods (18 months), both MK and PFA enhance strength and the difference in strengths achieved with the different blends at 10% and 30% replacement (Fig. 4a and c) is relatively small. In fact, the PC–PFA blend concrete performs as well or slightly better than the PC–PFA–MK blends concrete. Thus, the effect that increasing MK content has on the strength versus time profiles of PC–PFA–MK concrete is to increase early strength and subsequently reduce the gradient of the strength versus time curve. The degree of strength enhancement over and above that of the PC control concrete reduces with increasing total replacement level, and at 40% replacement (10% MK, 30% PFA), the strength of the concrete is slightly below that of the control at all curing periods (28 days–18 months). It is suggested that at these very high replacement levels, the amount of calcium hydroxide (CH) available is too small to provide sufficient pozzolanic reaction to compensate for the large PC deficiency.

Air-cured concrete (Fig. 5) shows overall strength reduction relative to that which is water cured. Early strengths (28 days) of air-cured concrete (Fig. 5) are significantly below those of water-cured concrete (Fig. 4), and the continued retardation in strength development leads to substantially lower strengths after 18 months. This is especially apparent at 30% replacement (Figs. 4c and 5c) where strength reductions are between 15% (control) and 25% (70% PC–30% PFA). The reduction in strength at 18 months is particularly large for concrete with binary PC–PFA binder (compare (Figs. 4a with 5a, and Figs. 4c with 5c)).

Fig. 6 compares the strength of the air-cured and water-cured concrete. At both 10% and 30% total replacement (Fig. 6b and c, and d and e), the advantages, at early ages (28 days), of employing PC–PFA–MK blends instead of PC–PFA blends, are clearly apparent, irrespective of the type of curing. At 18 months, although with 10% replacement, the PC–PFA concrete performs better than the PC–PFA–MK concrete when water cured, the latter performs significantly better than the former when air cured (Fig. 6b and c). The PC–PFA–MK ternary blend concrete also performs better than the PC–PFA concrete at 30% replacement when air cured, whereas when water cured, the

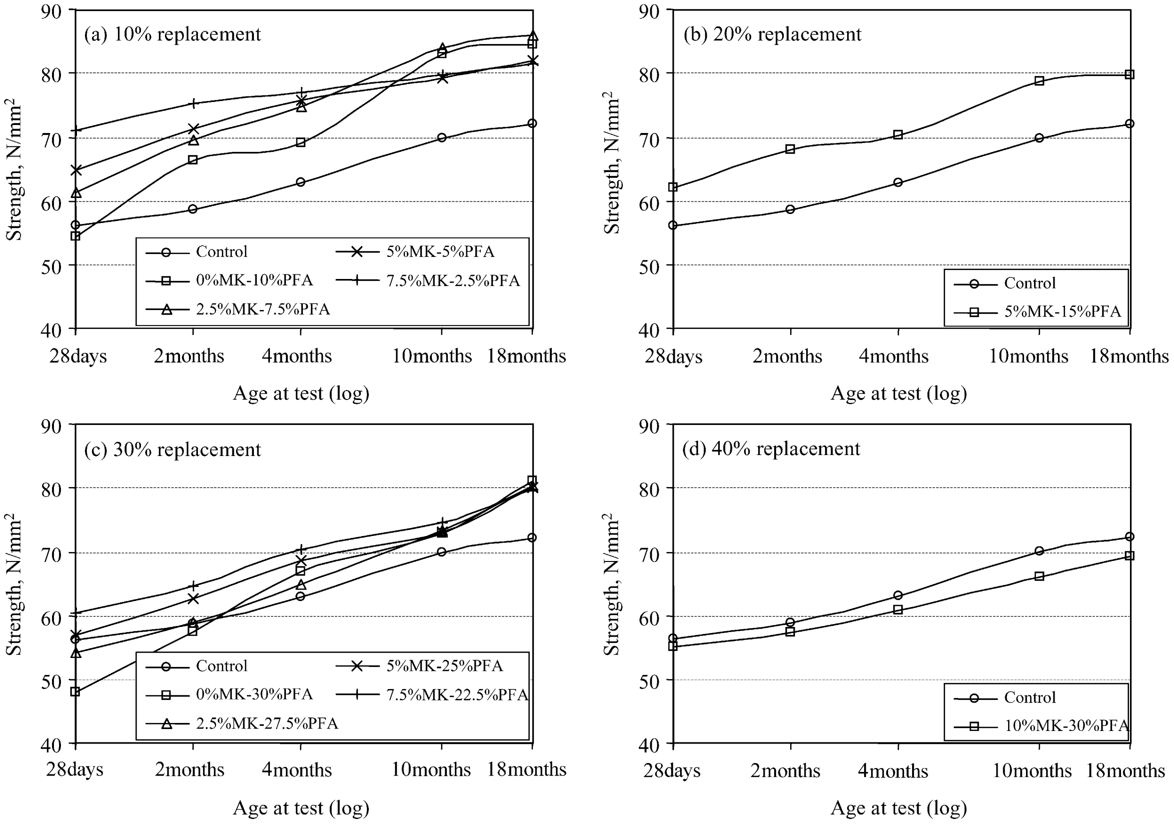

Fig. 4. Compressive strength with age at 10%, 20%, 30% and 40% cement replacements for water cured concrete.

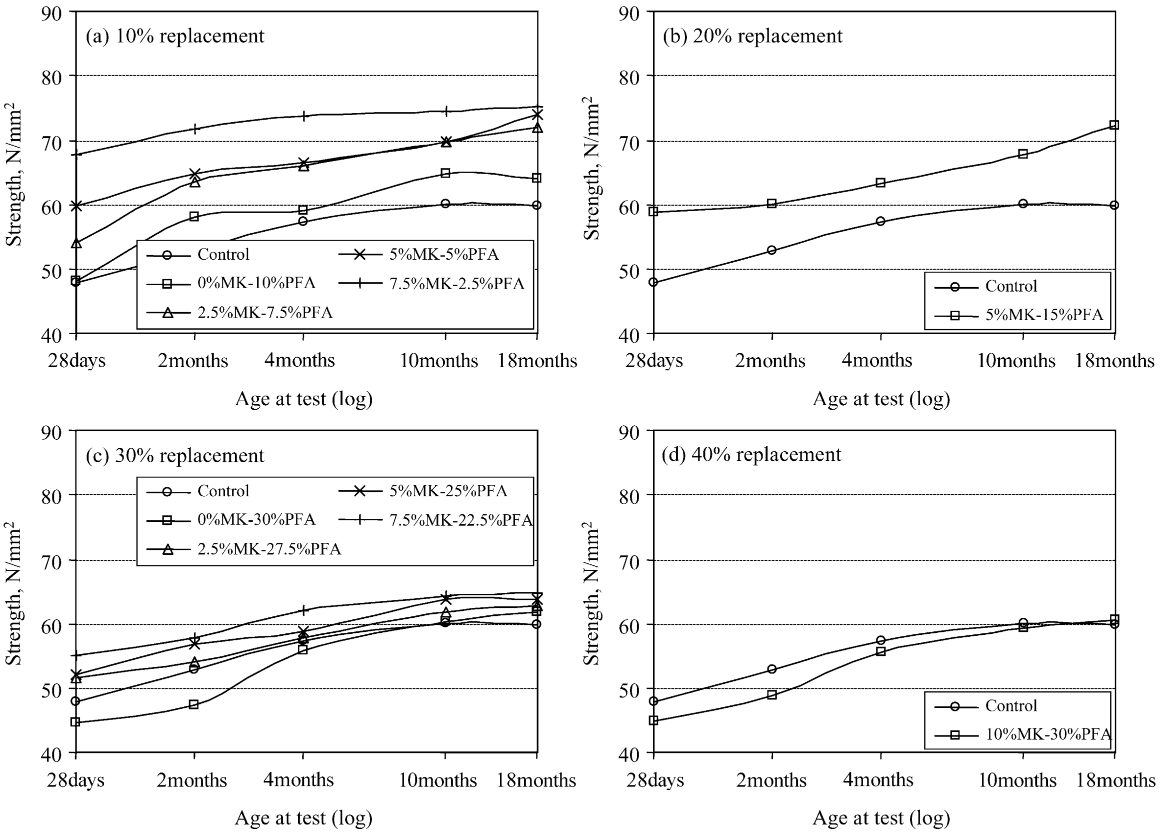

Fig. 5. Compressive strength with age at 10%, 20%, 30% and 40% cement replacements for air-cured concrete.

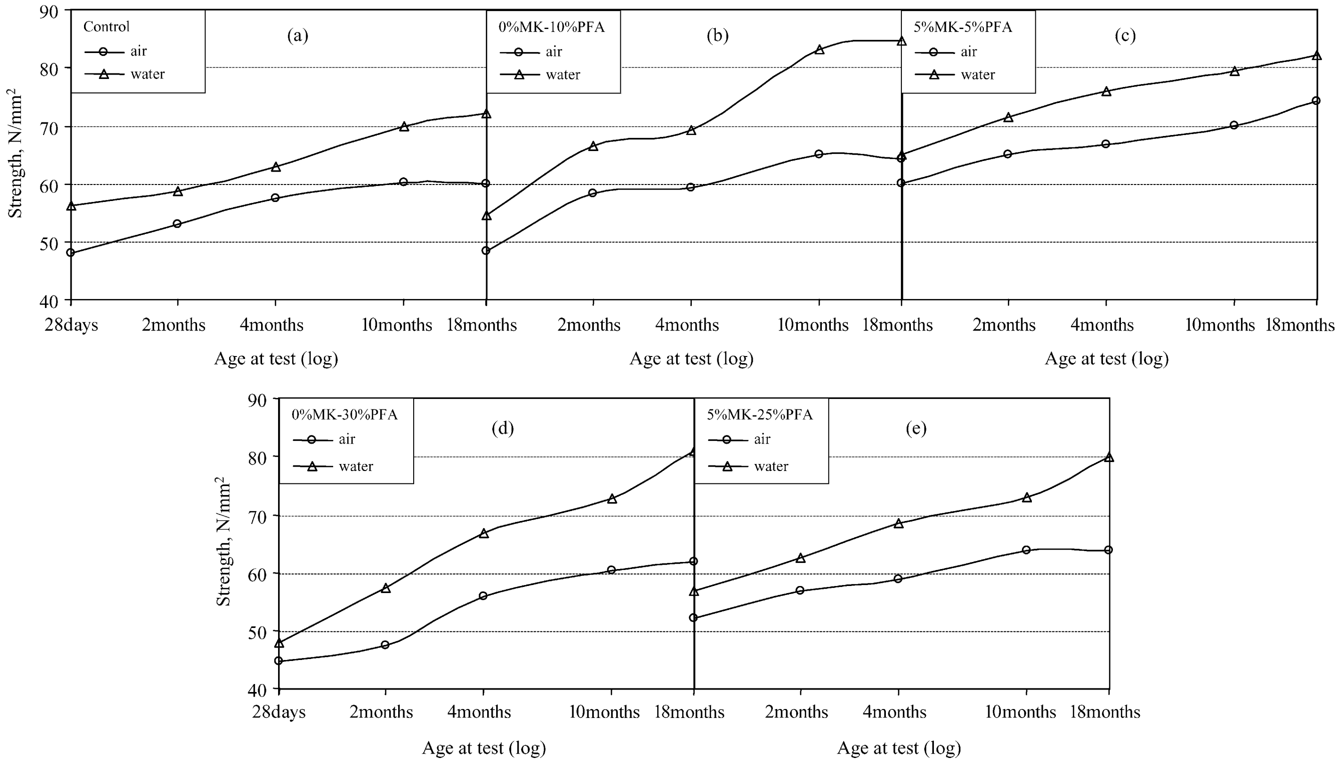

Fig. 6. Strength of air-cured and water-cured PC–PFA–MK concrete.

performance of the binary and ternary blend concretes are similar (Fig. 6d and e).

The change in sorptivity with age of the water-cured MK–PFA and PC–PFA–MK concrete for all cement replacement levels (10%, 20%, 30% and 40%) cured up to 18 months is given in Fig. 7. In each case, sorptivities are compared with those of the control PC concrete. It is apparent that sorptivity decreases systematically with an increase in curing period, and the gradients of the sorptivity versus age curves tend to decrease with increase in MK content (Fig. 7a and c).

At early ages (28 days), the relative sorptivity values are clearly reflected in the strength values (Figs. 4a and c, and 7a and c). Thus, the water-cured concretes with the highest sorptivities have the lowest strengths (i.e. the PC–PFA blend), and the concretes with the lowest sorptivities have the highest strengths (i.e. the PC–PFA–MK blends with the highest MK content). However, concrete with 40% cement replacement, deviates from this pattern in that the water-cured control concrete (Fig. 4d) gives both strength values and sorptivity values consistently above those for the water-cured 10% MK–30% PFA concrete. This may be due to the influence of particle packing on the initial capillary pore structure that develops, in that a wide distribution of binder particle sizes in the 60% PC–30% PFA–10% MK binder will result in denser packing than in the PC binder and hence reduced sorptivity. In contrast, the reduced availability of CH, due to the high cement replacement level, will limit the extent of pozzolanic activity and cementation and will limit strength gain. Increasing the MK content reduces the 28-day sorptivity of the concrete to values below that of the control, whereas the sorptivity values of the PC–PFA concrete exceed those of the control (Fig. 7a and c). This shows the value of using a ternary PC–PFA–MK blend rather than a binary PC–PFA blend. This reduced sorptivity reflects a finer pore structure that will, for example, inhibit ingress of aggressive elements into the pore system.

Air-cured concrete (fig. 8) exhibits generally higher sorptivity than that of water-cured concrete (Fig. 7), which might be expected due to the reduced level of hydration in the surface layers of the air-cured concrete. This difference in sorptivity is substantial for both the control and the PC–PFA concrete and reduces systematically as the PFA is

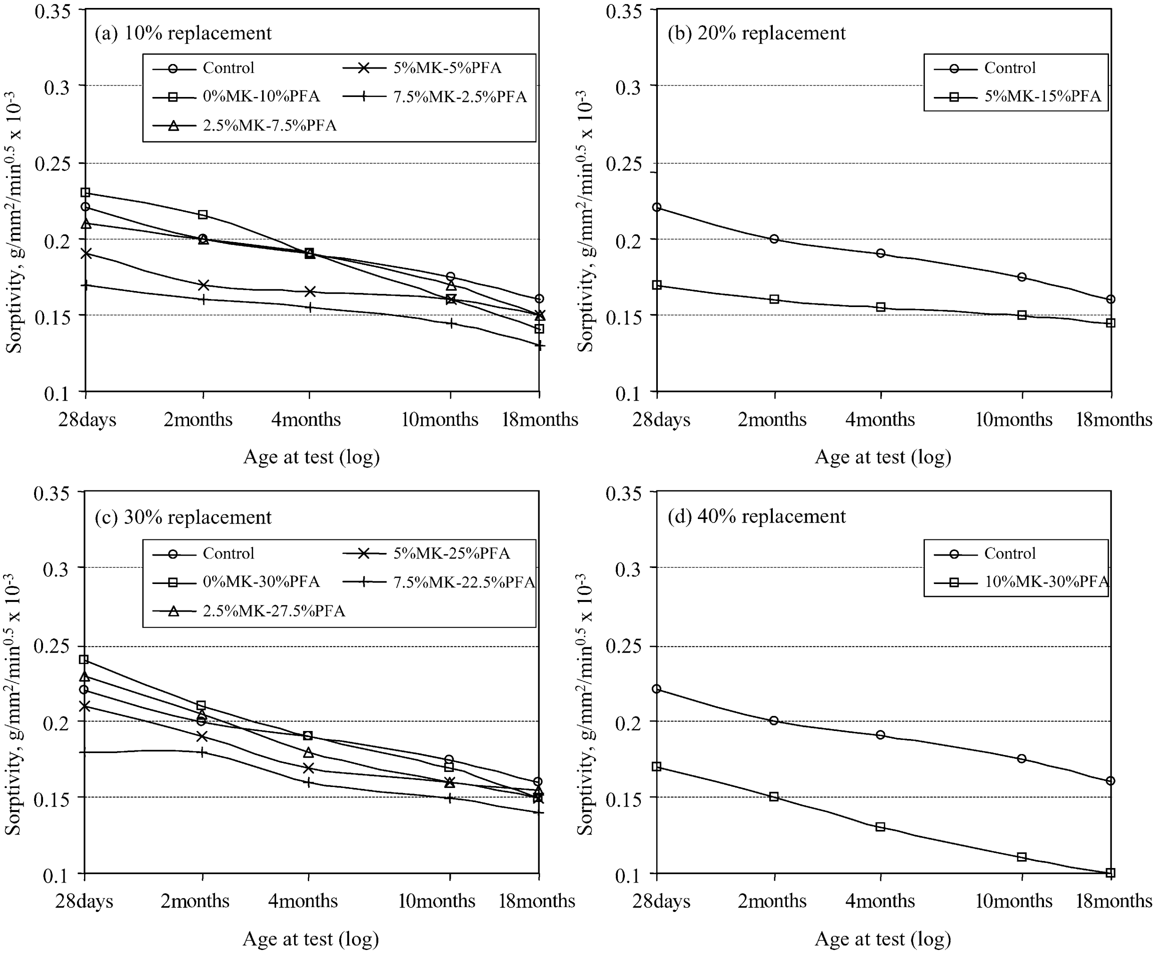

Fig. 7. Sorptivity with age at 10%, 20%, 30% and 40% cement replacements for water-cured concrete.

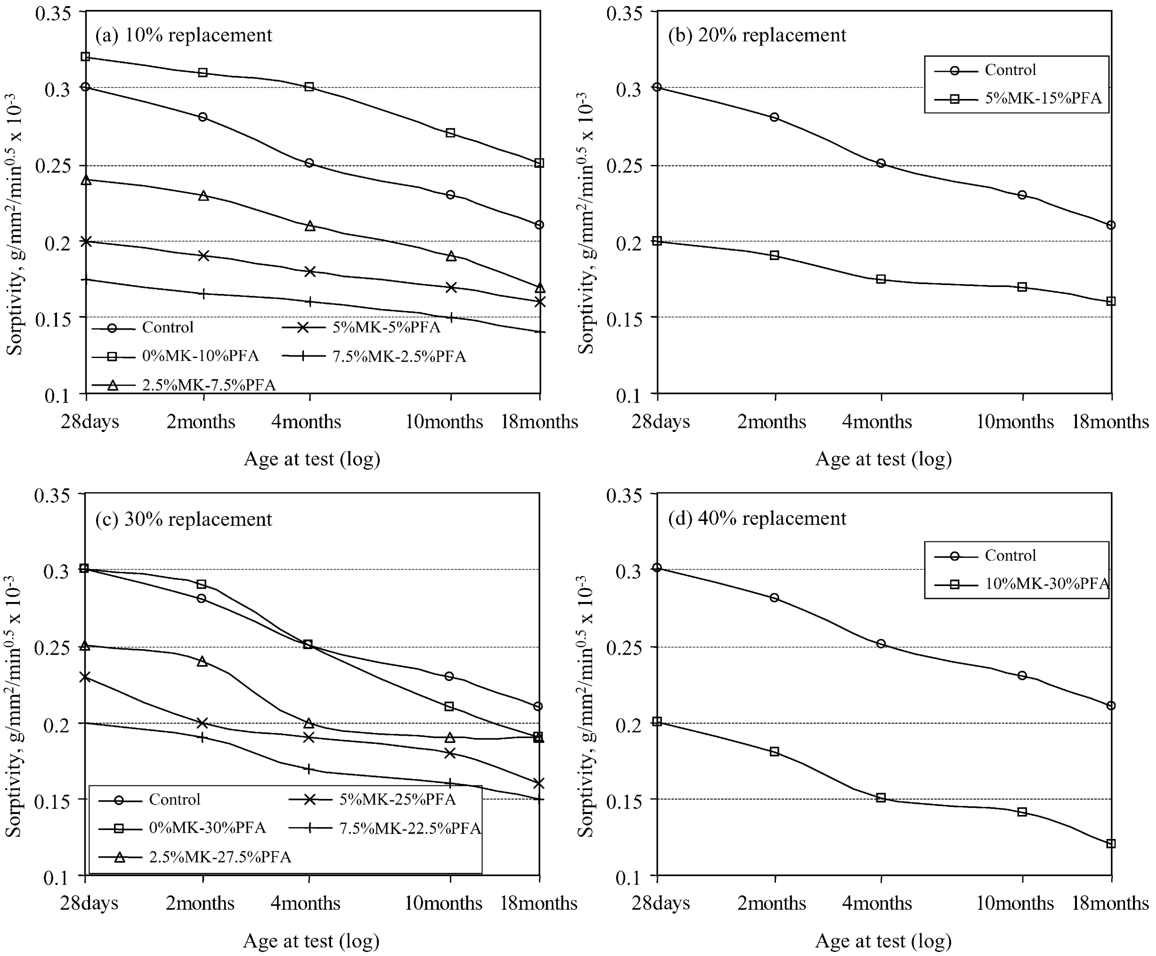

Fig. 8. Sorptivity with age at 10%, 20%, 30% and 40% cement replacements for air cured concrete.

replaced with MK, such that both water- and air-cured concrete containing 7.5% MK (Figs. 7a and c, and 8a and c) show similar sorptivities. It is suggested that this is a result of the much finer pore structure of the paste in concrete that contains MK, which will reduce surface evaporation of water in air-cured concrete and allow hydration to proceed uninhibited.

A comparison of air-cured and water-cured concrete sorptivity with age for the control, 10% replacement (0MK–10PFA, 5MK–5PFA) concrete and 30% replacement (0MK–30PFA, 5MK–25PFA) concrete is given in Fig. 9. The advantage of blending PFA with MK to reduce sorptivity of air-cured concrete is apparent by comparison of Fig. 9b with c, and d with e. For water-cured concrete, the advantages are mainly at young ages, and there are very minor differences in sorptivity at extended ages.

The carbonation depths for PC–PFA–MK concrete (PC replacement levels 0%, 10%, 20%, 30% and 40%) exposed to normal air (0.035% CO_2, 20 °C, 55% relative humidity) for 12 months and CO_2-rich air (4% CO_2, 20 °C, 65% relative humidity) for 6 months are shown in Fig. 10. The two principal trends apparent are (i) increasing replacement of PC with PFA increases carbonation depth and (ii) systematically substituting the PFA with increasing levels of MK reduces carbonation depth. There is also a strong correlation between carbonation depth and sorptivity. For example, at 10% replacement of PC with PFA–MK blends, concrete carbonation depth decreases in the order 90% PC–10% PFA, 100% PC–control, 90% PC–7.5% PFA–2.5% MK, 90% PC–5% PFA–5% MK 90% PC–2.5% PFA–7.5% MK, which is exactly the order in which the sorptivities of these concretes decrease (Fig. 8a). For 30% replacement of PC with PC–MK blends, increasing substitution of PFA with MK again leads to decreasing carbonation depth and corresponds with decreasing sorptivity. However, the carbonation depths for the concretes containing the blended binders are substantially greater than that for the control concrete (other than for the concrete with the highest MK content), whereas the sorptivities of these concretes are substantially below that for the control concrete. This increased carbonation depth and decreased sorptivity relative to the control at high PC replacement levels is attributed to a much reduced CH content in the blended binder concretes as a result of the

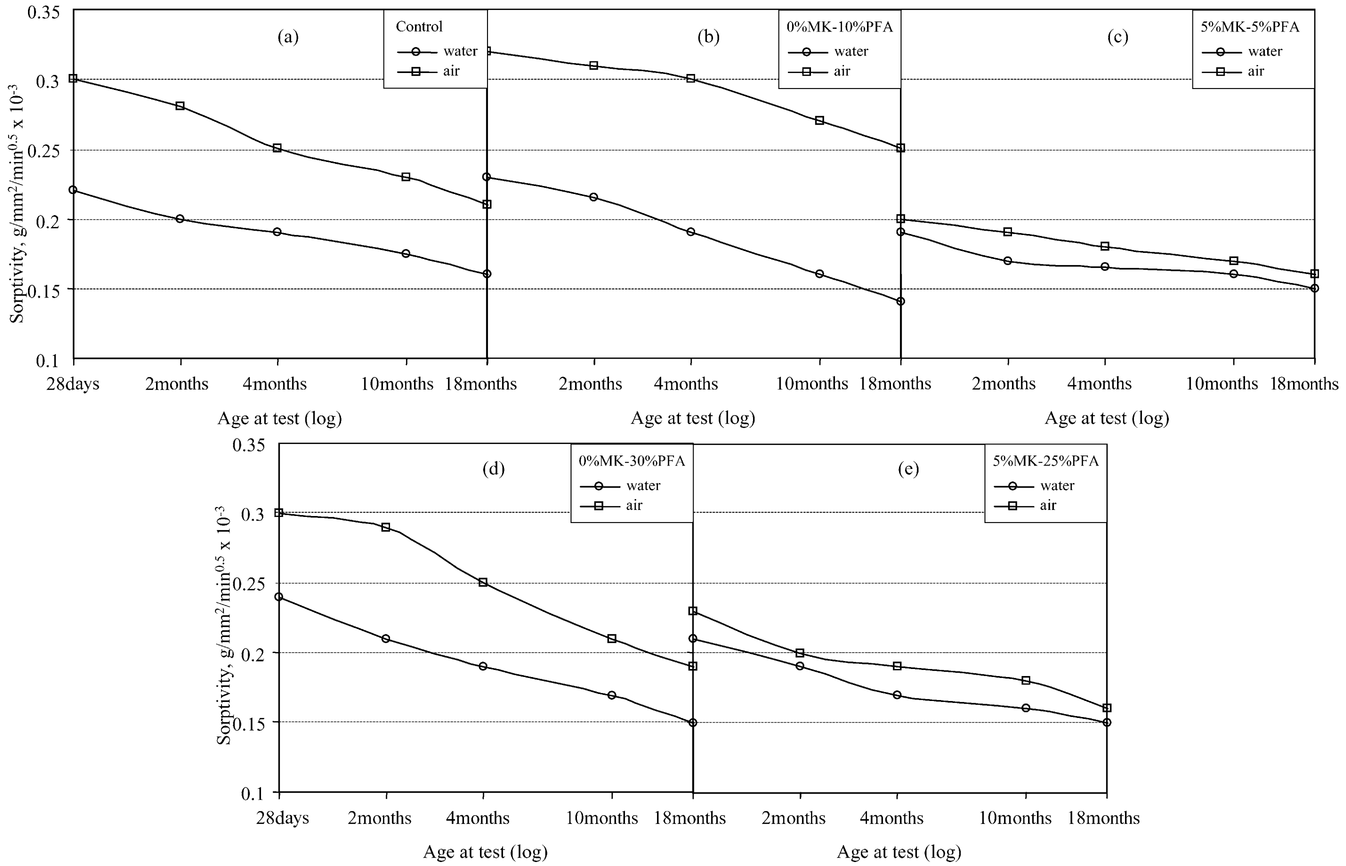

Fig. 9. Sorptivity of air-cured and water-cured PC–PFA–MK concrete.

pozzolanic reaction, coupled with reduced sorptivity derived from the carbonation process itself over a prolonged period (see Dias [9]). In fact, there is a tendency for the water-cured and air-cured sorptivity versus age curves to converge rather than diverge, with increasing age particularly at 30% PC replacement (see Fig. 9d). This is opposite to what might be expected, as the surface hydration of the concrete cured in air in the laboratory would be expected to be much less than that for the water-cured concrete, and, thus, sorptivity would be expected to decrease only very slowly with time if at all. It is therefore suggested that the surface carbonation of the air-cured concrete results in enhanced reduction in sorptivity.

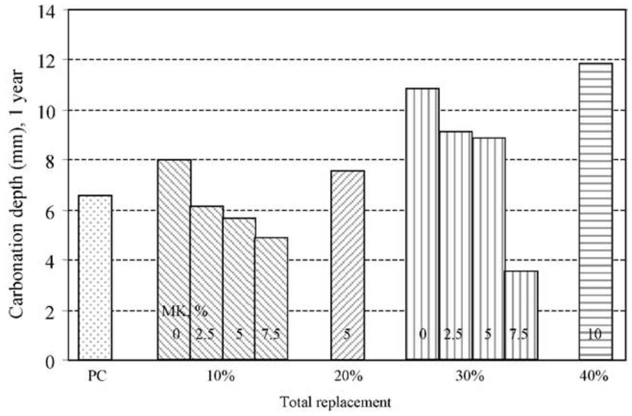

Fig. 10. Carbonation depth (1 year) of PC–PFA–MK concrete at 10%, 20%, 30% and 40% cement replacements.

4. Conclusions

The following conclusions may be drawn from the results of the work.

- In water-cured concrete made with PC–PFA–MK binder, the MK enhances early (28 days) strength, and PFA retards early strength.
- Air-cured concrete shows a loss in strength relative to equivalent concrete that is water cured and the strength difference increases with curing period. The difference is enhanced in concrete made with PC–PFA binder at high replacement levels, which show a much reduced strength gain with time when air cured, whereas for PC–PFA–MK concrete, this difference is reduced as the MK content increases.
- Increasing the MK content of water-cured PC–PFA–MK concrete reduces the sorptivity to values below that of

the control, whereas the sorptivities of PC–PFA concrete exceed that of the control.

- Air-cured concrete shows higher sorptivity than equivalent water-cured concrete, and this difference is substantial both for PC concrete and PC–PFA concrete. In contrast, for PC–PFA–MK concrete, the difference reduces as the MK content increases, such that at high MK levels, the air-cured and water-cured concrete sorptivities are similar.
- Increasing replacement of PC with PFA in PC–PFA air (CO_2 enriched)-cured concrete increases carbonation depth whereas systematically replacing the PFA with MK in PC–PFA–MK concrete reduces carbonation depth.
- There is a strong correlation between carbonation depth and sorptivity as the binder composition of PC–PFA–MK concrete is varied. However, other than for concrete with high MK contents, concrete containing blended binders shows greater carbonation depths than that of the PC concrete but lower sorptivities. This anomaly is attributed to a much reduced CH content in the blended binder concretes coupled with reduced sorptivity deriving from surface layer carbonation over a prolonged period.

Acknowledgements

The authors would like to thank EPSRC for providing a research grant to carry out the work and Ash Resources and Imerys (formally ECCI) for their continued support both in kind and in helpful discussions. In addition, the authors would like to thank the School of Technology at the University of Glamorgan for the provision of technical support and facilities.

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