Pergamon

Cement and Concrete Research, Vol. 28, No. 6, pp. 803–809, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00045-3

METAKAOLIN AS A POZZOLANIC MICROFILLER FOR HIGH-PERFORMANCE MORTARS

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(Received March 5, 1998; in final form March 30, 1998)

ABSTRACT

Superplasticized mortars containing metakaolin (MK) as 15% replacement of cement and with a water/binder ratio of 0.33 have been characterized. Four commercially available MK samples have been studied and compared to silica fume. Three of the four MK samples give, at early ages, a compressive strength enhancement that is more pronounced than that of silica fume. The fourth and coarser sample gives a lower strength at early ages, but at 90 days and later the difference is reduced. Compressive stength enhancement differences between the specimens with microfillers and the control decrease after 28 days, as the control shows a slighter slowdown of the hydration rate. The DTA calcium hydroxide peak heights show that three of the MK samples have a remarkable pozzolanic activity, comparable to that of silica fume even if slightly lower at longer ages. A 24-h treatment at 90°C of the mortar specimens, after a 7-day moist room curing, causes a loss of water whose extent is different for all types of specimens and can be related to the fineness of the microfiller for the MK-containing specimens.

Introduction

Metakaolin (MK) is a supplementary cementing material for high-performance concrete and mortars (1–5). Its properties and uses as a pozzolanic microfiller are similar to those of silica fume (SF). However, while SF is widely used and the related literature is abundant, MK has been to date much less studied, although interest in its applications has been growing in the last years. Ambroise et al. (6) followed the concentration of CH in the hydration of C_3S and ordinary Portland cement in presence of MK and identified the reaction products. Compressive strength and durability is improved when 10–20% by weight of cement is replaced by MK (3–5). The suppression of alkali silica reaction by MK has been also reported (7). Zhang and Malhotra (4) have compared the mechanical properties and the durability of MK-containing concrete with those of SF concrete. Recently Wild et al. (8) have concluded that

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Communicated by F. Massazza.
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TABLE 1
Properties of cement, metakaolins, and silica fume.

	Cement	MK1	MK2	MK3	MK4	SF
Specific gravity, g/cm^3	3.10	2.50	2.50	2.50	2.50	2.22
Specific surface, Blaine m^2/kg	476	—	—	—	—	—
Composition, weight %						
SiO_2	20.77	51.89	51.42	55.0	53.0	96.0
Al_2O_3	5.02	43.52	44.81	40.0	44.0	0.3
Fe_2O_3	2.43	1.49	1.15	0.6	1.0	0.2
CaO	64.52	—	—	<0.1	0.1	0.3
MgO	1.23	0.48	0.43	0.4	0.3	0.5
K_2O	0.90	0.27	0.22	2.4	2.0	0.4
Na_2O	0.48	0.36	0.25	<0.1	<0.1	0.3
SO_3	3.43	—	—	—	—	—
LOI	1.16	0.94	1.08	—	—	0.2

the influence of MK on concrete strength is confined to the first 2 weeks of age. Mercury intrusion porosimetry studies indicated that MK incorporation brings about a significant decrease of the average pore size (6,9).

In this work, we have prepared and characterized mortars incorporating metakaolins of different origin and fineness, together with a control mortar and one containing SF. To emphasize the comparative aspect of the work, all mortars had the same composition and were mixed with the same amount of water.

Experimental

Materials

A Portland cement classified as CEM I 52.5 R (European standard ENV 197/1) was used. The metakaolins, hereafter indicated as MK1, MK2, MK3, MK4, are commercially available products, as is silica fume (SF). Compositions are given in Table 1. Alluvial siliceous-type sands were used as aggregates, a coarser one (0.5–4 mm) and a finer one (0.065–0.5 mm). Both were washed and dried at room temperature to the free flowing state before use. The naphtalene sulphonate formaldehyde-based superplasticizer and the deaerating agent employed are both commercially available powders.

Procedures

The mix proportions are reported in Table 2. M1, M2, M3, M4, and S contain 5% of MK1, MK2, MK3, MK4, and SF respectively, corresponding to a cement replacement level of 15%. The water was 11% of dry weight for all mixes, which gives a water/binder ratio of 0.33. The mortars were mixed in a Hobart-type laboratory apparatus for 10 min. and cast into 40 × 40 × 160 mm molds, which were stored at 20°C and relative humidity >98%. The specimens

TABLE 2
Dry mix compositions (weight %).

Mix	C	M1	M2	M3	M4	S
Cement	33.0	28.0	28.0	28.0	28.0	28.0
Microfiller	—	5.0	5.0	5.0	5.0	5.0
Fine sand	23.0	23.0	23.0	23.0	23.0	23.0
Coarse sand	42.2	42.2	42.2	42.2	42.2	42.2
Superplasticizer	1.0	1.0	1.0	1.0	1.0	1.0
Deaerating agent	0.8	0.8	0.8	0.8	0.8	0.8

were demolded after 24 h and left in the moist curing room until compressive strength measurement were carried out after 7, 28, 90, and 180 days. Pozzolanic activity was determined on mixtures of 80% cement and 20% MK or SF according to EN 196/5. In this method the concentration of calcium hydroxide in the liquid that has been in contact with the binder at 40°C for a given time (usually 8 days, as in this work) is compared with that of a saturated solution of the same alkalinity at the same temperature taken as unity. Setting measurements were performed, with the usual Vicat needle method, on the mixes without the aggregates and employing the same amount of water for all the samples (120 g for 500 g of solids). Density, air content, and flow table spreading (15 drops) of the fresh mortars were measured with the usual standard methods.

Immediately after the samples had been broken in the compressive strength test, a few grams were taken from the inner part, ground, and used for thermal analysis. A part of the samples, after 7 days curing in the moist room, was treated for 24 h at 90°C and the weight loss was determined.

Results and Discussion

Densities of the mortars were 2400 Kg/m^3 (C), 2370 Kg/m^3 (S), and 2380 Kg/m^3 (M1-M4). Air content was in the range 0.5–1.5%, setting times 185–200 min. (initial) and 305–320 min. (final). In Table 3, the weight loss after 24 h at 90°C per single 40 × 40 × 160 mm specimen

TABLE 3
Some properties of the mortars and the relative microfillers.

Properties of the mortars			Properties of microfillers		
Mix	Weight loss at 90°C, g	Flow table spreading, %	BET m^2/g	Bulk density (kg/m^3)	Pozzolanic activity
C	20.4	176	—	—	—
S	14.4	140	18.2	205	0.16
M1	12.2	130	19.8	245	0.23
M2	12.5	142	13.9	365	0.21
M3	12.9	138	14.7	417	0.24
M4	14.1	162	12.7	512	0.47

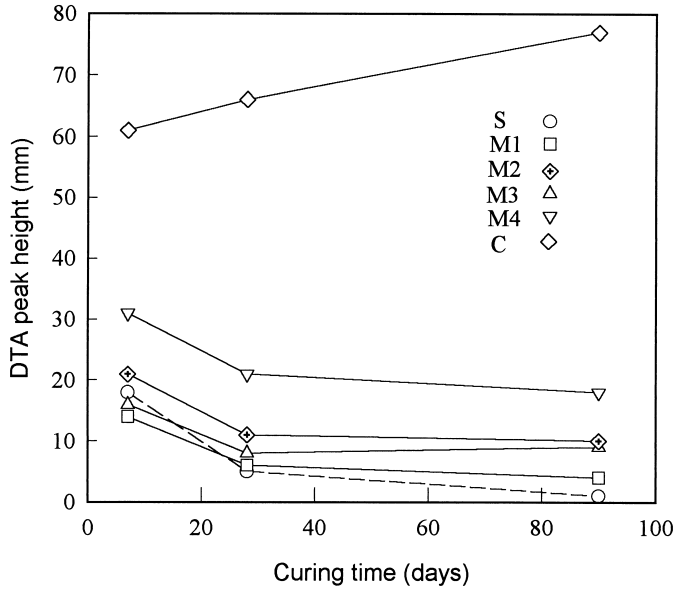

FIG. 1.
DTA $Ca(OH)_2$ peak height vs. curing time.

and the flow table spreading for the six mixes are reported. Pozzolanic activity, measured as described above, bulk density and BET specific surface area of the microfillers are also given.

The weight loss data are the averages of three measurements referring to different preparations and each carried out on two specimens. They are highly reproducible (within ± 0.2) and indicate a definite pattern over the six mixes. Such a pattern is preserved if the temperature is 105°C or the time is 48 h, the figures being obviously different. The water content of each specimen is about 60g, so the losses are 34.0% (C), 24.0% (S), 20.3% (M1), 20.8% (M2), 21.5% (M3), and 23.5% (M4). The removal of water takes place above all from the outer part of the sample, down to a depth of about 10 mm from the surface, as can be seen in the broken specimens. For a given mix composition and water/binder ratio, and a fixed room temperature curing time before the 90°C treatment, the extent of water loss depends on the permeability of the medium and on the amount of uncombined water. SF and MK accelerate cement hydration (5,9,10), a fact that brings about a faster decrease in the amount of free water. The drastic reduction of the amount of CH due to the high pozzolanic activity of the microfillers and the formation of a C-S-H with a very fine microstructure determine a pore refinement and a reduced permeability. A similar situation has been described for cement pastes containing fly ashes (11). The larger loss of the control sample (C) is easily explained on the basis of the above considerations. The difference between S and M1 can be attributed to the different hydrated species that are formed, assuming a similar pore structure in the two samples, which seems reasonable in view of a comparable fineness of SF and MK as inferred from BET specific surface area and bulk density. On the other hand, the different fineness of the four metakaolins, clearly resulting from Table 3, gives differences in the reactivities, in the pore size distributions, and, therefore, in the permeabilities of the resulting materials. DTA and compressive strength data at the 7-days curing time (Fig. 1 and 2) seem

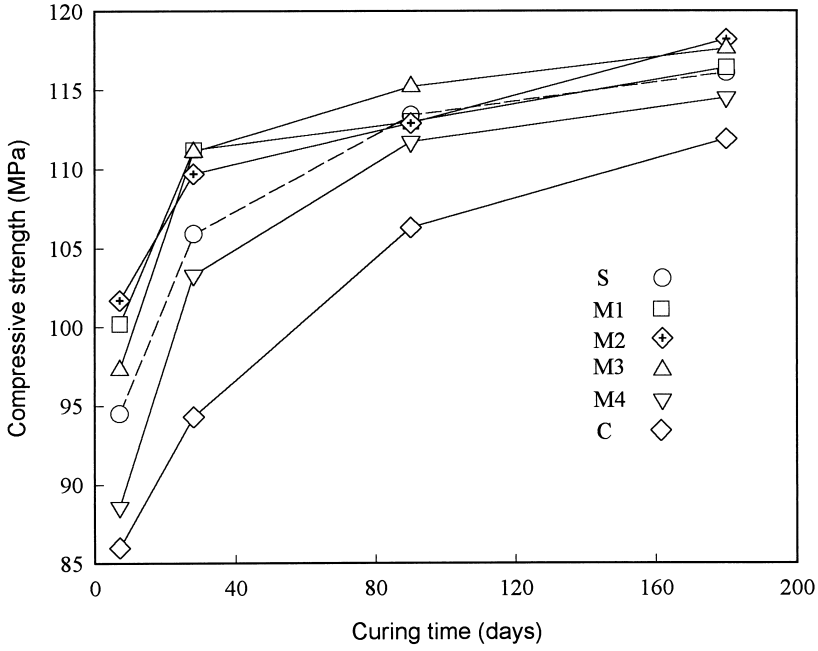

FIG. 2.
Compressive strength vs. curing time.

to indicate that differences in the reactivities are present.

The flow table test indicates that the coarse MK4 does not change much the workability of the mix, while the influence of MK1 is noticeable. MK1, MK2, and MK3 have identical pozzolanic activity, only slightly lower, if any, than SF, while MK4 is less active.

Figure 1 reports the height of the DTA peak of CH, occurring around 485°C, as a function of the curing time for the six mixes. The drastic decrease of the intensity of the peak caused by the microfillers is apparent, in substantial agreement with the pozzolanic activity data. The 180-days data, not reported, are the same as those at 90 days. The amount of CH changes very little after 28 days for the samples with metakaolins, slightly more for that with SF. MK1, MK2, and MK3 have a remarkable pozzolanic activity, comparable to that of SF, even if slightly lower at longer ages. MK4 has a lower, but not at all negligible, activity.

The compressive strengths vs. curing time are reported in Figure 2. The spread of the data at earlier ages can be readily seen. The finer and more reactive metakaolins (MK1, MK2, MK3) give a faster strength development than SF at 7 and 28 days. A similar behavior has been noticed by Zhang and Malhotra (4) and can also be inferred from the comparison of the data on MK and those on SF of Wild et al. (8,12). MK4 is the least active, but it comes close to the others at 90 days and later. From the data on of the specific surface area (Table 3) a lower reactivity at short ages of MK4 is not unexpected. The compressive strength curves of M1, M2, and M3 parallel those of the CH peak heights from DTA measurements (Fig. 1); after 28 days there is a slow increase in strength and a slow decrease of CH. The difference between the samples with the microfillers and the control decreases after 28 days. This can be ascribed to a smaller slowdown of the hydration for the control sample. The presence of microfillers with pozzolanic activity gives an accelerated hydration at early ages and gen-

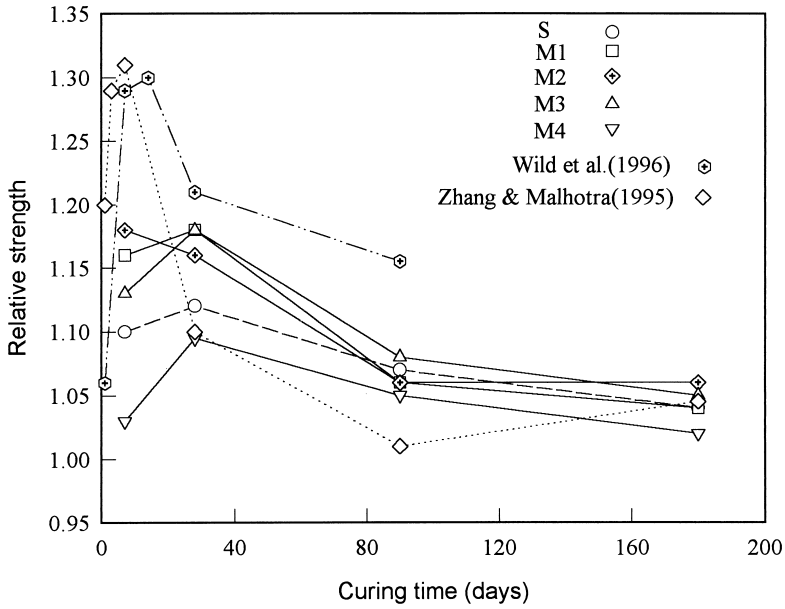

FIG. 3.
Relative strength vs. curing time.

erates a denser microstructure with fine pores and low water permeability. In this situation there is less available water with a lower mobility and, as a consequence, a lower hydration rate at longer curing times.

The higher rate of strength development at earlier ages of MK as compared to SF may seem surprising. On the basis of the data on specific surface area and pozzolanic activity one would expect a similar, if not higher, reactivity for SF. The initial higher reactivity of MK is most likely due to its Al_2O_3 moiety, which is known to contain 4- and 5-coordinated Al (13). The formation of alumina containing phases, particularly C_2ASH_8 (hydrated gehlenite), has been established (6,14).

The data of Figure 2 can be plotted as relative strengths (ratios of the strengths to that of the control sample) (Fig. 3). This facilitates the comparison with the results for the 15% sample of Wild et al. (8) reported in the graph. The points obtained from the data for a 10% cement replacement sample of Zhang and Malhotra (4) are also included. It can be clearly seen that the peak at ages below 28 days is much more pronounced for the data from both papers. Unfortunately our work had been planned without the 14-days measurements; however, the 7-days data seem adequate for the comparison. Our samples are quite different from those of refs. 4 and 8. One could mention the water/binder ratio (0.33 vs. 0.40 and 0.45), the amount of cement in the mix (33% vs. 14.8% and 16.6%), and the air content (0.5–1.5% vs. 5.6%). However, the difference in the relative strength patterns at shorter curing ages seems to depend mainly on the type of cement employed. Both Wild et al. (8) and Zhang and Malhotra (4) used an ordinary Portland while we used an “early strength” Portland (52.5 R as defined by ENV 196/1). From Figure 3 we see that a 10–15% cement replacement by MK increases the compressive strength at 1–14 days, with respect to the control sample, of about 30% with ordinary Portland cement and of 10–20% with an “early strength” Portland.

Conclusions

From our work on mortars with 15% cement replacement by four metakaolin products several concluding remarks can be made.

Specimens containing three of the four metakaolin samples have a higher rate of compressive strength development as compared to that of the control at ages below 28 days, a consequence of the higher hydration rate. Silica fume and the fourth and coarser metakaolin have a less pronounced effect. At 90 and 180 days metakaolin and silica fume specimens give similar strengths.

The difference in the compressive strength between the specimens with microfillers and the control decreases after 28 days, because of a smaller slowdown of the hydration rate in the control.

The extent of strength enhancement at short curing ages is influenced by the type of cement; it is lower for early strength Portland as compared to ordinary Portland.

The DTA calcium hydroxide peak heights on mortars and the pozzolanic activity test on mixtures of 80% cement and 20% microfiller show that three of the four metakaolins have a remarkable pozzolanic activity comparable to that of silica fume, even if slightly lower at longer ages. The fourth and coarser metakaolin sample is less reactive.

The amount of water that is lost after 24 h at 90°C is different for all types of specimens and is dependent on the differences of the hydration products formed and on the permeability of the materials. It can be related to the fineness of the microfiller in the specimens with metakaolin.

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