JOURNAL OF MATERIALS SCIENCE 28 (1993) 1345–1350

# The pozzolanic reaction of metakaolinite and its effects on Portland cement hydration

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Metakaolinite was prepared from kaolinite by thermal treatment. Subsequent reaction of the metakaolinite with calcium hydroxide and water resulted in a cementitious material whose reaction kinetics were followed at a molecular level at both ambient and elevated temperatures using trimethylsilylation. Metakaolinite as a mineral admixture to ordinary Portland cement was also investigated.

## 1. Introduction

The thermally activated clay metakaolinite, ($AS_2$, $A = Al_2O_3$; $S = SiO_2$) acts as a pozzolan in the presence of lime and water to give a cementitious product containing calcium silicate and calcium aluminate hydrates [1].

Trimethylsilylation (TMS) produces $Q_xM_y$ ($Q = SiO_{4/2}$; $M = (CH_3)_3SiO_{1/2}$) polyorganosiloxanes which give information on the polymerization of the original silicate anions present in the silicate hydrate [2]. The study of polycondensation of pozzolanic materials by trimethylsilylation has been restricted to the effects of pulverized fuel ash or silica fume on Portland cement hydration [3, 4]. This is the first attempt at a mechanistic interpretation of the pozzolanic reaction of metakaolinite alone and in the presence of ordinary Portland cement.

The hydration of metakaolinite–calcium hydroxide–water pastes was carried out. Differential thermal analysis (DTA) and TMS revealed the presence of a variety of calcium silicate hydrate phases.

Unhydrated metakaolinite and prehydrated (20 and 95 °C) metakaolinite–lime pastes were added to ordinary Portland cement (OPC) and accelerated the hydration of the cement silicates at ambient temperature. Prehydration did not improve the accelerating efficiency as the effects were indistinguishable to that of unhydrated metakaolinite.

## 2. Experimental procedure

Ordinary Portland cement (Rugby Portland Cement plc) and metakaolinite (54% $SiO_2$), prepared by calcining well-crystallized impure kaolinite (6.5 h, 750 °C), were characterized using infrared spectroscopy, DTA, and XRD.

### 2.1. Preparation of metakaolinite–lime pastes

Metakaolinite was dry-mixed with an equal weight of calcium hydroxide (gpr grade) and a predetermined amount of deionized distilled water. The pastes were mixed by hand and were hydrated under a variety of water/solid ratios and curing conditions (Table I).

Specimens of the type MKCH 1 (see Table I) were moist-cured (4 days, 20 °C), demoulded and stored subsequently in a saturated lime–water solution until required. Specimens of the types MKCH 2 and MKCH 3 were cast in porcelain crucibles and stored in a moist atmosphere (90 °C) prior to analysis.

### 2.2. Preparation of metakaolinite–Portland cement pastes

A metakaolinite–calcium hydroxide–water paste (water/solid 0.94) was hydrated (24 h, 20 °C), crushed, extracted with methanol and dried. The pre-hydrated paste (10.07 g) was tumble mixed with Portland cement (15.00 g), then mixed with water (16.45 g) to give composition PCPH1. These mix proportions were designed to replace the extracted water from the pre-hydrated paste, bring the water/cement ratio to 0.47, and maintain the metakaolinite/cement ratio at 0.33. A similar paste (PCPH2) was prepared where the pre-hydrated paste had been hydrated for 28 days (90 °C).

Specimens were stored (24 h, 20 °C, 100% relative humidity), demoulded and stored prior to analysis in a saturated lime–water solution (20 °C).

### 2.3. Trimethylsilylation analysis

Samples (~ 20 g) were prepared for trimethylsilylation by grinding with 50 ml methanol to remove free water. The powder was vacuum dried (2 mm Hg, 1 h, 20 °C) and then ground to pass a 200 μm sieve. Trimethylsilylation was carried out using modifications in scale to the original method of Tamas *et al.* [5] which are described elsewhere [6]. Insoluble residue was separated by filtration and washed with chloroform.

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TABLE I Mixing proportions and hydration conditions of pastes containing metakaolinite

| Paste number | Constituents (wt %) | | | | | W/S[a] | Ratio of solid constituents by weight[b] | Curing conditions |
|---|---|---|---|---|---|---|---|---|
| | $H_2O$ | CH | Metakaolinite | Portland cement | Pre-hydrated paste | | | |
| MKCH 1 | 48.5 | 25.8 | 25.8 | – | – | 0.94 | MK:CH = 1:1 | 20 °C humid cure and immersion |
| MKPC | 32.0 | – | 17.0 | 51.0 | – | 0.47 | MK:OPC = 1:3 | 20 °C humid cure and immersion |
| MKCH 2 | 48.5 | 25.8 | 25.8 | – | – | 0.94 | MK:CH = 1:1 | 90 °C humid cure |
| MKCH 3 | 65.3 | 17.4 | 17.4 | – | – | 1.88 | MK:CH = 1:1 | 90 °C humid cure |
| PHPC 1[c] | 48.4 | – | – | 30.9 | 20.7[c] | 0.93 | PH:OPC = 1:0.7 | 20 °C humid cure |
| PHPC 2[d] | 48.4 | – | – | 30.9 | 20.7[d] | 0.93 | PH:OPC = 1:0.7 | 20 °C humid cure |

[a] Water/solids ratio.

[b] MK, metakaolinite; OPC, ordinary Portland cement; CH, calcium hydroxide; PH, prehydrated calcium hydroxide/metakaolinite paste used as an admixture.

[c] Prehydrated paste is an MKCH 1 type paste hydrated for 24 h.

[d] Prehydrated paste is an MKCH 2 type paste hydrated for 28 days.

The soluble polyorganosiloxanes were quantitatively analysed by high-performance liquid chromatography (h.p.l.c.) using a Waters Associates model 501 chromatograph fitted with seven microstyrogel columns with toluene as the mobile phase. Tert-butylbenzene was employed as an internal standard and the system recalibrated every week for molecular weight accuracy using polyorganosiloxanes derived from the mineral suzorite, a phlogopite-type mica.

Differential thermal analysis of the methanol-extracted pastes was carried out using a Stanton Redcroft DTA 673-4 instrument equipped with platinum crucibles and alumina as the reference material. Calcium hydroxide was determined by comparison of the height of the calcium hydroxide decomposition endotherm at about 450 °C with a calibration curve plotted using mixtures of calcium hydroxide and alumina.

## 3. Results and discussion

### 3.1. The hydration of metakaolinite–calcium hydroxide pastes

Trimethylsilylation of unhydrated metakaolinite gave very disappointing yields of polyorganosiloxanes of the type. Only 14% of the theoretical yield of soluble product was obtained, which was predominantly $QM_4$ derived from the $SiO_4^{4-}$ anion, together with a large yield of insoluble residual mineral, largely unreacted metakaolinite. However, the trimethylsilylation of the metakaolinite–calcium hydroxide–water (MK–CH–H) paste showed an increase in polyorganosiloxane products with hydration time together with a decrease in the insoluble material (residual mineral + interfacial (see Figs 1 and 2). Both the metakaolinite and unhydrated (MK–CH–H) are fairly unreactive towards trimethylsilylation (Table II). However, on reaction with lime the metakaolinite gives a partially trimethylsilylated material (interfacial) and an increased proportion of polyorganosiloxanes derived from the silicate hydrate phases.

The trimethylsilylation studies of Portland cement hydration have shown that the hydrated silicate phases dissolve fully and are derivatized. On this basis the hydrate phases formed by the pozzolanic reaction are also likely to be totally converted to polyorganosiloxanes leaving unreacted metakaolinite, as shown

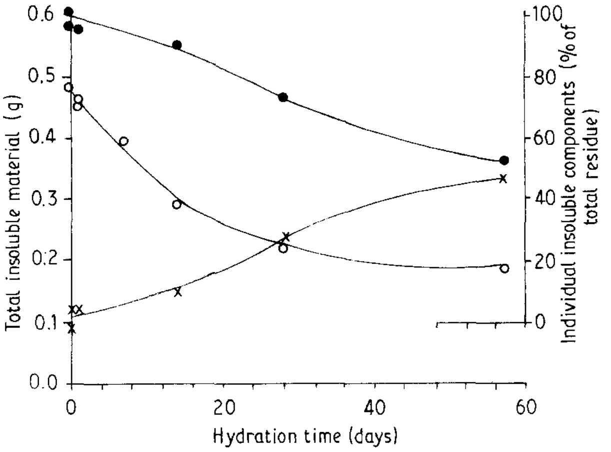

*Figure 1* The variation in amounts of insoluble trimethylsilylation residues formed with hydration time in MK–CH–H pastes. (●) Residual mineral (wt %), (×) interfacial (wt %), (○) total weight of insoluble material (g).

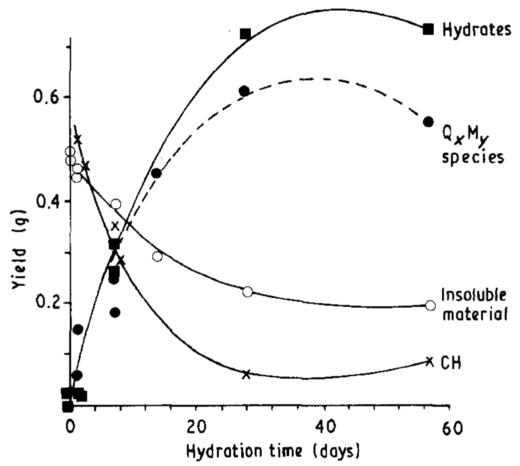

*Figure 2* Graph illustrating the pozzolanic reaction between metakaolinite and calcium hydroxide during the hydration of MK–CH–H paste.

TABLE II Trimethylsilylation of metakaolinite (MK) and unhydrated (MK/CH) mixture. Samples 1 and 2 were trimethylsilylated for 15 min, Sample 3 for 105 min

| Sample | Polymer ($\mathrm{wt\,g^{-1}}$)[a] | Residue ($\mathrm{wt\,g^{-1}}$)[a] | Polyorganosiloxanes (wt %) | | | | |
|---|---|---|---|---|---|---|---|
| | | | $QM_4$ | $Q_2M_6$ | $M_8$ | $M_{10}$ | $> M_{10}$ |
| 1. MK | 0.08 | 1.01 | 78 | 8 | 10 | 4 | 1 |
| 2. MK-CH | 0.18 | 0.50 | 69 | 13 | 14 | 3 | 0 |
| 3. MK-CH | 0.18 | 0.50 | 67 | 12 | 14 | 5 | 2 |

[a] Weight per gram of metakaolinite.

in Table II. The relationship between the amount of calcium hydroxide (CH) present and the unreacted metakaolinite (MK) indicated a stoichiometry of the CH : MK as 5 : 1 which together with a calculation of the amount of bound water present in the hydrates lead to the following equation for the overall pozzolanic reaction

$$AS_2 + 5CH + 5H \rightarrow C_5AS_2H_5 \qquad (1)$$

where $C_5AS_2H_5$ is an average composition representing a mixture of CSH, $C_4AH_{13}$, $C_3AH_6$ and $C_2ASH_8$.

This stoichiometry is similar to that proposed by Murat [1] in the formation of tetracalcium aluminate, tricalcium aluminate, and hydrated gehlenite as shown below

$$AS_2 + 6CH + 9H \rightarrow C_4AH_{13} + 2CSH \qquad (2)$$

$$AS_2 + 5CH + 3H \rightarrow C_3AH_6 + 2CSH \qquad (3)$$

$$AS_2 + 3CH + 6H \rightarrow C_2ASH_8 + CSH \qquad (4)$$

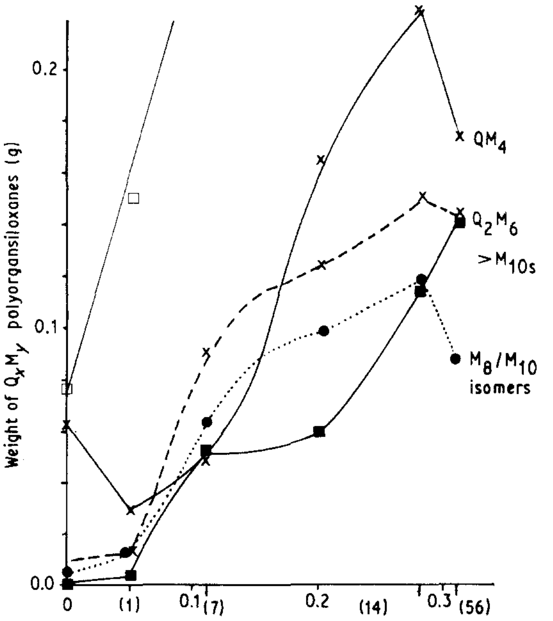

*Figure 3* The variation in the $Q_xM_y$ polyorganosiloxane distribution derived from MK-CH-H pastes with weight of metakaolinite consumed. (□) Total weight of $Q_xM_y$ species, best fit for six points (two shown) correlation coefficient = 0.98. Values in parentheses are hydration times (day), non-linear scale.

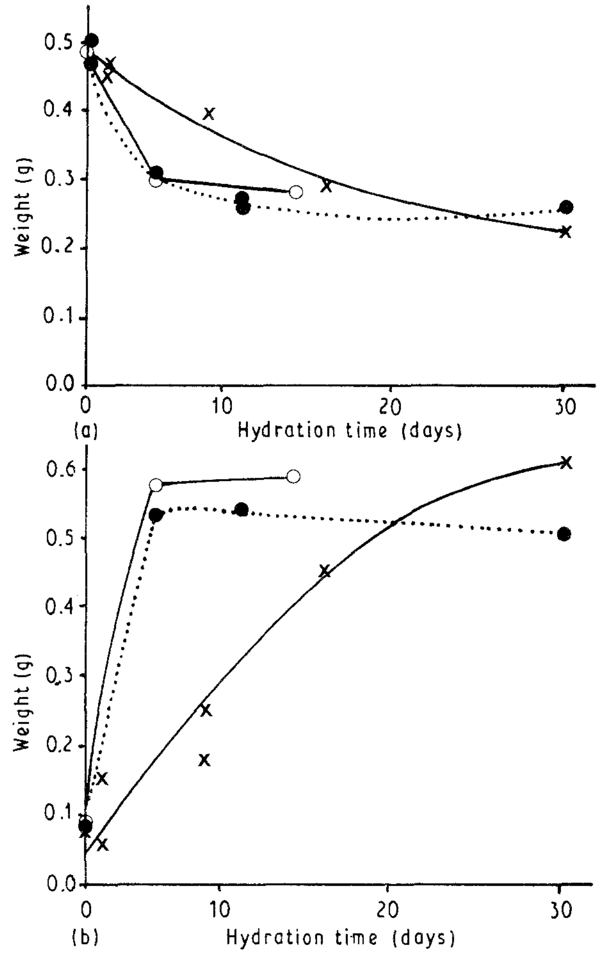

*Figure 4* The weight of trimethylsilylation products derived from MK-CH-H pastes hydrated at 20 and 90° C. (a) Insoluble material, (b) $Q_xM_y$ polyorganosiloxanes. (×) MKCH 1, 20 °C; (○) MKCH 2, 90 °C; (●) MKCH 3, 90 °C.

The absolute amount of polyorganosiloxanes produced is shown against the amount of metakaolinite consumed and time (Fig. 3). This indicates that the reaction between calcium hydroxide and the highly disordered metakaolinite commences within 24 h as the high pH encourages silica solubility [7]. Additionally the presence of aluminium atoms in tetrahedral sites provides break points for the silicate lattice and as Lentz has shown the high pH encourages the formation of $SiO_4^{4-}$ ions [7]. As Fig. 3 shows, the $SiO_4^{4-}$ ions dimerize and precipitate as gehlenite between 24 and 48 h (confirmed by DTA) together with the formation of CSH as shown below

$$2(SiO_4^{4-}) \rightarrow Si_2O_7^{6-} \; (\equiv Q_2M_6) + H_2O \qquad (5)$$

and subsequently

$$SiO_4^{4-} + Si_2O_7^{6-} \rightarrow Si_3O_{10}^{8-} \; (\equiv Q_3M_8) \qquad (6)$$

$$2(Si_3O_7^{6-}) \rightarrow Si_4O_{13}^{10-} \; (\equiv Q_4M_{10}) \qquad (7)$$

$$SiO_4^{4-} + Si_4O_{13}^{10-} \rightarrow Si_5O_{16}^{12-} \; (\equiv Q_5M_{12}) \qquad (8)$$

TABLE III The hydration of calcium hydroxide/metakaolinite at 90 and 20 °C for different ageing times

| | Hydration temperature and type[a] | | | | | | |
|---|---|---|---|---|---|---|---|
| | 20 °C, MKCH1[b] | | 90 °C, MKCH2[c] | | | 90 °C, MKCH3[b] | |
| | 7 days | 14 days | 4 days | 9 days | 9 days | 4 days | 12 days |
| $QM_4$ (%) | 19.6 | 36.9 | 38.0 | 38.5 | 36.5 | 37.3 | 36.3 |
| $Q_2M_6$ (%) | 35.7 | 27.7 | 20.0 | 21.1 | 20.5 | 20.7 | 21.8 |
| $M_8$ isomers (%) | 8.9 | 10.0 | 7.7 | 7.6 | 8.2 | 7.6 | 9.1 |
| $M_{10}$ isomers (%) | 16.9 | 12.0 | 8.3 | 7.8 | 8.2 | 9.1 | 8.4 |
| $> M_{10}$ (%) | 18.9 | 13.1 | 26.0 | 25.0 | 26.6 | 25.2 | 24.3 |
| Total (%) | 100.0 | 99.9 | 100.0 | 100.0 | 100.0 | 99.9 | 99.9 |

[a] See Table I.
[b] w/s = 1.88.
[c] w/s = 0.94.

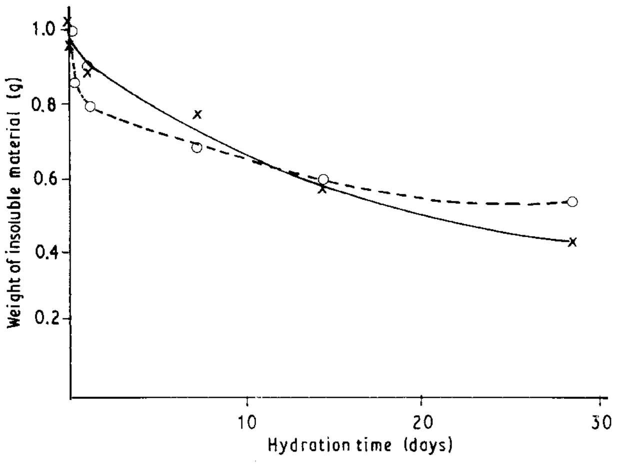

*Figure 5* The variation in the amounts of insoluble trimethylsilylation residues with hydration time obtained from (×) MK–CH–H and (○) OPC–MK–H pastes. Weight of insoluble material recalculated on the basis of equal metakaolinite contents at zero hydration time.

The initial release of $SiO_4^{4-}$ from metakaolinite leads to a ten-fold increase of $QM_4$ in the first 28 days of hydration. As Reactions 5–8 also consume $SiO_4^{4-}$, the production of $SiO_4^{4-}$ ($\equiv QM_4$) is larger and faster than Fig. 4 suggests.

The hydration of MK–CH–H pastes at 90 °C gave a quite different set of hydrate phases and consequently a different molecular weight distribution of polyorganosiloxanes, Table III. The rate of reaction in terms of polyorganosiloxane formation was more than twice that of an equivalent paste at ambient temperatures (see Fig. 4). A wide molecular weight spread of $Q_xM_y$ polyorganosiloxanes than at ambient temperatures was obtained giving a maximum molecular weight of $1.6 \times 10^4$.

A more crystalline form of calcium hydroxide (Type II) was identified using DTA by a peak at 509 °C in addition to the normal Type I at 494 °C. These data for the hydrate phases agree with those quoted by Taylor [8] who reported that a hydrated hydrogarnet $C_3AS_{1/3}H_{5\frac{1}{3}}$ is formed at temperatures > 50 °C in preference to hydrated gehlenite. The formation of crystalline CSH at elevated temperatures has also been reported [9].

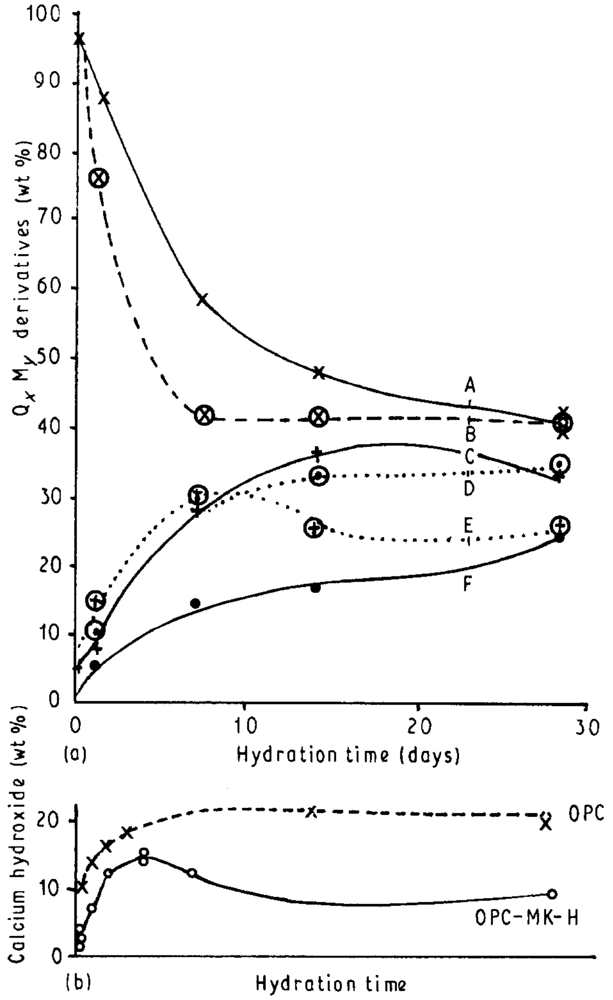

*Figure 6* The variation of (a) $Q_xM_y$ polyorganosiloxane distribution and (b) calcium hydroxide precipitation with hydration time in OPC–MK–H paste. (×) OPC, $QM_4$, A; (+) OPC, $Q_2M_6$, C; (●) OPC, $Q_3M_8$, F; (⊗) OPC–MK–H, $QM_4$, B; (⊕) OPC–MK–H, $Q_2M_6$, E; (○) OPC–MK–H, $Q_3M_8$, D.

## 3.2. The hydration of ordinary Portland cement metakaolinite–water pastes

The results of the investigation into the ME–CH–H pastes were applied to the study of the metakaolinite as a cement admixture as shown in Table I. The cement provides the source of calcium hydroxide and

TABLE IV The effects of metakaolinite on Portland cement hydration

| | Hydration time | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 24 h | | | 14 days | | | 28 days | | |
| | [a] | [b] | [c] | [a] | [b] | [c] | [a] | [b] | [c] |
| $QM_4$ (%) | 87.7 | 86.6 | 76.7 | 47.3 | 44.9 | 41.6 | 41.7 | 39.7 | 40.9 |
| $Q_2M_6$ (%) | 7.7 | 8.1 | 13.8 | 36.0 | 34.1 | 25.2 | 33.8 | 31.2 | 25.0 |
| $M_8$ isomers (%) | 3.3 | 3.5 | 4.4 | 9.3 | 9.5 | 10.1 | 5.3 | 6.5 | 9.3 |
| $M_{10}$ isomers (%) | 1.0 | 1.3 | 3.3 | 6.1 | 7.5 | 10.1 | 10.1 | 10.8 | 10.9 |
| $> M_{10}$ isomers (%) | 0.3 | 0.5 | 1.8 | 1.4 | 4.2 | 12.8 | 9.1 | 11.9 | 14.0 |
| Total (%) | 100.0 | 100.0 | 100.0 | 100.1 | 100.2 | 100.1 | 100.0 | 100.1 | 100.1 |

[a] Ordinary Portland cement.
[b] Calculated composition of polyorganosiloxanes if the cement and metakaolinite were hydrating independently.
[c] Found composition.

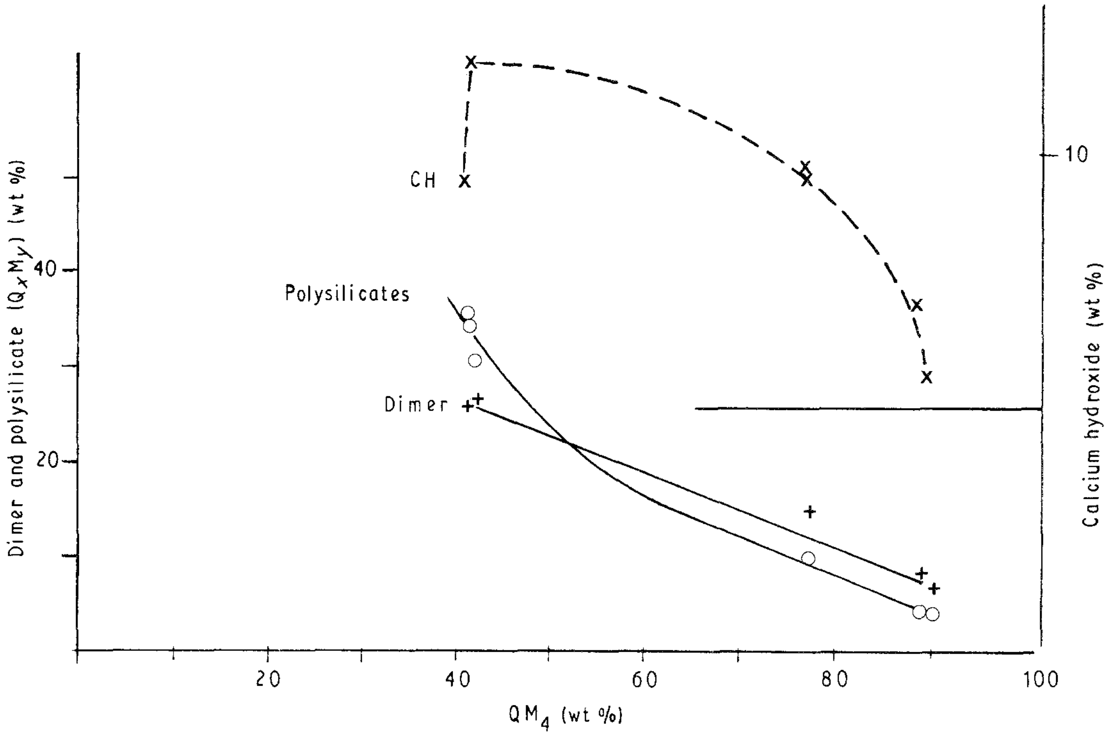

*Figure 7* Results of a time-independent study of silicate anion condensation and calcium hydroxide precipitation during the hydration of OPC–MK–H paste.

the rate of pozzolanic reaction is approximately equal to that observed in the model system (see Fig. 5).

Metakaolinite also significantly accelerates the hydration of silicate pastes in OPC. The acceleration of silicate hydration is a real effect as shown by the differences between the observed composition and the predicted composition if the cement and metakaolinite were hydrating independently as shown in Table IV.

After 24 h hydration, the rate of consumption of $SiO_4^{4-}$ monomer (Equation 5), is faster in the metakaolinite–OPC pastes than in the OPC pastes. After 7 days the amount of dimer has decreased. This phenomenon is accompanied by a reduction in the amount of calcium hydroxide and an increase in the amount of higher molecular weight $Q_xM_y$ polyorganosiloxanes (see Fig. 6).

Obviously the hydration products of OPC–MK–H pastes are derived from two distinct processes, the hydration of OPC, and the pozzolanic reaction between calcium hydroxide and metakaolinite. The cement hydration may be represented as follows:

$$2SiO_4^{4-} \rightarrow Si_2O_7^{6-} + 2OH^- \qquad (9)$$

$$Si_2O_7^{6-} \rightarrow [SiO_3]_n^{2-} \qquad (10)$$

Both these reactions are accelerated during the first 7 days of hydration, and calcium hydroxide released by hydration of OPC is consumed by the pozzolanic reaction, reducing the amounts of calcium hydroxide relative to the control.

These findings are confirmed by a time-independent study. The method of presenting experimental data used here is to plot the percentages of calcium hydroxide, dimer and polymer derivatives against the percentage of orthosilicate derivative $QM_4$. This enables the results to be presented as a time-independent study so that the concept of acceleration is eliminated (see Fig. 7).

The data show that metakaolinite reduces the amount of dimer and increases the proportion of higher molecular weight silicates at a given degree of hydration relative to the control. At higher degrees of hydration ( $< 50\%$ $QM_4$), the polysilicate overtakes the dimer curve and this is accompanied by a sharp reduction of 5% in the amount of calcium hydroxide.

Two types of MK–CH–H paste (which were pre-hydrated at 20 and 95 °C, respectively), were used as cement admixtures (for details of mixing proportions and hydration conditions, see Table I). The hydration of the cement silicates was accelerated although the effect was indistinguishable to that of unhydrated metakaolinite. The admixture which had been hydrated at the higher temperature seeded the formation of two forms of calcium hydroxide (Types I and II). Pre-hydration of metakaolinite therefore influences calcium hydroxide precipitation by seeding crystal nucleation, but does not influence seeding of C–S–H.

## Acknowledgements

The authors acknowledge the funding from the British Technology Group and the gift of Suzorite from Marietta Resources International Limited.

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*Received 13 March*
*and accepted 16 June 1992*