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PORTLANDITE CONSUMPTION IN METAKAOLIN CEMENT PASTES AND MORTARS

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ABSTRACT

Cement mortars and pastes containing 0, 5, 10 and 15% replacement of cement with metakaolin and with a water/binder (w/b) ratio of 0.55 have been moist cured for periods from 3 to 365 days. The Portlandite content at different ages has been determined by thermogravimetric analysis and this has been related to changes in relative strength. $Ca(OH)_2$ in mortars was found to be less than that in pastes. In the metakaolin mortars and pastes removal of Portlandite by pozzolanic reaction reached a maximum at about 14 days, corresponding with a maximum in relative strength. Beyond 14 days severe retardation of the pozzolanic reaction was observed and relative strength rapidly declined. *Copyright © 1997 Elsevier Science Ltd*

Introduction

Portlandite Formation in Cement and Mortar. On complete hydration up to 28% by weight of ordinary Portland cement (OPC) is converted to Portlandite (CH) although in practice complete hydration is never achieved and values at extended ages are typically in the range 16-20% [1]. Portlandite is partially water soluble (1.76g/l at 10°C) and is chemically reactive particularly when exposed to acidic environments, and it therefore contributes substantially to the generally poor durability of mortar and concrete. Hence, the removal or partial removal of CH and its replacement by a less chemically reactive cementitious product produces improved durability, particularly in relation to sulphate resistance [2] and alkali silica reaction [3,4]. Pozzolanic materials when partially replacing cement in concrete and mortar react with the Portlandite to produce additional cementitious gel the formation of which has the added effect of pore blocking and permeability reduction [5], thus further improving material durability.

The CH content of a hydrating paste at a given temperature and curing time is controlled by the initial water to cement (w/c) ratio and by the local environment. For example, Zhang and Gjørv [6] observed CH contents (expressed as a percentage of dry cement) of 8, 12 and 16% for cement pastes of w/c ratios of respectively 0.2, 0.3 and 0.4, after curing in sealed containers for 550 days at 20 ± 1°C. This is in good agreement with similar work on silica fume paste by Yogendran et al. [7] who observed CH contents, depending on curing time, from

9.7% to 12.3% at a w/c ratio of 0.28 and 15.7% to 17% at a w/c ratio of 0.48. The local environment is influenced significantly when aggregate is present and its influence on CH production is not well understood or easily predictable.

The surface adsorption of water by the aggregate, the tendency towards bleeding and the lower packing density of cement grains at the cement paste-aggregate interface inevitably lead to an initially enhanced w/c ratio in the interfacial zone region [8,9]. In addition, the aggregate particle surfaces provide nucleation sites for CH nucleation and growth [10] and massive deposits of oriented CH crystals are often observed at the cement paste-aggregate interface. Some investigators report that for a given w/c ratio and curing time, the CH content of paste in mortar is greater than that of the equivalent paste alone [11] whereas other authors [12] find the opposite to be the case. Curing time appears to be a critical factor in determining the relative amount of CH produced in mortar pastes and equivalent neat pastes. For example, Huang Cheng-Yi and Feldman [12] have shown that in very early stages of curing (up to 8 hours), ground quartz sand actually accelerates the production of CH. However, their work on paste and mortar of w/c ratio 0.45 shows that for curing times between 1 and 28 days, the CH content per ignited weight of binder in mortar is lower than in paste and from 90 to 180 days it is equivalent to that in the neat paste. This can be explained in terms of a reduced hydration rate within the denser and less permeable cement paste matrix relative to that in the neat paste.

No detailed work has been reported on the change in CH content with curing time for metakaolin mortars and pastes, unlike the case for condensed silica fume (CSF) [13-17]. Reports of the amount of metakaolin required to fully remove all the CH vary. Kostuch et al. [18] have reported that 20% replacement of cement by metakaolin is required to remove all the CH in a standard concrete at 28 days, whereas Oriol et al. [19] report that between 30 and 40% metakaolin is required to remove all the CH in cement-metakaolin paste at a water/binder (w/b) ratio of 0.5 when cured in lime-saturated water for 28 days. This indicates that metakaolin may be less effective in removing CH from OPC systems than is CSF. Although this might be predicted due to the lower SiO_2 content of metakaolin relative to CSF, it is not necessarily the case because the Al_2O_3 component in metakaolin also reacts with CH. The aim of the current investigation is to determine the effectiveness of metakaolin in removing CH from hydrating pastes and mortars.

Experimental

Materials. The cement used for this investigation was ordinary Portland cement, which complied with BS12 and the metakaolin was supplied by ECC International (Europe) under the commercial name MetaStar. The compositions of cement and metakaolin are given in Table 1. The specific surfaces of the cement and metakaolin were respectively 363m^2/kg and 12000m^2/kg and the specific gravities were 3150 kg/m^3 and 2490 kg/m^3. The sand used was a "Leighton Buzzard" quartz sand (97% SiO_2). It has a saturated porosity of 0.41% and a particle size ranging from 0.25 to 0.71 mm. The sieve analysis on the sand is presented in Table 2.

Mix Proportions. Details of the four mortar mixes (A-D) are given in Table 3. The control mix (A) was of proportions by weight 1 cement : 2.5 sand : 0.55 water. In mixes B, C and D, cement was partially replaced (by weight) with respectively 5, 10 and 15% metakaolin. Mixing was performed in a pan mixer. The dry sand was added first followed by the pre-

TABLE 1

Composition of Cement and Metakaolin

OXIDE	CEMENT	METAKAOLIN
	%	%
SiO2	20.2	52.1
Al_2O_3	4.2	41.0
Fe_2O_3	2.0	4.32
CaO	63.9	0.07
MgO	2.1	0.19
SO_3	3.0	----
Na_2O	0.14	0.26
K_2O	0.68	0.63
TiO_2	----	0.81
L.O.I	2.81	0.6

blended cement and metakaolin. The constituent materials were mixed dry for about 1.5 minutes. The water was then added slowly and mixing was continued for a total period of 4 minutes.

Four different pastes, equivalent to the hydrated binder phase of the mortar mixes with water to binder ratio (w/b) of 0.55 and replacement levels of 0, 5%, 10% and 15% with metakaolin, were also prepared.

Specimen Preparation, Curing and Testing. Specimens were cast in 100 × 100 × 100mm steel moulds and compacted by vibration. A small amount of bleeding was observed during vibration. After casting, the cubes were covered with cling film to prevent water loss and after 24 hours the specimens were demoulded, weighed and quickly wrapped with cling film and placed in plastic bags. The bags containing the specimens were placed on a stand in a plastic container at a temperature of 20 ± 2°C for periods of 3, 7, 14, 28, 90 and 365 days. To prevent loss of water from the specimens, wet hessian was placed around the inner walls of the container and draped around the specimens, and this in turn was covered with plastic sheeting.

Before testing, the cubes were weighed to check that there was negligible moisture change during curing and they were then tested in compression at a loading rate of

TABLE 2

Particle Size Distribution of Sand

SIEVE SIZE	PASSING (%)
5.00mm	100
2.36mm	100
1.18mm	100
600μm	87
300μm	4
150μm	0
Pan	0

TABLE 3

Mix Proportions of Mortar

MIX	MK %	PROPORTIONS (Kg/m^3)			
		CEMENT	MK*	SAND	WATER
A	0	552.2	0	1380.6	303.7
B	5	523.4	27.5	1377.4	303.0
C	10	494.7	55.0	1374.2	302.3
D	15	466.1	82.3	1371.0	301.6

* metakaolin

40kN/min. Three cubes were tested at each curing time and the average strength determined (other than for paste at 365 days where one cube only was tested). Individual values varied within ± 6% of the average. Immediately after testing, pieces of up to 5g in weight were carefully taken from the middle (core) of the broken cubes and dried in a sealed drying cabinet at 40°C under silica gel. Prior to placing the samples, carbosorb was put in the cabinet overnight to eliminate any carbon dioxide present. When samples reached constant weight (usually within 48 hours), they were placed in an air tight container and were subsequently analysed using thermogravimetric analysis (TG) to determine their calcium hydroxide content. The results were also used to determine the free (evaporable) water. This was calculated from the difference between the sample weight (as cured) and the sample weight after drying.

The instrument used for thermal analysis was a Perkin-Elmer TG47 thermal analyser. Before testing, a part of each dried sample was ground. Thermal analysis was conducted on ground samples (weight of samples ranged from 30–60mg) in a dry nitrogen atmosphere at a heating rate of 20°C/min up to 1025°C. The calcium hydroxide content was determined using the method described by Marsh and Day [20]. This involved drawing two tangents to the linear portion of the TG curve on either side of the temperature region over which weight loss due to CH decomposition occurred. The vertical drop in weight at the mid value was then used to determine the weight of CH present in the sample. The temperature region over which CH decomposed ranged from 425–600°C. The amount of CH was expressed, for both the pastes and the mortars, as a percentage by weight of the original cement content of the sample.

The original cement content in each sample was calculated from the final ignited weight. However, it could not be assumed that the finial ignited weight represented the sum of the initial weights of the dry solid materials in the mix. This is because although TG analysis of the raw materials showed the sand to be completely inert, the metakaolin was found to con-

TABLE 4

Free Water of Control Paste and Mortar

	FREE WATER (% by weight of Cement)					
	3d	7d	14d	28d	90d	365d
Paste	36.91	35.13	33.79	32.82	31.86	30.97
Mortar	32.72	32.08	28.94	30.33	29.44	26.47

TABLE 5

Strength Development of Metakaolin Mortar and Paste

MIX	MK %	COMPRESSIVE STRENGTH (N/mm^2)					
		3d	7d	14d	28d	90d	365d
A	0	27.8	36.0	40.0	44.3	51.4	53.4
B	5	29.3	37.8	44.9	47.4	56.6	57.7
C	10	30.2	46.6	56.7	61.8	65.9	66.3
D	15	26.1	46.0	56.4	58.4	56.8	60.4
PA	0	21.9	30.2	34.5	40.5	48.0	52.1
PB	5	21.2	32.5	39.6	42.9	45.6	50.5
PC	10	25.5	37.8	48.0	51.5	56.3	59.6
PD	15	22.0	41.8	47.5	54.5	58.5	61.6

tain 0.5% of adsorbed water and the cement to contain 5% of calcium carbonate. However, using the original mix proportions and correcting for the adsorbed water in the metakaolin and the $CaCO_3$ in the cement it was possible, by applying a correction factor, to determine the initial dry weight of OPC (excluding the $CaCO_3$ contaminant) in the mortar and in the paste samples. Although calcium carbonate was present in the cement initially, there was no evidence from the TG analysis of any further significant increase in the carbonate content of the mortars and pastes during curing and this was confirmed by weight change monitoring.

Results and Discussion

Table 4 gives the free (evaporable) water expressed as percentage of the cement content for the control paste and the control mortar. Table 5 gives the calculated strength values for the mortar and paste mixes and Figure 1a and 1b respectively show the change in relative strength of the mortar and paste mixes against curing time. Relative strength is the ratio of the strength of the test specimen to that of the control at the same age. It should be noted that in all cases a maximum in relative strength occurs at around 14 days.

Figure 2 compares the change in CH content (expressed as a percent of the dry weight of the cement) of the control mortar and the control paste, with curing time. Figure 3a and 3b respectively show the change in CH content with age for the metakaolin mortars and pastes. It should be noted that clearly defined minima occur at about 14 days in all cases.

Comparison of the weight percent CH (expressed as the percent by weight of OPC) for the control paste and mortar paste at different curing times (Figure 2) clearly illustrates that for a fixed w/c ratio CH production in the control paste at early ages is much greater than in the mortar paste. However, as curing time advances the CH content in the mortar paste increases at a slightly greater rate than in the control paste, and there is a tendency for the two curves to converge. This type of behaviour has also been observed by Huang and Feldman [12] in their work on silica fume paste and mortar. In the current work, observed weight changes during curing were negligible. Also specimens for analysis were taken from the central region of the cubes. Thus it is unlikely that any movement of water into or out of the specimens occurred during curing. Therefore, the fact that CH contents detected in the mortar paste are much less than those in the control paste, is indicative of a much lower degree

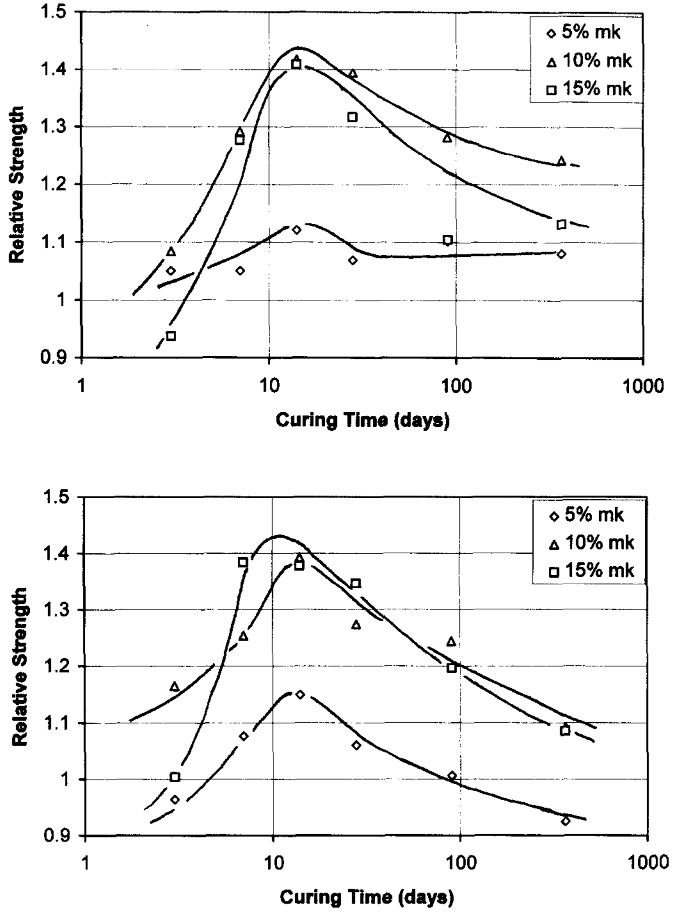

FIG. 1.

Change in relative strength versus curing time for metakaolin (a) mortar and (b) paste.

of hydration in the former particularly at early ages, although a second explanation should also be considered. This is the probable occurrence of a much wider range of crystallite sizes of CH within the mortar [10], with much coarser crystals being present than in the neat paste. This would result in a much broader and diffuse weight loss versus temperature relationship during thermogravimetric analysis shifting the peak weight loss to higher temperatures and leading to an underestimate of the CH present. However careful examination of the TG curves for mortar and paste and consideration of the method employed to determine the CH content does not support this explanation.

The control paste comprises a relatively homogenous uniform system where the water is evenly distributed throughout the whole mass. The mortar forms a much more heterogeneous system in which the cement paste separating the sand grains is much less uniform. The interfacial zones at adjacent sand grains are characterised by a low density of cement particles and a high water content and these are separated by a much denser bulk paste matrix of lower w/c ratio. The interfacial zone normally forms the "weak link" in mortar (and concrete) and observations of mortar strengths by a number of authors [12,21] are generally below those of the equivalent neat paste with the same w/c ratio. This strength difference

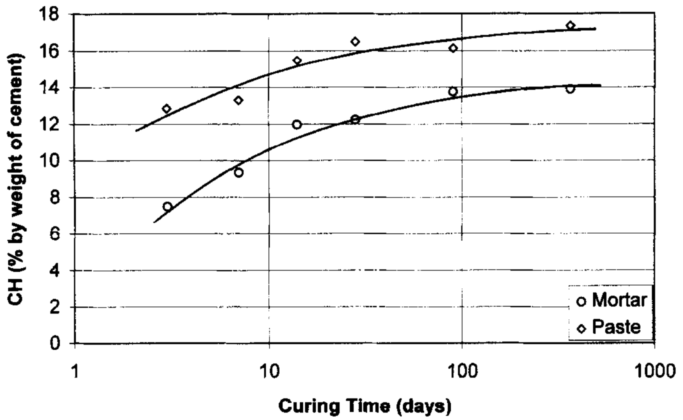

FIG. 2.
Change in CH content versus curing time for control mortar and paste.

however decreases with increase in w/c ratio and is also influenced by aggregate type [21]. In addition if there is chemical interaction between the aggregate and the cement paste the weak link is strengthened and concrete made from such reactive aggregate has been shown [21,22] to exhibit significantly higher strengths relative to that made with unreactive aggregate. The fact that in the current work the mortar strengths are consistently greater than those of the equivalent cement paste is therefore unusual and requires some discussion.

The possible phenomena which are considered could result in this effect are absorption of water by sand, chemical interaction between the CH and the sand, acceleration of cement hydration by the sand, and differences in the degree of compaction between the control mortar and the control paste. The observations indicate that it is the final phenomenum which is producing the observed discrepancy between mortar and paste strength.

Rheologically the control paste (which is a colloidal system containing only very fine solid particles) will behave under vibration in a different way from the control mortar (which contains a large proportion of much coarser particles). During vibration it is often more difficult to fully compact paste and remove entrapped air than it is in the mortar. If, as is likely, more water per unit volume of paste was lost from the control mortar than from the control paste due to bleeding, then this would lead to a better compacted less porous paste structure in the mortar. This would be expected to result in reduced w/c ratio, increased strength, reduced free water (see Table 4), reduced hydration and reduced CH in the control mortar, relative to the control paste and would therefore be in accordance with the observations.

When metakaolin is used to partially replace the cement, the change in CH content (expressed as the percent by weight of OPC) with curing time for both mortar and paste is much more complex (see Figure 3). At short curing periods the CH contents of the mortar pastes are (in common with metakaolin free material) significantly below those of the control pastes, whereas at long curing periods the difference is less pronounced.

At 3 days curing there is, particularly in the mortar, a relatively small variation in CH content with change in metakaolin content and there is, as might be expected, a general trend for CH content to decrease with increase in metakaolin content. At extended curing periods a distinct pattern of behaviour emerges in both the mortar pastes and the control pastes. After reaching a maximum (between 0 and 7 days) the CH content falls to a well defined mini-

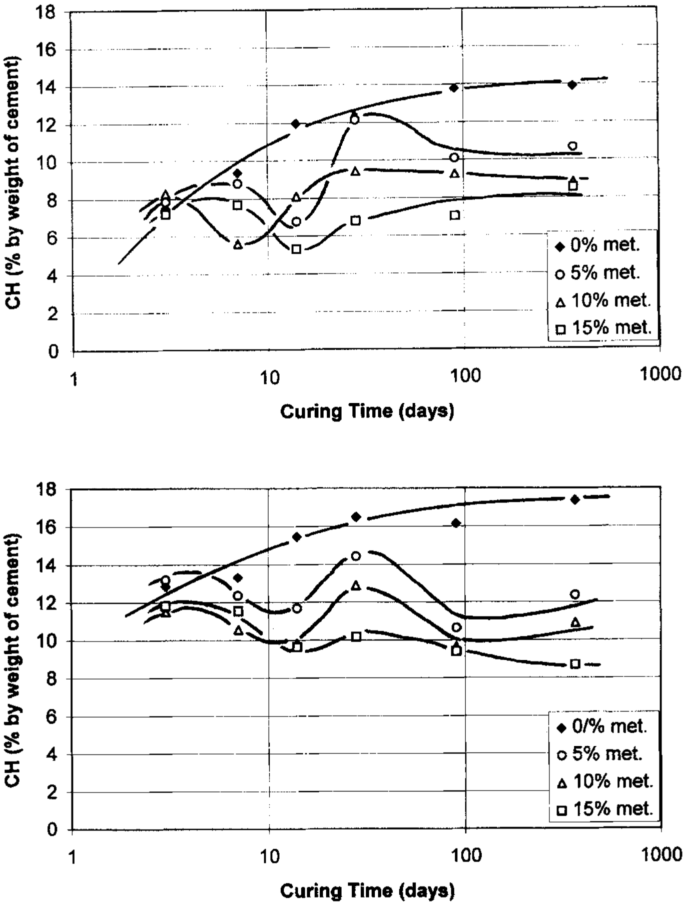

FIG. 3.

Change in CH content versus curing time for metakaolin (a) mortar and (b) paste.

mum. This minimum occurs at about 14 days for all mortar and paste compositions (with the exception of mortar with 10% replacement of cement by metakaolin where it occurs rather earlier). It is significant that, within the limits of accuracy of the measurements, this minimum coincides for both mortar and paste with the equivalent maximum in relative strength shown in Figure 1. The minimum is clearly a result of the pozzolanic reaction which is removing CH from the system more rapidly than it is being produced by hydration of the OPC (see Figure 2 for reference).

Surprisingly, between 14 and 28 days curing and irrespective of metakaolin content, the CH content shows a marked increase corresponding with (see Figure 1) the initial decline in relative strength. A similar pattern of behaviour in relative strength with age has also been reported by Wild et al. [17] for silica fume concrete. In this case the fall in relative strength beyond 21 days was explained in terms of the development of an inhibiting layer of reaction product around the CSF particles which severely retarded the lime—CSF reaction. The current results also indicate a similar process.

Between 28 days and 365 days the change in CH content with time shows a slightly different pattern of behaviour between the mortar pastes and the control pastes. For mortar pastes with 15% cement replacement with metakaolin the CH content gradually increases with time, with 10% replacement it decreases very slightly with time, and for 5% replacement it decreases more steeply with time. In the case of the aggregate free pastes the CH contents during this period decline significantly for all three cement replacement levels, particularly at the the low replacement levels. This would suggest that beyond 28 days there is in the aggregate free pastes a greater degree of secondary reaction of lime with metakaolin than in the mortar paste, although this does not appear to be reflected (see Figure 1) in any further enhancement in relative strength, which for 5% cement replacement with metakaolin actually falls below 1. However, it has been reported by numerous authors [12,21] that the partial replacement of cement by pozzolans only provides long term strength enhancement in aggregate-paste systems, where it modifies the nature of the interfacial zones, and not in systems based on paste alone.

These observations support the hypothesis that in the mortar paste there is formed a denser and less permeable cement paste matrix which is more effective in blocking diffusion processes and in inhibiting further reaction with lime, particularly at the higher metakaolin levels. Porosity and pore size distribution measurements are currently being carried out on the metakaolin mortars and pastes to provide additional information at the microstructural level.

Conclusions

The following conclusions may be drawn from the results obtained:

1. The amounts of CH detected in young mortar pastes (both with and without metakaolin) are less than those detected in the equivalent aggregate free pastes. This is explained in terms of reduced initial hydration in the mortar pastes due to the formation of a denser bulk cement paste matrix of lower w/c ratio than the cement paste in the equivalent aggregate free pastes. It is suggested that this may have been caused as a result of better compaction of the paste matrix in the mortar and greater loss of water due to bleeding, relative to the neat paste.
2. The CH contents of both metakaolin mortar pastes and their equivalent standard pastes show a minimum at about 14 days which coincides with a maximum in relative strength. This is attributed to a peak in pozzolanic activity for which more CH is being removed from the paste than is being generated by cement hydration.
3. Reaction of metakaolin with lime between 14 and 28 days appears to be severely retarded, as evidenced by a further sharp increase in CH content. This retardation can be explained in terms of formation of an inhibiting layer of reaction product on the metakaolin particles.
4. Beyond 28 days there is evidence of further secondary reaction of metakaolin with CH particularly for the aggregate free pastes, although this is not reflected in any additional enhancement of relative strength.
5. At the age of one year for paste with 15% replacement of cement by metakaolin, the amount of CH present relative to the cement is still 50% of that present in the equivalent metakaolin free paste. This suggests that replacement levels considerably in excess of 15% would be required to fully consume all the CH.

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