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SULPHATE RESISTANCE OF METAKAOLIN MORTAR

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ABSTRACT

The partial substitution of cement (both high C_3A and intermediate C_3A) with metakaolin (MK) is investigated in terms of resistance of MK mortar to sodium sulphate (Na_2SO_4) solution. Results on strength, porosity, pore size distribution, and calcium hydroxide (CH) contents are also reported. The sulphate expansion results demonstrate that the sulphate resistance is increased as the replacement level of cement with MK increases, up to at least 25% replacement. Refinement in pore structure and reduction in CH content increase with increase in MK content (for moist-cured mortar), and these two factors are considered to be the principal factors affecting improvement in sulphate resistance. Also, although after prolonged periods of exposure to Na_2SO_4 solution, there is (relative to water-cured specimens) significant strength loss of PC mortars and mortars with low levels of MK (5 and 10%); for mortars with high levels of MK (15, 20 and 25%), there is consistent strength gain. *© 1998 Elsevier Science Ltd*

Introduction

Metakaolin (MK) is an ultra-fine pozzolan (1) similar in its pozzolanic properties to condensed silica fume (CSF). Recent work (2–4) has shown that when MK is used as a partial cement replacement in concrete, it gives significantly enhanced early strength and increased long-term strength. This is because it acts as a filler, it accelerates initial cement hydration, and in the early stages of curing, it rapidly consumes the hydrated lime produced by cement hydration to produce additional cementitious reaction products (2,5). It is claimed that it also increases resistance to alkali-silica reaction; it prevents efflorescence, and it increases resistance to acid attack (6,7). Porosity and pore size distribution measurements have demonstrated (8) that the early strength enhancement is associated with substantial pore refinement. MK is most efficiently utilised (with respect to strength enhancement and pore refinement) at small replacement levels (0–15%) and in the very early stages of curing (up to about 14 days). Thermogravimetric analysis has indicated that beyond this period curtailment of the hydrated lime, MK reaction occurs even though both reactants are still in excess

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(5). Based on this information, it might be expected that MK concrete will show good resistance to sulphate attack.

A fine discontinuous pore structure and low levels of calcium hydroxide (CH) (9,10) are two of the necessary ingredients for promoting high sulphate resistance. This is because the former inhibits transport of reactive species into the cement paste, and the latter limits the level of ettringite and gypsum produced, which are the principal components implicated in the expansion and disruption of the cement-paste matrix. Sulphate attack is normally associated with expansion and is frequently accompanied by strength reduction, properties which result from ettringite and/or gypsum formation in particular chemical environments. Thus, mortars containing highly active pozzolans, such as CSF, which are very efficient in consuming CH, show much smaller expansions and strength reductions when immersed in Na_2SO_4 solution than do control mortars without pozzolan (11). Also, expansion generally decreases with increasing level of substitution of cement by pozzolan, although strength reduction may actually increase.

Al-Amoudi et al. (11) reported the effect of different pozzolans on the strength reduction of mortars made up with Type 1 cement exposed to Na_2SO_4 solution relative to the strength of equivalent water-cured mortars. For PC mortars, the strength reduction after 1 year was 39%, and for mortars with 20% replacement of cement with PFA, the strength reduction was 21%. Also, there was a small (5%) strength gain within the first 28 days. For mortars containing CSF, the strength reduction at 1 year was 10% for 10% cement replacement and 18% for 20% cement replacement. There was also a small strength gain (7–9% relative to the water cured samples) within the first 28 days. However, the mortar containing 10% CSF showed siginificantly more expansion at 1 year than that containing 20% CSF. Similar observations have also been made by Cohen et al. (12) for PC-CSF pastes with CSF contents of 0–15% by weight. Using a Type 1 cement ($C_3A = 10.52\%$), the neat paste without CSF expanded substantially (.83%) after 140 days exposure to Na_2SO_4 solution, whereas the paste containing 15% CSF showed negligible expansion. However, the strength loss, relative to the equivalent control paste cured in saturated lime-water solution, was substantial for both the neat paste (38.2% loss) and the CSF paste (32.4% loss). Cohen et al. suggested that the absence of any significant expansion in the PC-CSF pastes exposed to sulphate solution, although there is a strength loss, may be due to a reduction in the amount of ettringite produced or to a change in ettringite morphology. Thus, low expansion does not in itself indicate low strength reduction, which means that testing programmes that rely solely on expansion measurements for assessing sulphate resistance are unreliable.

The reported properties of MK suggest that it should also be highly effective in promoting sulphate resistance. In fact, a recent report by Asbridge et al. (13) on large scale trials of MK concrete in aggressive environments (up to 3 years) does indicate that MK concrete has good sulphate resistance. However, MK is chemically different from many other pozzolans in that it has a very high alumina content (42% Al_2O_3: 51% SiO_2), and the reaction products on reaction with CH, are not only C-S-H gel but include C_4AH_{13}, C_2ASH_8, and C_3AH_6 (14). Also, if sulphate is present, ettringite rapidly forms and subsequently converts to monosulphate during the early stages of hydration. Such reactions, if not complete before the system has set and hardened could, in themselves, lead to substantial expansion. In fact, Wild et al. (15) has shown that when kaolin (which, although much less active than MK, possesses the same oxide composition) reacts with lime and gypsum, very large expansion occurs and that this expansion is a result of ettringite formation. However, lime-stabilised clay systems are

TABLE 1
Composition of cement.

OXIDE %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	L.O.I
Cement 1	20.2	4.2	2.0	63.9	2.1	3.0	0.1	0.7	–	2.8
Cement 2	20.4	5.8	2.1	65.2	1.1	3.2	0.2	0.6	–	1.0
MK	52.1	41.0	4.3	0.1	0.2	–	0.3	0.6	0.8	0.6

much more weakly bonded than cement systems and are thus much more sensitive to internal volume changes.

Therefore, if MK is to find future use in a wide range of concrete applications, it is necessary to establish its effect on the sulphate resistance of concrete and mortar. It is intended that the data reported in this paper contribute to the existing knowledge in this field.

Experimental

Materials

For the sulphate resistance test, two types of Portland cement class 42.5 (PC) were used; the first type (Cement 1) has an intermediate C_3A content of 7.8% and the other type (Cement 2) has a high C_3A content of 11.7%. For the other tests, (compressive strength, pore size distribution, and calcium hydroxide determination) only Cement 1 was used. The metakaolin was supplied by ECC International (Europe). The compositions of metakaolin and both types of cement are given in Table 1. The specific surface of the metakaolin was 12,000 m^2/kg. The quartz sand used had a particle size ranging from 0.25 to 0.71mm.

Mix Proportions

Six different mortar mixes were investigated. The control mix (M0) had composition of 1 cement: 2.5 sand: 0.55 water (by weight). In mixes M5, M10, M15, M20, and M25, cement was partially replaced (by weight) with, respectively, 5, 10, 15, 20, and 25% metakaolin. For the sulphate tests, all mixes were tested; however, for the other tests only mixes M0, M5, M10, and M15 were tested.

Specimen Preparation, Curing, and Testing

For the sulphate study, bars with dimensions of 25 mm × 25 mm × 285 mm were produced with stainless steel inserts cast into their ends to allow the change in length to be accurately measured. After casting, the moulds were covered with cling film to avoid any loss of water from the specimens. After 24 h, the bars were demoulded, weighed, and quickly wrapped with a few layers of cling film at 20 ± 1.5°C. Eight mortar bars were made up for each mix composition and for each cement type (high C_3A and intermediate C_3A).

The wrapped specimens were moist-cured in air for 14 days, and their length measured before immersing 5 bars in 5% Na_2SO_4 solution and 3 bars in water from each mix. The dial gauge used was sensitive to 0.002 mm. The sulphate solution was renewed every 2 months, and the length changes of specimens and their weights were monitored (at between 3-week and 3-month intervals).

Mortar cubes (100 mm × 100 mm × 100 mm) made from the same mixes and moist-cured (using the identical procedure to that used for the mortar bars) for periods of up to 1 year, were used for compressive strength determination, mercury porosimetry, and thermogravimetric analysis. Both the mortar bars and the cubes were compacted on a vibrating table, ensuring good compaction of the high MK mortars, which were much less workable than the low MK mortars. The cubes were weighed before testing to monitor any change in weight. Observed weight changes were found to be negligible (±0.15%). After crushing, small samples weighing up to 5 g were taken from the middle of the crushed cubes for the determination of calcium hydroxide using thermogravimetric analysis and porosity and pore size distribution measurements using mercury porosimetry. The specimens were dried to constant weight before testing. The drying was performed in a cabinet at 40°C under silica gel. The gel was renewed daily. The samples were then put in an air-tight container until testing. Further details about the testing procedure are given in (5,8). Only data from the 14-day and 365-day cured specimens were considered in this study, although the results of the CH determinations, which have been published previously (see (5)) are available from 3 to 365 days. The reason for this is that 14 days is the period of moist-curing of specimens before immersion in sulphate solution, and the 365-day strength data represent the ultimate strength.

In addition to testing moist cured cubes for strength, strength measurements were also made at 520 days on the mortar bars that had been exposed to sulphate solution and those that had been water-cured. Two bars were tested for each mix and exposure/curing conditions. The ends of the bars containing the stainless steel inserts were cut away, and the remaining section was cut into four equal sized pieces (eight pieces in total). Each test piece was located centrally between two 25-mm square section polished steel plates, and a self adjusting ball and socket unit was positioned between the top plate and the upper platten to ensure uniaxial application of the load. Specimens were tested in an Instron 250 KN testing machine at a compression rate of 2.5 mm/min. Each compressive strength value reported is the mean of eight separate values.

Results and Discussion

Sulphate Expansion and Strength Changes

The sulphate expansions of mortar specimens containing different levels of replacement of cement with metakaolin are shown in Figure 1a and Figure 1b for Cements 1 (high C_3A) and 2 (intermediate C_3A), respectively. The results show that expansion decreases systematically with increase in MK content for both types of cement. For mortars containing high C_3A cement, the control mix and mixes containing 5% and 10% MK showed rapid expansion and deterioration between 40 and 70 days exposure to sulphate solution. It should be noted that bars (M15 and M20) containing 15% and 20% MK showed small but quite sharp expansions also between 40 and 70 days, but subsequently stabilised and even contracted slightly, although the bars M15 disintegrated after 290 days with little further expansion. By 520 days,

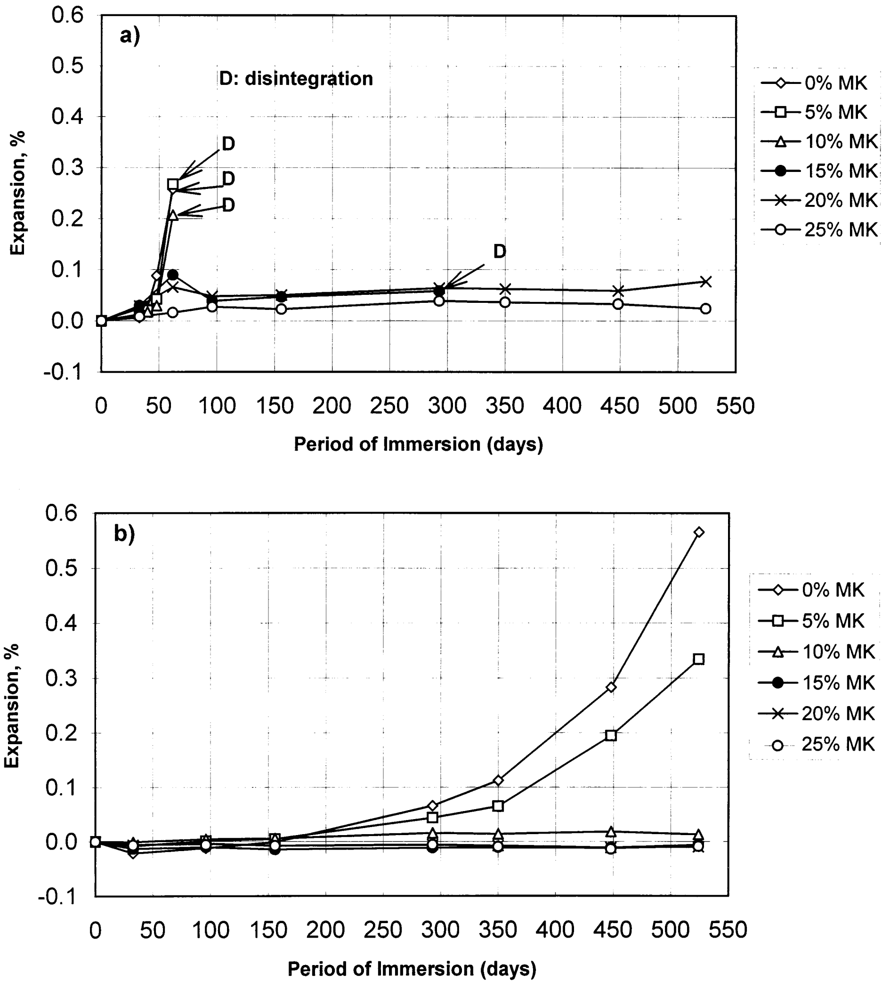

FIG. 1.
Expansion of MK mortar bars vs exposure time in sodium sulphate solution for a) high C_3A PC-MK mortar and b) intermediate C_3A PC-MK mortar.

mortar bars containing 20% and 25% MK showed no significant changes in length and no apparent signs of distress.

Figure 1b, where intermediate C_3A cement was used, shows similar trends to those observed in Figure 1a but with a much delayed expansion process. The control mix showed significant expansion followed by the 5% MK mix, and cracks were observed on specimens of the latter (i.e., 5% MK). Mortars containing 10% MK exhibited little expansion, and the other MK compositions (i.e., 15, 20, and 25%) were extremely stable, showing little overall change (after an initial minor contraction) and no signs of deterioration after 520 days of exposure.

Figure 2a compares the strength (at 520 days) of mortar bars exposed to Na_2SO_4 solution with those of identical mortar bars that were water cured, and Figure 2b presents similar data

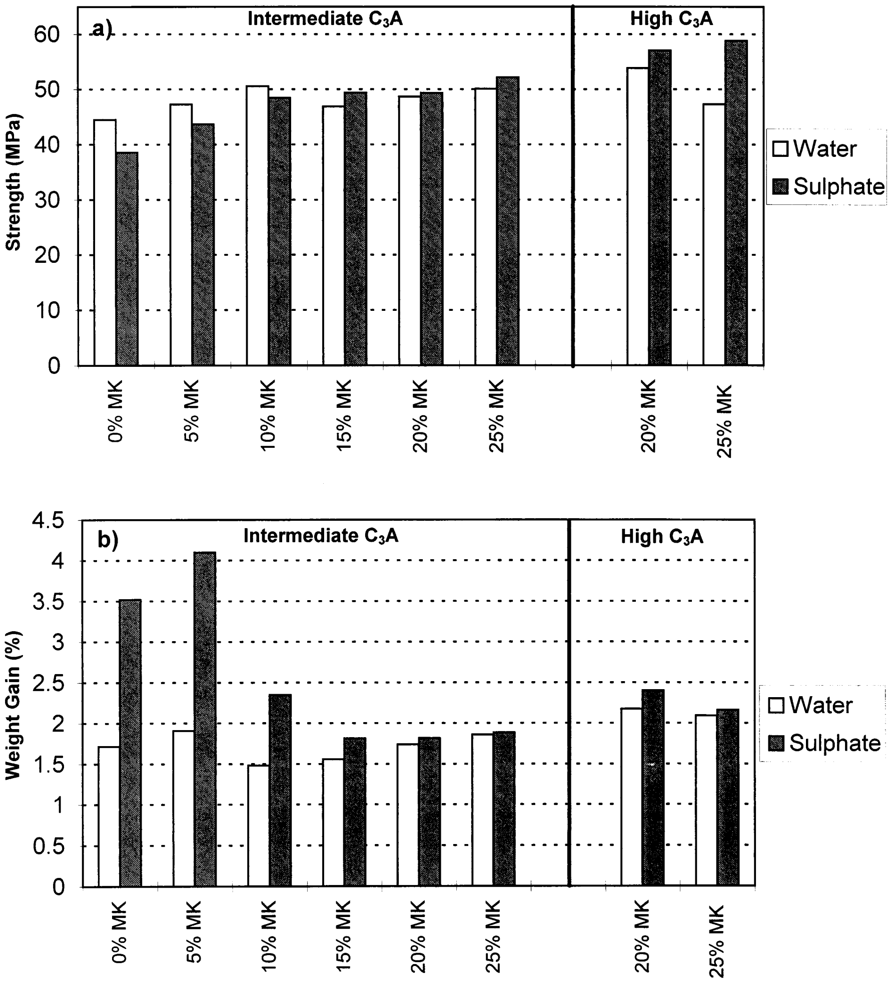

FIG. 2.

Comparison of a) compressive strength and b) weight changes, of MK mortar bars immersed in either sodium sulphate solution or water for 520 days, using both high C_3A and intermediate C_3A cement.

on percent weight change. Strengths are only available over the full range of compositions for mortars with intermediate C_3A cement. This is because compositions with high C_3A cement, other than those with 20% MK and 25% MK, had disintegrated by 520 days. For intermediate C_3A cement mortars, specimens containing between 0 and 10% MK showed significant strength losses in Na_2SO_4 solution relative to the equivalent water-cured specimens whereas specimens containing between 15 and 25% MK showed consistent strength gains. For high C_3A cement mortars, specimens containing between 0 and 10% MK expanded substantially and disintegrated within 70 days, but specimens containing 20 and 25% MK again showed consistent strength gains at 520 days relative to the equivalent water-cured specimens. This suggests that to obtain good sulphate resistance the MK level

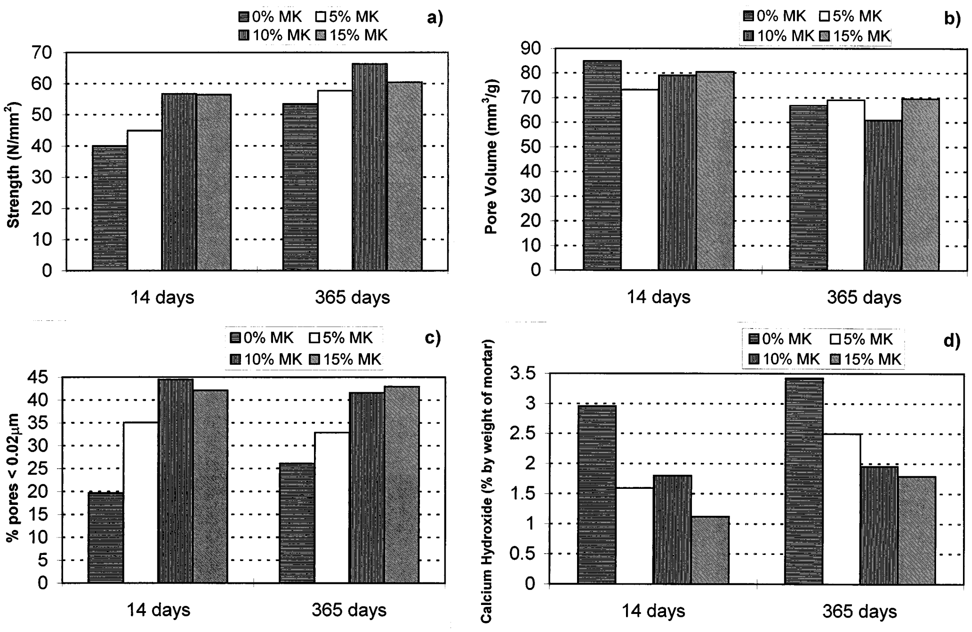

FIG. 3.
The effect of the MK content of mortar (cement type 1) after 14 and 365 days of moist curing, on a) compressive strength, b) total intruded pore volume, c) percent volume consisting of pores < 0.02 μm radius and d) CH content.

should be greater than 15%. Strength differences between specimens that were water-cured and those exposed to sulphate solution, although small, in general exceeded the standard deviations, which were in the range of 1.4 to 5 N/mm^2.

The weight gains of specimens containing between 0 and 10% MK (Fig. 2b) in sulphate solution are substantially higher than those of specimens cured in water, and these high weight gains correspond both with strength loss and high expansions. In contrast, at replacement levels between 15 and 25%, the relative weight gains of specimens are much less, length change is negligible (Fig. 2b), and relative strength is greater (Fig. 2a).

Strength, Porosity, and CH Content of Moist Cured Mortars

Figure 3 shows a) compressive strength, b) porosities, c) percentages of micropores (<0.02 μm), and d) CH contents of mortar cubes (mixes M0, M5, M10 and M15), which have been moist cured for 14 and 365 days, respectively. At both curing ages, the presence of MK contributed significantly to strength (Fig. 3a), but particularly at 14 days. In fact, previous work by the authors (2,5) has shown, both for MK mortar and concrete, that strength enhancement by the MK reaches a maximum at 14 days and subsequently declines.

As might be expected, the intruded pore volume (Fig. 3b) at 365 days is less than that at 14 days for all mortars, although the presence of MK in the mix does not have much influence on the total intruded pore volume. However, the percentage of the pore volume occupied by fine pores (i.e., pores less than 0.02 μm in radius, Fig. 3c), in general increases with increase in MK content, the effect being particularly pronounced at 14 days. In fact, for mortars containing MK, the percentage of fine pores is slightly higher at 14 days curing than it is at 365 days. This confirms that the major part of the pore refinement process occurs at a very early age. In contrast, for the control mortar, the percent of the pore volume containing fine pores increases between 14 and 365 days, confirming increased pore refinement during this period.

Figure 3d shows that there is a sharp decrease in CH content relative to the control (M0) when cement is partially replaced by MK, and the reduction in CH is greater at 14-day curing than at 365-day curing. In fact, CH contents are greater at 365 days than at 14 days for all the MK mortars, as well as for the control mortar. This is, of course, expected for the control mortar because there is no component to remove the CH produced by the continued hydration of cement with time. The fact that for the MK mortars the CH content increases between 14 and 365 days confirms that the MK is not very efficient at removing CH over this period. In fact, this was previously confirmed by Wild et al. (5), who showed that in both paste and mortar, maximum consumption of CH by MK occurred at 14 days and subsequently CH contents increased. The authors suggested that this was due to the formation of an inhibiting layer of reaction product around the MK particles, although this is yet to be confirmed using microanalytical methods. However, at 365 days, as the MK content increases, there is clearly both a consistent reduction in CH content (Fig. 3d) and a consistent increase in the degree of pore refinement (Fig. 3c), although there is little variation in intruded pore volume (Fig. 3b). Although data are not available for compositions M20 and M25, this trend would be expected to continue but needs to be confirmed by further measurements.

Discussion

Both of the basic requirements for high sulphate resistance discussed in the introduction (i.e., fine pore structure and low levels of CH) are achieved by the partial replacement of cement with MK. They are also achieved after relatively short periods, and in fact the CH content actually increases between 14 and 365 days in moist-cured mortar and the percentage pore volume occupied by fine pores decreases, although the total pore volume also decreases slightly. These data suggest that the sulphate-resisting properties of the MK mortar are developed at a very early stage. For mortars made with high C_3A cement (Fig. 1), expansion in Na_2SO_4 solution is very rapid for compositions containing up to 10% MK (M0, M5, and M10), and disintegration occurs within 70 days. Composition M15, although also showing an initial but smaller expansion within the first 70 days, subsequently contracts and then fails due to crack formation within 300 days. It is perhaps significant that at 14 days of moist curing the porosity and degree of pore refinement of specimen M10 is very similar to that of M15 (Figs. 3b and 3c), but the CH content of the latter is significantly less than the former. This suggests that the reduction in CH content is acting as the principal contributor to the sulphate resistance. In fact, the primary and the critical expansive phase for all these specimens appears to occur within the first 70 days with expansion at 70 days systematically declining with increase in MK content. The damaging cracks, which resulted in the failure of the M15 sample, may well have been initiated during this first 70-day period. For the M20 and M25 specimens, no cracking is visible, and at 520 days there is significant strength enhancement relative to the equivalent water-cured samples. For mortars made with intermediate C_3A cement, significant expansion does not appear until about 300 days and only specimens with low MK levels (M0, M5, and M10) actually expand. Specimens M15, M20, and M25 show an initial contraction that is maintained up to 520 days. This distinction in behaviour is also reflected in the 520 day strengths of these bars, in that specimens M0, M5, and M10 show strength reductions and specimens M15, M20, and M25 show strength gains. In addition, the formation of sulphate containing reaction product is indicated from the marked weight increases of the M0, M5, and M10 specimens exposed to sulphate solution (Fig. 2b) relative to the water-cured specimens, whereas specimens with MK contents above 15% give only minor relative increases in weight.

The strength reduction can be attributed to microcracking induced by the expansive ettringite forming reaction. However, the strength gain at 520 days for the high MK mortars is surprising in that Al-Amoudi et al. (11) observed significant loss in strength of both PFA mortars and CSF mortars after 1 year in Na_2SO_4 solution. Possibly, at high MK levels and substantially depressed CH levels, the absorbed sulphate reacts to form a product that contributes to rather than reduces the strength, for example by filling empty pores without disrupting the overall microstructure. This, however, can be substantiated only by detailed analytical work, which is beyond the scope of this paper.

Conclusions

The following conclusions can be drawn from the observations:

1) MK produces a reduction in CH content of PC mortars and a refinement of pore structure, and these effects are more pronounced after 14 days moist curing than after 365 days.
2) Increasing levels of MK in PC mortars exposed to Na_2SO_4 solution produce reduced levels of expansion and increased resistance to cracking.
3) Mortars exposed to Na_2SO_4 solution and containing MK levels of up to 10% exhibit a loss in strength, and those containing MK levels greater than 15% exhibit a gain in strength, relative to equivalent water-cured specimens.
4) Reduction in CH content is considered to be the principal factor by which MK improves sulphate resistance, and it is suggested that the nature of the sulphate containing reaction product formed at high MK levels and low CH contents is different from that formed at low MK levels and consequently higher CH contents.
5) At least 15% replacement of cement with MK is considered to be necessary to provide good sulphate resistance.
6) It is suggested that at low MK contents (0–10%), there is excess CH available, therefore, the onset and magnitude of expansion is controlled by the amount of C_3A available to react to form an expansive product. Hence, the high C_3A content PC mortars show early and rapid expansion, whereas the intermediate C_3A content PC mortars show much later expansion and slower expansion rates. At high MK contents (15–25%), CH availability becomes restricted, and the magnitude and rate of expansion is very much smaller and less sensitive to C_3A content. In this case, expansion is controlled by CH content, and the difference in expansion between the two PC systems is much smaller.

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