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RELATIVE STRENGTH, POZZOLANIC ACTIVITY AND CEMENT HYDRATION IN SUPERPLASTICISED METAKAOLIN CONCRETE

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ABSTRACT

The role of metakaolin (MK) in enhancing the strength of concrete is reviewed and the principal mechanisms identified. Metakaolin concretes with a range of MK contents (0-30%) have been cured for periods of 1 to 90 days. The change in relative strength with both curing time and metakaolin content is discussed in relation to the 'filler effect', acceleration in OPC hydration and the pozzolanic reaction. The observed results establish that there is an optimum OPC replacement level of 20 wt% MK and that the contribution which MK makes to strength is restricted beyond 14 days. *Copyright © 1996 Elsevier Science Ltd*

Introduction

The manner in which finely divided highly active pozzolans such as condensed silica fume (CSF) and metakaolin (MK) influence the rate of strength development of concrete is highly complex.

Replacement of cement in concrete by mineral admixtures produces an immediate dilution effect such that if the replacement material was totally physically and chemically inert, concrete strength would be reduced in approximate proportion to the degree of replacement. However, finely divided mineral admixtures, even if chemically inert, do have a physical effect in that they behave as fillers. This is particularly significant in the interfacial zone regions where they produce more efficient packing at the cement paste-aggregate particle interface, reduce the amount of bleeding and produce a denser, more homogeneous, initial transition zone microstructure and also a narrower transition zone [1,2]. Thus relative to no cement replacement, partial replacement by ultra-fine solids results in a reduction in the strength of pastes (due to the dilution effect) but an increase in the strength of concrete (due to an improved transition zone).

If the finely divided mineral replacements are highly active pozzolans such as CSF or MK then they rapidly remove calcium hydroxide (CH) from the system and accelerate the ordinary Portland cement (OPC) hydration. This is apparent from observations that in the very early stages of curing CH contents (expressed as a percentage of the OPC content) are often of the same order or higher in OPC-CSF mortars and pastes [3] and OPC-MK mortars and pastes [4] than in the equivalent OPC systems whereas they might be expected to be lower due to removal of CH by the pozzolan. The increase in strength resulting from this acceleration in cement hydration will offset, to various degrees the loss in strength due to the dilution effect, particularly at low dilution levels.

The acceleration in OPC hydration is also apparent in the observed increased rates of heat evolution in OPC-CSF and OPC-MK systems. For example, Ambroise et al. [5] attribute the increased temperature rise of metakaolin mortars relative to that of plain OPC mortar to the accelerating effect of metakaolin on OPC hydration. It is significant to note that the maximum observed temperature rise occurs for 10% replacement of OPC by MK. Zhang and Malhotra [6] also observed enhanced temperature rises in MK concrete (10% replacement) and CSF concrete (10% replacement) relative to plain concrete. They however attribute the particularly high and early temperature rise of the MK concrete to the high reactivity of MK with CH. This explanation of the increased level of early heat evolution is also put forward by Sanchez de Rojas and Frias [7] in their study of the heat of hydration of mortars containing different silica fumes. They attribute the observed fall in heat output at CSF replacement levels above 10% (which gives maximum heat output) as being due to the predominance of the dilution effect over the heat output from the pozzolanic reaction. These two different explanations are, however, not incompatible in that there is good evidence that finely divided pozzolans, which react exothermically with CH [8] contribute to early heat evolution both by accelerating the hydration of OPC [3,5] and by rapidly reacting with CH released by the OPC hydration [9].

The degree to which each reaction contributes to the heat output (and also to the strength development) at a particular time will depend on both the enthalpy changes [8] and the kinetics of the two reactions. Also, it is the OPC hydration reaction that supplies the CH which feeds the pozzolanic reaction. This fact, coupled with the observations of a number of authors [5,7] that within the first forty-eight hours the peak observed in heat evolution is at its highest for 10% OPC replacement by pozzolan and then falls for higher replacement levels, suggest that in the very early stages of reaction, acceleration in OPC hydration is the predominant contributor to enhanced heat output and hence to increased strength development.

The efficiency of both reactions relies on effective and even dispersion of the two binders, a problem commented upon by numerous authors [3,4,5,6,9] who also emphasise that high levels of replacement of both CSF and MK substantially increase water demand. The dispersion and workability problems are, however, effectively overcome by use of superplasticisers. Wild et al. [9] have shown that in a well dispersed superplasticised CSF concrete, relative strength at extended ages (90 days) increases systematically with increase in CSF level up to at least 28% replacement. However, the initial increase in relative strength with curing time exhibited at all replacement levels studied is not maintained beyond 28 days for replacement levels below 20% and relative strength only continues to increase with curing time beyond 28 days for CSF replacement levels above 20%. This behaviour is explained in terms of the increased time required for an inhibiting layer of reaction product to form around CSF particles as the CSF level increases. At elevated curing temperatures (50°C) very rapid acceleration of OPC hydration occurs and the effects of the two reactions are more clearly resolved on relative strength curing time plots. Thus, as the CSF level increases, a well defined minimum develops on relative strength curing time curves at about 7 days, separating the effect of the early, highly accelerated OPC hydration from the later optimum effect (14-21 days) of the CSF-CH reaction.

Metakaolin, which like CSF is an ultra-fine highly active pozzolan, might be expected to behave in a similar way to CSF when replacing OPC in concrete. The object of the current

TABLE 1
Composition of Cement and Metakaolin

Oxide	Cement (mass%)	Metakaolin (mass %)
SiO_2	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

study is to determine the manner in which metakaolin replacement of OPC in concrete influences relative strength-curing time profiles and relate the observed behaviour to the reaction processes occurring.

Experimental Work

Materials. The materials used were as follows: Ordinary Portland Cement complying with BS12:1989. Metakaolin supplied by ECC International (Europe) under the commercial name 'Metastar'. Compositions are given in Table 1. The specific surfaces were $363m^2/kg$ (OPC) and $12000m^2/kg$ (MK).

The sand used was a fine natural sea dredged sand which complied with grade F of BS882:1983 and 10mm and 20mm size crushed limestone aggregate was employed. The superplasticiser used was Cormix SP1 which is a Naphthalene Sulphonate based liquid superplasticiser with a 60% water content and a density of $1.19g/cm^3$.

Mix Design, Workability and Strength Testing. Replacement levels of OPC by MK chosen for the concrete mixes were 0, 5, 10, 15, 20, 25 and 30% and the water to binder ratio (w/b)

TABLE 2
Mix Proportions (kg/m^3), Water/Binder = 0.45

Binder		Aggregate				Superplasticiser
MK (kg/m^3)	OPC (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	10mm (kg/m^3)	20mm (kg/m^3)	SP1 (wt% of binder)
0	350.2	157.6	810.4	360.2	840.4	0.0
17.5	332.2	157.3	809.2	359.7	839.2	0.6
34.9	314.2	157.1	808.0	359.1	837.9	1.2
52.3	296.3	156.9	806.8	358.6	836.7	1.8
69.6	278.5	156.7	805.6	358.1	835.5	2.4
86.9	260.7	156.4	804.5	357.5	834.3	3.0
104.1	243.0	156.2	803.3	357.0	833.0	3.6

TABLE 3
Workability of Metakaolin Concretes

MK (mass%)	SP1 (mass% of binder)	Slump (mm)	Compacting Factor	Vebe Time (seconds)
0	0	5	0.81	26
5	0.6	10	0.84	15
10	1.2	15	0.88	10
15	1.8	25	0.89	9
20	2.4	75	0.89	7
25	3.0	75	0.89	4
30	3.6	90	0.90	5

used was 0.45. This value does not include the small amounts of water contributed to the mixes by the superplasticiser. The amount of superplasticiser added to each mix was in direct proportion to the amount of metakaolin replacement, in order to offset the increased water demand at increased metakaolin levels. The mix proportions based on a constant mix volume of $1m^3$ are given in Table 2. The superplasticiser which is added as a percentage by weight of binder is in addition to this.

In order to ensure good dispersion of the metakaolin, the specified amounts of metakaolin and superplasticiser were first mixed with the water and stirred to produce a slurry which was added to the coarse aggregate and mixed for 1 minute (see Massazza [10]). The sand was then added and mixed for 2 minutes and finally the cement was added and mixed for a further 2 minutes. The concrete was cast under vibration into 100mm cube moulds which were then covered by cling film and demoulded after 24 hours. For the lower workability mixes, particularly the control mix, additional vibration was used to ensure full compaction. Three cubes were then tested in compression for each mix. The remaining cubes were cured in water at 20 ± 1°C and three cubes from each mix were tested in compression to BS1881:1983 at ages of 7, 14, 28 and 90 days. Densities were also determined by displacement. Also standard workability tests were performed on the concrete in compliance with BS1881 pt.102:1983 (slump), pt.103:1993 (compacting factor) and pt.104:1983 (Vebe).

TABLE 4
Compressive Strengths and Densities of Metakaolin Concretes

MK (%)	Density (kg/m^3)	Compressive strength (N/mm^2)				
		1 day	7 days	14 days	28 days	90 days
0	2490	19.07	50.23	57.10	62.60	72.43
5	2440	21.50	53.80	58.97	63.50	71.63
10	2460	22.43	62.30	69.23	71.00	80.07
15	2470	20.23	64.80	74.67	76.00	83.70
20	2480	19.33	66.47	75.73	82.47	85.13
25	2470	15.73	62.50	69.77	73.93	82.23
30	2480	14.53	60.53	72.33	76.73	81.80

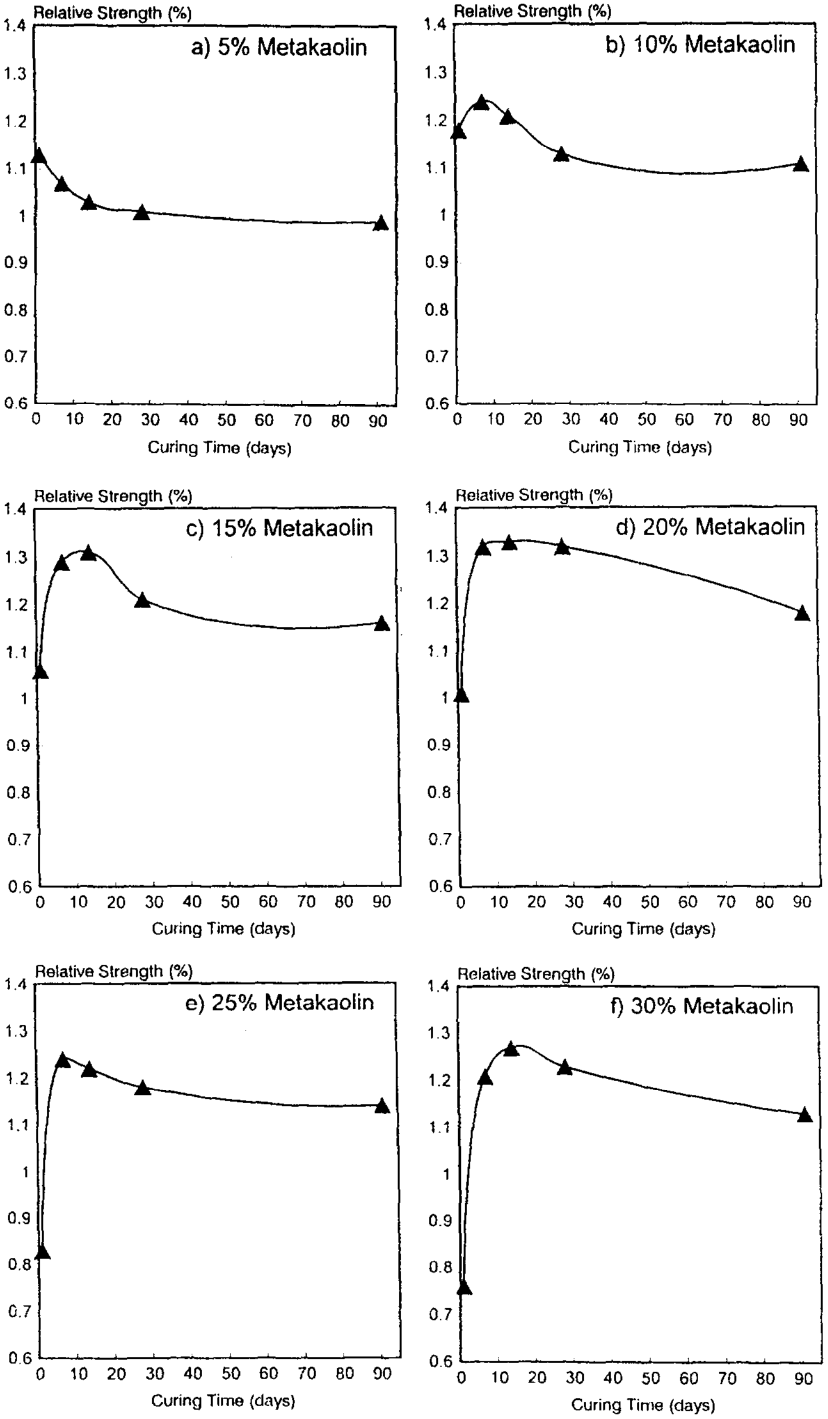

FIG. 1.
Relative strength versus age for metakaolin concrete with different metakaolin contents.

Results and Discussion

Table 3 gives the slumps, vebe times and compacting factors for the different mixes. Table 4 gives the densities and cube compressive strengths of the different concretes. Each strength value is the average of 3 tests (individual values varied to within ±5% of the mean). Each density value is the average measured density of all 15 cubes for that particular mix (individual values varied to within ±1% of the mean).

Figure 1 gives plots of relative strength versus curing time at the different metakaolin contents. Relative strength is the ratio of the strength of the metakaolin concrete to the strength of the control concrete at each particular curing time. As the gain in strength with time for OPC concrete is principally dependent on the rate of OPC hydration and that for OPC-MK concrete is principally dependent on a combination of the rates of OPC hydration and the MK-CH reaction, relative strength-time plots provide an insight into the rates of reaction in the blended system relative to the plain OPC system.

For 5% replacement, (see Figure 1a) the dilution effect and the contribution by any pozzolanic reaction would be expected to be very small as also would any filler effect [1] and these would tend to be self compensating. Therefore the fact that relative strength starts at above 1 (at 1 day) and shows a continuous and smooth reduction to slightly below 1 at 90 days suggests that the early enhancement in relative strength is principally a result of the initial acceleration in OPC hydration, the effect of which is lost at extended curing times. Further increase in metakaolin level results in the development at between 7 and 14 days, of a maximum in relative strength. This maximum has previously been reported by Wild et al. in paste [4], mortar [4] and concrete [11] systems containing metakaolin. It corresponds to a minimum in CH content, and is interpreted [4] in terms of a maximum in the rate of pozzolanic activity. Subsequently relative strength declines and tends to approach a constant value by 90 days.

The effect that metakaolin content has on relative strength at both 90 days and 1 day is illustrated in Figure 2. At 1 day (Figure 2a) where the contribution due to pozzolanic activity

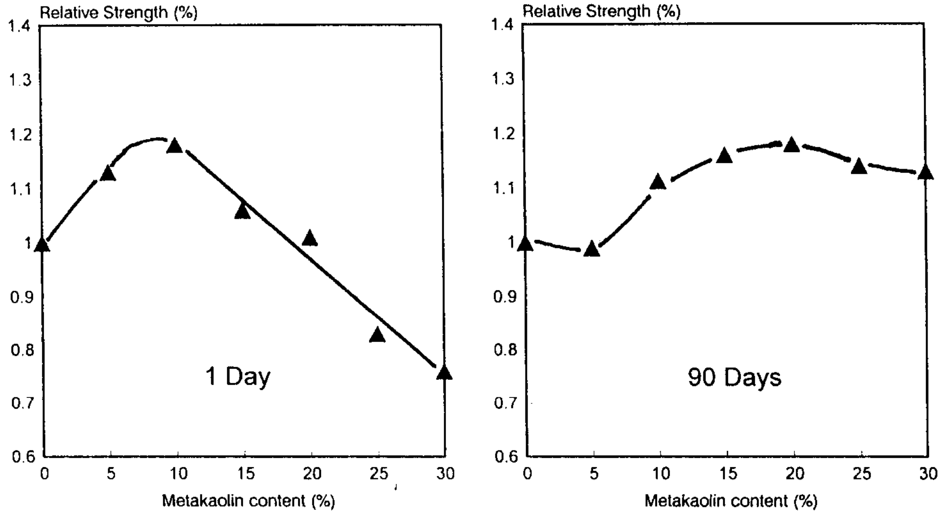

FIG. 2.

Relative strength versus metakaolin content at (a) 1 day and (b) 90 days.

is expected to be small, relative strength increases with increase in MK content up to a maximum of 1.18 at 10% replacement, and then falls linearly to 0.76. The increase in relative strength at 1 day is interpreted as being due principally to the increased acceleration of OPC hydration combined with the contribution from the filler effect, and the fall in relative strength at high MK contents must clearly be a result of the dilution effect. At 90 days all cementitious reactions are close to completion and the short term effect of strength enhancement due to acceleration of OPC hydration has been lost. Therefore Figure 2(b) represents the long term effect that pozzolanic activity and the filler effect have in enhancing concrete strength.

Unlike the behaviour of concrete containing CSF [9], where there is a continuous increase in relative strength with increase in CSF content up to at least 28% replacement, concrete with metakaolin shows a maximum in relative strength at 20% replacement and then a reduction. This difference results because for silica fume concrete, containing above 20% silica fume, relative strength continues to increase up to at least 90 days whereas for metakaolin concrete relative strength decreases after 14 days regardless of metakaolin content. This indicates that there is a critical change in the CH-MK reaction at around 14 days which inhibits further reaction of MK even though it is in ample supply. Such a change is also apparent from observations of the change in CH content and pore volume of metakaolin mortars and pastes with time. Wild and Khatib have reported that the CH content of metakaolin mortars and pastes [4] drops to a minimum between 7 and 14 days and then increases between 14 and 28 days. This increase in CH content also corresponds with a sudden increase in pore volume [12]. The current observations on concrete therefore confirm and reinforce previous observations on paste and mortar.

Conclusions

The following conclusions can be drawn from the current study.

1. There are three elementary factors which influence the contribution that metakaolin makes to concrete strength when it partially replaces cement in concrete. These are the filler effect, the acceleration of OPC hydration, and the pozzolanic reaction of MK with CH.
2. The filler effect is immediate, the acceleration of OPC has its major impact within the first 24 hours and the maximum effect of the pozzolanic reaction occurs at between 7 and 14 days.
3. The optimum replacement level of OPC by MK to give maximum long term strength enhancement is about 20%. This differs from silica fume which continuously enhances strength at extended ages up to replacement levels of at least 28%.
4. The positive contribution which metakaolin makes to strength enhancement of concrete does not continue beyond about 14 days irrespective of the replacement level. It is suggested that this is a result of an elementary change in the MK-CH reaction beyond 14 days.

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