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A conduction calorimetric study of early hydration of ordinary Portland cement/high alumina cement pastes

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Conduction calorimetry was applied to an investigation of the early hydration of ordinary Portland cement (OPC)/high alumina cement (HAC) pastes. Three different rate of heat-evolution profiles were observed, depending on the HAC/OPC ratio. Relevant processes affecting heat development include ettringite formation, HAC and OPC hydration. Results from SEM examination and X-ray diffraction studies are also presented. An acceleration of OPC hydration was observed in pastes containing less than 12.5% HAC. A similar acceleration effect on HAC hydration was also obtained with the addition of OPC. A large amount of ettringite was formed and OPC hydration delayed in the pastes containing 15%–30% HAC. The latter could be one of the factors attributed to poor strength development in these HAC/OPC systems. Early hydration mechanisms of OPC/HAC systems are also discussed.

1. Introduction

Setting of ordinary Portland cement (OPC) mixed with high alumina cement (HAC) occurs rapidly [1–3]. These binary cement mixtures develop strength within a few hours. This characteristic has been utilized in various applications including the sealing of leaks, fabrication of emergency bulkheads, rapid wall and road pavement repair and waste solidification [3, 4]. The longer term strength development is, however, relatively poor. Miller [5] followed the strength development of the binary cement systems up to 1 year. Compressive strength development was slow compared with either pure OPC or HAC. Pure OPC/HAC systems have therefore not been widely used. Chemicals and pozzolanic additives have been used to modify its strength and other properties [6]. The reasons for slow strength development remain unclear.

Scanning electron microscopy revealed that needle-type ettringite formed in a 20%HAC–80%OPC paste within the first 30 min. [7]. It was one of the major factors causing quick-set. A systematic investigation of the OPC/HAC system was undertaken as a basis for development of a rapid-hardening repair material for highway and airport runway repairs. The study addressed (a) hydration mechanism changes associated with OPC/HAC ratio, (b) the hydration process associated with slow strength development; (c) improvement of the strength and microstructure of the binary cement systems by chemical additives. Conduction calorimetry results are presented here to elucidate factors affecting changes in the hydration mechanism with OPC/HAC ratio.

2. Experimental procedure

The OPC and HAC (Fondu) used in this study was obtained from the St Mary's Cement Co. The chemical composition is given in Table I. Pastes containing various percentages of HAC (ranging from 0–100%) were prepared.

A conduction calorimeter manufactured by the Institute of Applied Physics, TNO-TU, Delft (The Netherlands), was employed for all calorimetry measurements. The calorimeter was placed in an isothermal water bath. The voltage signals from each thermopile were recorded by a Datataker DT100 data logger (from Data Electronics Ltd, Australia). The logged data were transferred to a 386 microcomputer and the voltage data converted to calories. Distilled water (4 ml) was added to 10.00 g blended cement giving a w/c ratio of 0.4. The samples were mixed and placed in the calorimeter which was sealed and submerged in a water bath maintained at 20.0 °C. Pastes prepared for SEM and X-ray analysis contained 7.5%, 20% and 80% HAC. A w/c ratio of 0.5 was used. Cold acetone was used to terminate the hydration reactions at selected times.

3. Results

The rate of heat development versus hydration time curves up to 72 h for pastes containing various

TABLE I Chemical composition (mass %) of Type 10 OPC and HAC

	CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
OPC	62.49	4.05	21.82	2.77	3.69	2.48	0.12	0.44
HAC	38.50	39.00	4.50	12.00	0.60	0.15	0.10	0.15

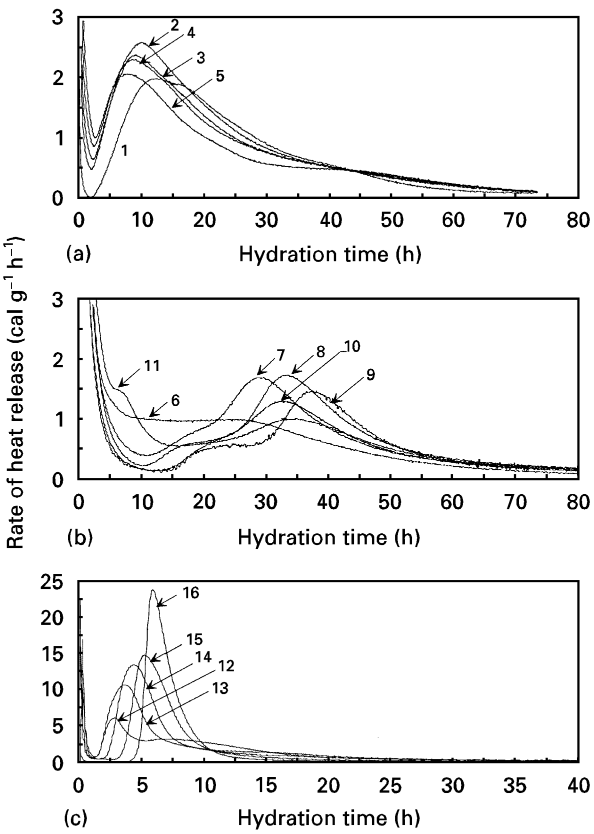

Figure 1 Plots of the rate of heat-development versus hydration time up to 72 h for OPC/HAC pastes containing (a) 0%–10%, (b) 12.5%–30% and (c) 40%–100% at 20 °C (w/c ratio = 0.40). (1) Pure OPC, and pastes containing various percentage of HAC; (2) 2.5% (3) 5%, (4) 7.5%, (5) 10%, (6) 12.5% (7) 15%, (8) 17.5%, (9) 20%, (10) 25%, (11) 30%, (12) 40%, (13) 60%, (14) 70%, (15) 80%, and (16) pure HAC.

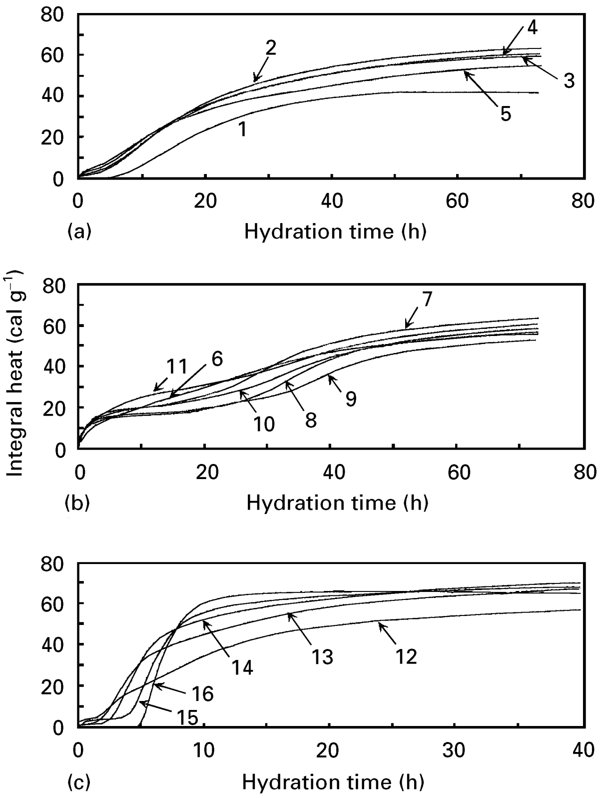

Figure 2 Plots of total heat evolution versus hydration time up to 72 h for OPC/HAC pastes containing (a) 0%–10%, (b) 12.5%–30% and (c) 40%–100% HAC at 20 °C (w/c ratio = 0.40). (1) Pure OPC, and pastes containing various percentage of HAC; (2) 2.5% (3) 5%, (4) 7.5%, (5) 10%, (6) 12.5% (7) 15%, (8) 17.5%, (9) 20%, (10) 25%, (11) 30%, (12) 40%, (13) 60%, (14) 70%, (15) 80%, and (16) pure HAC.

percentages of HAC ranging from 0%–100% are illustrated in Fig. 1a–c, respectively. Plots of total heat evolution versus time for the corresponding pastes shown in Fig. 1 are given in Fig. 2a–c. The heat-evolution pattern changes as the amount of HAC increases. The experimental observations are described below.

3.1. Pastes containing less than 12.5% HAC

The heat-evolution behaviour of OPC/HAC cement pastes containing 2.5%, 5%, 7.5% and 10% HAC (curves 2–5, Fig. 1a) is very similar to that of pure OPC paste (curve 1). The curves exhibit an initial exotherm within the first hour of hydration, attributed to complex reactions occurring during the wetting process. These reactions include hydration of free lime, formation of low Ca/Si ratio C–S–H and ettringite. Only part of the exothermic peak was recorded in Fig. 1a owing to the time requirement for the pre-mixing procedure outside the calorimeter. The induction period associated with pure OPC paste hydration is about 2.5 h. This is followed by an exothermic peak associated with C_3S and/or C_2S hydration. The maximum values of the rate of heat evolution for pastes containing 0%, 2.5%, 5.0%, 7.5% and 10% HAC are 1.99, 2.58, 2.37, 2.30 and 2.05 cal g^{-1} h^{-1} respectively, and the corresponding times are at 12.6, 10.1, 9.1, 9.1 and 8.5 h. The total heat-evolution curves of these pastes (curves 2–5, Fig. 2a) are very similar to pure OPC (curve 1, Fig. 2a). An enlarged plot of total heat from 0–2 h is also shown in Fig. 3a. The heat evolved during the initial hydration period increases with HAC content. The heat evolution is slow in pure OPC paste compared with others (curves 2–5, Fig. 2a). A slight acceleration effect is observed when a small amount of HAC is present.

3.2. Pastes containing 12.5%–30% HAC

The rate of heat-evolution curves for OPC/HAC cement pastes containing 12.5%, 15%, 17.5%, 20%,

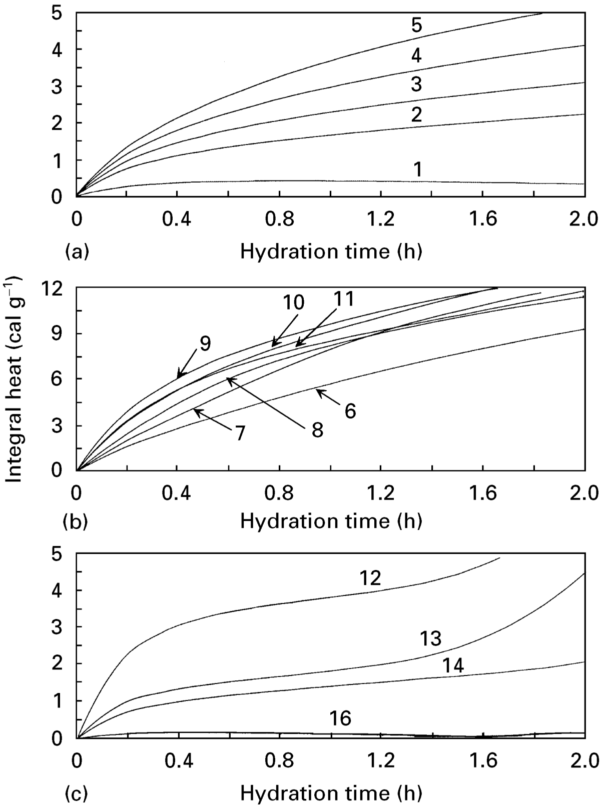

Figure 3 Enlarged plots of total heat evolution versus hydration time up to 2 h for OPC/HAC pastes containing (a) 0%–10%, (b) 12.5%–30% and (c) 40%–100% HAC at 20 °C (w/c ratio = 0.40). (1) Pure OPC, and pastes containing various percentage of HAC; (2) 2.5% (3) 5%, (4) 7.5%, (5) 10%, (6) 12.5% (7) 15%, (8) 17.5%, (9) 20%, (10) 25%, (11) 30%, (12) 40%, (13) 60%, (14) 70% and (16) pure HAC (curve 15 for 80% is not shown).

25% and 30% (Fig. 1b) of HAC illustrate a major difference from those curves obtained from pastes containing less than 12.5% HAC. There is a significant delay in the appearance of the main hydration peak. A transient stage was observed in the 12.5% HAC–87.5% OPC paste (curve 6, Fig. 1b). Instead of a peak at 12.6 h (curve 1, Fig. 1a), the rate remains at about 1 $\mathrm{cal\,g^{-1}\,h^{-1}}$ until 27 h. A longer induction period was observed for pastes containing 15%–25% HAC, depending on the percentage of HAC present. The 75% OPC–25% HAC and 80% OPC–20% HAC pastes seem to have the longest induction time, i.e. about 10 h. The rate increases at about 10–15 h followed by a "shoulder" and a peak. Maximum values of the rate for pastes containing 15%, 17.5%, 20%, 25% and 30% HAC are 1.69, 1.71, 1.43, 1.32 and 1.01 $\mathrm{cal\,g^{-1}\,h^{-1}}$ respectively, and the corresponding times are 29.3, 34.3, 38.8, 32.6 and 32.4 h. The total heat-evolution curves (Fig. 2b) are quite dissimilar to pure OPC (curve 1, Fig. 2a). A typical example is 80% OPC–20% HAC paste (curve 9, Fig. 2b) which reveals two stages of heat evolution – one at the first few hours (an enlarged plot up to 2 h is given in Fig. 3b) and another at 20–40 h respectively. The curve for OPC is continuous and does not have two distinct regions.

3.3. Pastes containing more than 30% HAC

Two changes were noticed in the rate of heat-evolution curves for the paste containing 30% HAC (curve 11, Fig. 1b). A hump appears at 5–10 h and there is a significant decrease (relative to others) of the main hydration peak which occurs at 32 h. The hydration peak at 32 h decays to zero as the HAC content increases (see curves 12–16, Fig. 1c). These curves exhibit a peak at 3–10 h and the amplitude increases with the amount of HAC in the paste. The maximum peak values are 5.94, 10.50, 13.28 and 23.75 $\mathrm{cal\,g^{-1}\,h^{-1}}$ for pastes containing 40%, 60%, 70%, 80% and pure HAC at the corresponding times of 3, 3.6, 4.5, 5.3 and 6 h, respectively. The heat evolution occurring within the first 2 h decreases as HAC content increases (Fig. 3c). Most of the heat evolution occurs between 3 and 10 h, as indicated in the total heat-evolution curves (Fig. 2c).

4. Discussion

The heat-evolution behaviour of OPC/HAC paste systems is dependent on the OPC/HAC ratio. Phenomena including ettringite formation, OPC and HAC hydration are important factors in understanding the chemical and physical processes relevant to the hydration of these materials. These are discussed below.

4.1. Early heat evolution and rapid ettringite formation

Ettringite can form when calcium aluminates, gypsum and water are present. It is a product of Portland cement paste hydration where C_3A reacts with gypsum and water [8]. It is also the main product of Type K, M and S cement paste hydration [9]. Ettringite can convert to monosulphoaluminate hydrate in a C_3A-rich environment, even though the solubility of ettringite (1.1×10^{-40} $\mathrm{mol^{-1}}$) is less than that of monosulphoaluminate (MS) (1.7×10^{-28} $\mathrm{mol\,l^{-1}}$) [10]. Ettringite is formed in a OPC/HAC paste system because HAC provides a rich source of calcium aluminates and OPC provides gypsum. The initial exotherm of the heat evolution curves within the first few hours of hydration (Fig. 3a–c) can be attributed to (a) hydration of free lime and early formation of low Ca/Si ratio C–S–H, (b) formation of CAH_{10} and/or C_2AH_8, and (c) ettringite formation. The pastes containing 15%–25% HAC have much larger total heat evolution at 30 min and 2 h than those of both pure OPC and HAC as shown in Fig. 4. For example, the paste containing 20%HAC has a total heat evolution of 12.6 $\mathrm{cal\,g^{-1}}$ at 2 h whereas the values are 0.38 and 0.14 $\mathrm{cal\,g^{-1}}$ for pure OPC and HAC pastes, respectively. Processes (a) and (b) are largely associated with pure OPC and HAC paste hydration. This large heat evolution within the first 2 h hydration is mainly attributed to process (c), ettringite formation. SEM examination of the morphology of pastes containing 7.5%, 20% and 80% HAC after 30 min hydration is illustrated in Fig. 5a–c. A large amount of needle-like

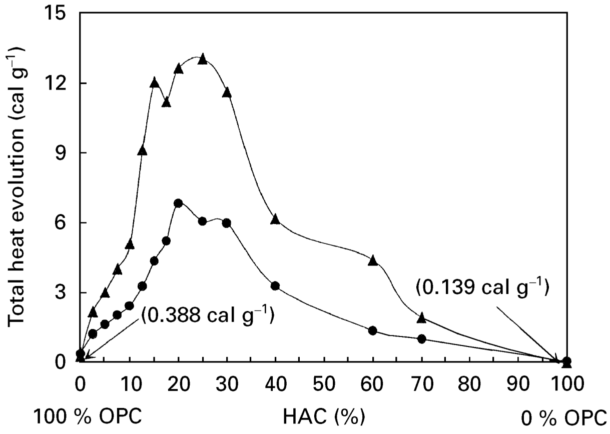

Figure 4 Plot of total heat evolution versus the percentage of HAC (●) at 30 min, and (▲) at 2 h.

crystals covering the surface of unhydrated cement grains is seen in the paste with 20% HAC (Fig. 5b). These crystals were not observed in the paste containing 7.5% HAC (Fig. 5a). A small amount was observed in the paste with 80% HAC (Fig. 5c). X-ray diffraction results support these observations. A distinguishable ettringite peak at $d = 9.73$ nm for the paste containing 20%HAC was detected at 30 min. It was not observed in the pastes containing 7.5% and 80% HAC (Fig. 6). This needle-like crystalline phase has been identified as ettringite elsewhere [7]. It appears that it is responsible for the quick-set behaviour of OPC/HAC mixtures.

A shoulder peak occurs between 10 and 30 h in the rate of heat-evolution curves (Fig. 1b) for the pastes containing 15%–30% HAC. This may be due to the conversion of ettringite to monosulphoaluminate hydrate. The size of this shoulder peak seems to have a maximum when the paste contains 20%–25% HAC. This appears to coincide with the observation of a maximum total heat evolution within first few hours (Fig. 4). This interpretation is also supported by the X-ray diffraction analysis of a 20%HAC–80%OPC paste hydrated 48 h, where a peak for monosulphoaluminate hydrate is clearly seen (Fig. 7b).

4.2. Heat evolution associated with ordinary Portland cement hydration

Hydration of OPC paste is a complex process. Physical and chemical changes involving mainly C_3S, C_2S, C_3A, ferrite and other minor phases occur [11, 12]. The hydration behaviour of pure OPC paste has been well characterized by conduction calorimetry [11, 12]. The heat-evolution behaviour of OPC/HAC pastes containing less than 12.5% HAC is very similar to that of pure OPC paste. This behaviour becomes more complex when the HAC content falls within the range 15%–30%. The OPC hydration peak appears to be delayed up to 20–40 h depending on the HAC content. X-ray diffraction analysis was used to determine the presence of $Ca(OH)_2$ in a 20%HAC–80%OPC paste hydrated 24 and 48 h. There was no clear evidence of a $Ca(OH)_2$ peak at 24h. A $Ca(OH)_2$ peak was detectable at 48 h (Fig. 7). The formation of lime is attributed to the hydration of C_3S and C_2S.

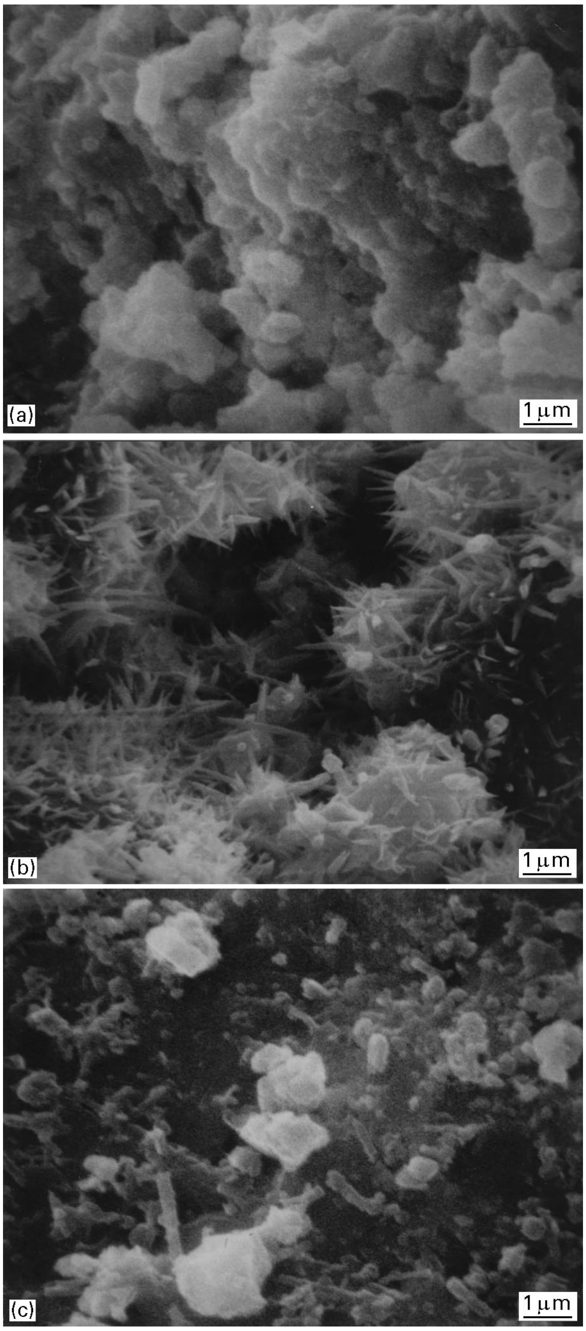

Figure 5 Scanning electron micrographs taken from OPC/HAC pastes containing (a) 7.5% HAC, (b) 20% HAC and (c) 80% HAC, at 30 min hydration time. The w/c ratio is 0.50.

4.3. Heat evolution associated with high alumina cement hydration

Comparing the similarity of the conduction calorimetric curve for pure HAC (curve 16, Fig. 1c) with other curves for OPC/HAC pastes containing more than 30% HAC (curves 12–15, Fig. 1c), the evidence for HAC hydration in the blended system is clear. X-ray results, taken at times before and after the occurrence of this peak from a 20% OPC–80% HAC paste, confirm that the sharp peak appearing between 4 and 8 h is due mainly to CA hydration. There is no clear indication of a CAH_{10} peak at 4 h as shown in Fig. 8;

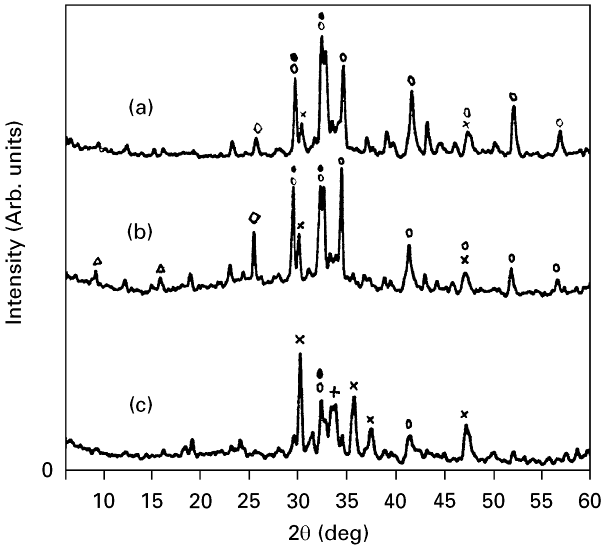

Figure 6 X-ray diffraction traces for pastes at a hydration time of 30 min. (a) 92.5% OPC–7.5% HAC, (b) 80% OPC–20% HAC, and (c) 20% OPC–80% HAC pastes. The w/c ratio is 0.50 (○) C_3S, (●) C_2S, (×) CA, (+) C_3A, (□) CAH_{10}, C_2AH_8, (△) ettringite, (▲) monosulphoaluminate, (◇) gypsum, and (■) CH.

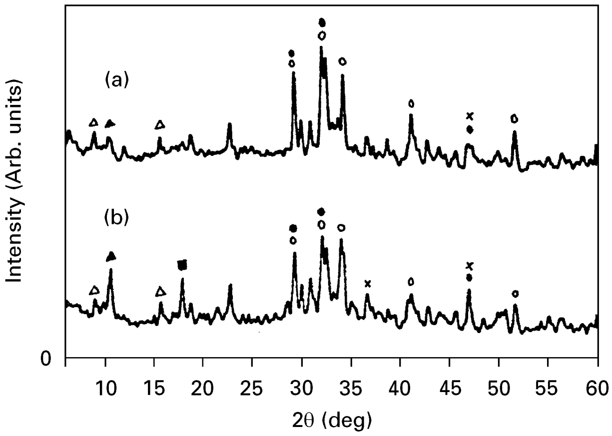

Figure 7 X-ray diffraction traces for an 80% OPC–20% HAC paste at hydration times of (a) 24 h, and (b) 48 h. The w/c ratio is 0.50. (○) C_3S, (●) C_2S, (×) CA, (+) C_3A, (□) CAH_{10}, C_2AH_8, (△) ettringite, (▲) monosulphoaluminate, (◇) gypsum, and (■) CH.

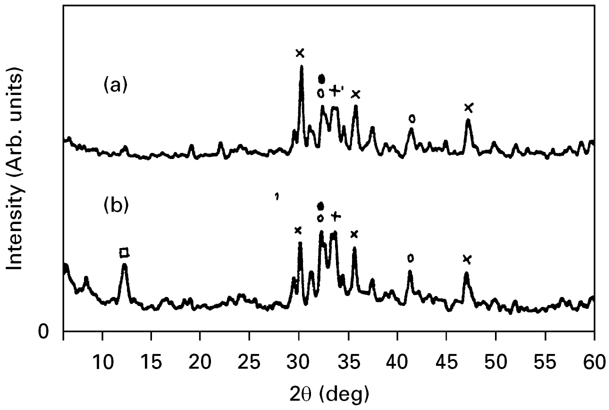

Figure 8 X-ray diffraction traces for an 20% OPC–80% HAC paste at hydration times of (a) 4 h, and (b) 8 h. The w/c ratio is 0.50. (○) C_3S, (●) C_2S, (×) CA, (+) C_3A, (□) CAH_{10}, C_2AH_8, (△) ettringite, (▲) monosulphoaluminate, (◇) gypsum, and (■) CH.

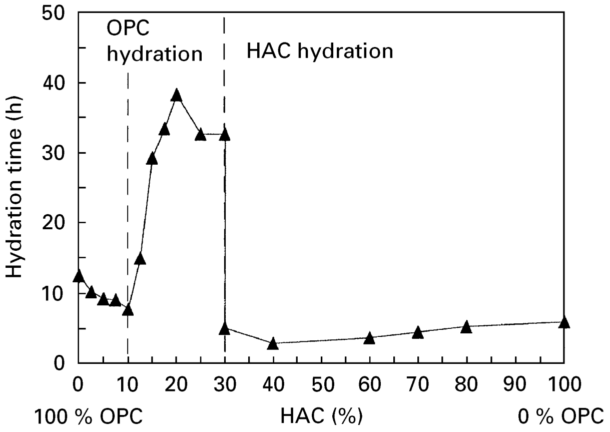

Figure 9 Plot of hydration time corresponding to the maximum rate of heat evolution versus the percentage of HAC.

a peak is observed at 8 h. It is also noted that OPC can hydrate at the same time even though a distinct separated peak cannot be observed. This is because the contribution from HAC to the rate of heat evolution is much larger than that of OPC. The heat evolved by HAC hydration may also accelerate OPC hydration.

It is evident that the OPC/HAC ratio has a significant influence on the hydration behaviour of the blended system. It may accelerate or delay the OPC or HAC hydration processes. An overall plot of hydration time corresponding to the maximum rate of heat evolution versus the percentage of HAC is given in Fig. 9. The presence of HAC in amounts less than 12.5% accelerates OPC hydration. The hydration time corresponding to the maximum rate decreases from 12.6 h to 8.5 h. However, once the HAC content reaches 12.5%, a significant delay of OPC hydration occurs, resulting in a change of the hydration mechanism. Behaviour related to the dominance of HAC hydration is not detectable until the HAC content is greater than 30%. The hydration of HAC is accelerated by the presence of OPC, which is in agreement with the literature [2].

4.4. Early hydration of OPC/HAC – barrier layer

Early OPC and HAC hydration has been widely studied. Hypothesis include mechanisms involving hydrate barriers [13–15], lattice defects [16, 17], interfacial or boundary layer reactions [18, 19] and electrical double-layer effects [20–22]. These have been used to explain the onset and termination of the induction period. The simple hydrate barrier effect explains the induction period well. The basic concept of a hydrate barrier is that a thin layer of hydration products rapidly covers the entire unhydrated grain when cement reacts with water. A physical barrier impedes further contact between water and the inner surface of the cement particles. The hydration reaction then becomes diffusion controlled. The paste does not set until the breakdown of this barrier by nucleation of C–S–H and/or $Ca(OH)_2$. The physical barrier concept can be used to explain the hydration behaviour of OPC/HAC pastes regardless of the specific type of

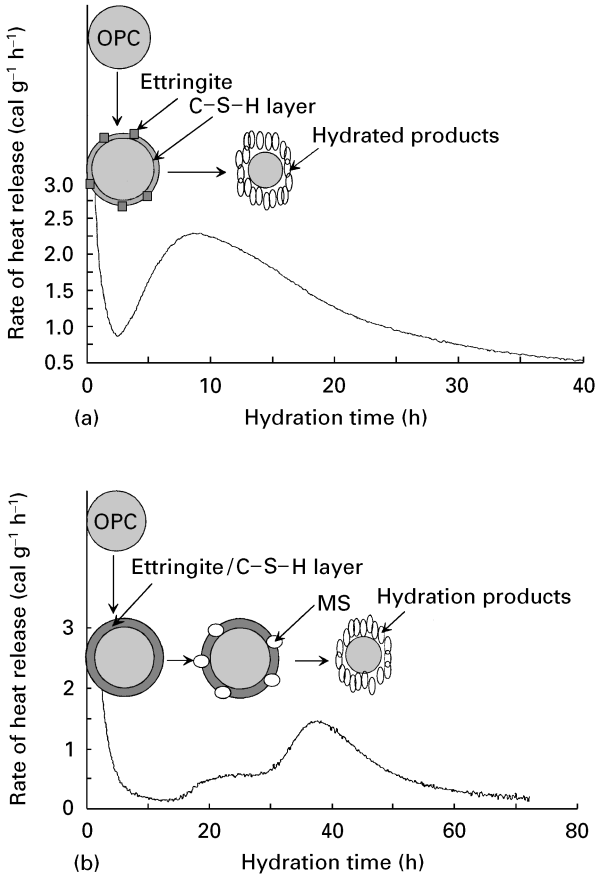

Figure 10 A schematic drawing illustrating early hydration mechanisms of OPC/HAC for (a) pastes containing less than 12.5% or more than 30% HAC, and (b) pastes containing 12.5%–30% HAC.

reactions occurring on the surface of cement particles. Schematic drawings of the early hydration mechanisms of OPC/HAC systems corresponding to various percentages of HAC are given in Fig. 10a and b. They are briefly described below.

(a) Hydration of OPC dominates in the OPC/HAC pastes containing less than 12.5% HAC as indicated by the heat-evolution curves. Lime and gypsum dissolution and C_3S, C_2S, C_3A and CA (from HAC) hydration occur as soon as the cement particle surface is in contact with water. A layer of hydrated cement quickly covers the entire surface and the system experiences an induction period. Ettringite also forms and co-deposits on the cement particle surfaces. This may introduce porous areas with reduced homogeneity adjacent to the hydrated barrier resulting in further OPC hydration (Fig. 10a).

(b) An increased amount of ettringite forms when the HAC content falls in the 12.5%–30% range. A mechanism for the delay of OPC hydration is illustrated in the schematic drawing in Fig. 10b. A large amount of ettringite (along with other minor components) is the primary hydration product covering the entire surface of the unhydrated particles. This barrier layer more effectively impedes further cement grain hydration. A long induction period is observed as a result. It is suggested that this delay is a contributing factor to poor strength development. The conversion of ettringite to monosulphoaluminate hydrate may cause the break down of the hydrated barrier hastening further OPC hydration.

The hydration behaviour of pastes containing more than 30% HAC is similar to that described in (a). Co-deposition of ettringite and hydration products of HAC and OPC form a porous area adjacent to the barrier layer. Increased water permeability results. The large amount of heat evolved during HAC hydration speeds up the break-down of the barrier layer on both OPC and HAC unhydrated cement grains. The result is an acceleration of the hydration reactions.

5. Conclusions

The early hydration mechanisms involved in OPC/HAC paste systems depend on the percentage of HAC present. A low HAC addition to OPC paste, or vice versa accelerates the OPC or HAC hydration. OPC hydration (mainly C_3S or/and C_2S) is significantly delayed with 15%–30% HAC addition. A semi-impermeable hydrated layer is formed, consisting mainly of ettringite covering the entire surface of unhydrated particles. This hydrated layer further impedes cement grain hydration. It is suggested that a delay of OPC hydration may result in poor strength of OPC/HAC binary systems.

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