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Early Strength Development and Hydration of Ordinary Portland Cement/Calcium Aluminate Cement Pastes

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The early strength development of ordinary Portland cement (OPC)/calcium aluminate cement (CAC) pastes (92.5/7.5, 80/20, and 20/80) was studied. Conduction calorimetry, X-ray diffraction, and scanning electron microscopy methods were used to monitor the heat evolution and microstructural changes of these pastes. It is apparent that ettringite formation contributes to the early "set strength" in the 80/20 paste. The OPC hydration seems to be delayed by the presence of CAC. ADVANCED CEMENT BASED MATERIALS 1997, 6, 53–58. *© 1997 Elsevier Science Ltd.*

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Repair technology has become increasingly important in modern construction practice. Demands for repair and protection of existing infrastructure have dramatically increased in the last decade due to the corrosion of steel reinforcement in concrete. This has resulted in severe damage of concrete structures and reduced service life. A quality repair material often requires rapid setting and hardening, good adhesion, compatibility with existing concrete, dimensional stability, and corrosion resistance. Binary cement based systems, e.g., mixtures of ordinary Portland cement (OPC) and calcium aluminate cement (CAC), are often considered, since rapid setting and appreciable strength can be developed within a few hours [1–3]. They have been utilized in sealing of leaks, rapid wall construction, and road pavement repair [3–5]. However, simply mixing these two cements can fail to provide satisfactory strength, especially in the range of composition that satisfies the quick-set requirement [6]. Therefore, it is important to understand the hydration behavior and strength development of the binary cement system to allow proper modification to enhance its strength performance. A previous study indicated that the OPC/CAC ratio has a significant influence on the rate of heat evolution behavior of the blended system [7]. In this article, three pastes with different OPC/CAC ratios, e.g., 92.5/7.5 (OPC/CAC mass percentage ratio), 80/20, and 20/80, were selected for the investigation. The ettringite formation, early strength development, and delayed hydration of OPC of the binary cement systems will be discussed.

Experimental Method

The OPC (Type 10) and CAC (Fondu) used in this study were obtained from the Lafarge Cement Co. The chemical composition (mass %) of the OPC is: $SiO_2 = 19.83$, $CaO = 61.21$, $Fe_2O_3 = 3.20$, $Al_2O_3 = 4.18$, $MgO = 4.09$, $SO_3 = 3.93$, $Na_2O = 0.45$, and $K_2O = 0.82$; and of CAC is: $SiO_2 = 4.50$, $CaO = 38.50$, $Fe_2O_3 = 12.00$, $Al_2O_3 = 39.00$, $MgO = 0.60$, $SO_3 = 0.15$, $Na_2O = 0.10$, and $K_2O = 0.15$.

Three binary cement pastes, containing 92.5/7.5, 80/20, and 20/80, were mixed at a water/cement (w/c) ratio of 0.40. Compressive strength was determined in accordance with a modified ASTM C39 procedure. Mini-cylindrical specimens, 14 mm in diameter ×25 mm long, were tested at ages up to 3 days.

The conduction calorimeter used was manufactured by the Institute of Applied Physics, TNO-TU, Delft, The Netherlands. Four mL of distilled water were added to 10.00 g of the binary cement systems. Pastes were mixed and placed in the calorimeter cells, which were sealed and submerged in a water bath maintained at 20.0°C.

Cement paste samples for scanning electron microscopy (SEM) and X-ray studies were prepared at w/c ratio of 0.5. The hydration of pastes was stopped at 0.5, 4, 8, 24, 48, and 72 hours using excess cold acetone. A

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TABLE 1. Compressive strength of the three OPC/CAC pastes

Hydration Hours	92.5/7.25 (MPa)	80/20 (MPa)	20/80 (MPa)
1	—	0.7	—
2	—	0.8	—
4	—	1.2	3.5
8	0.7	1.7	25.5
16	4.5	2.8	36.1
21	5.8	2.7	36.8
24	8.2	2.7	43.8
48	16.2	2.6	40.7
72	23.5	10.7	46.7

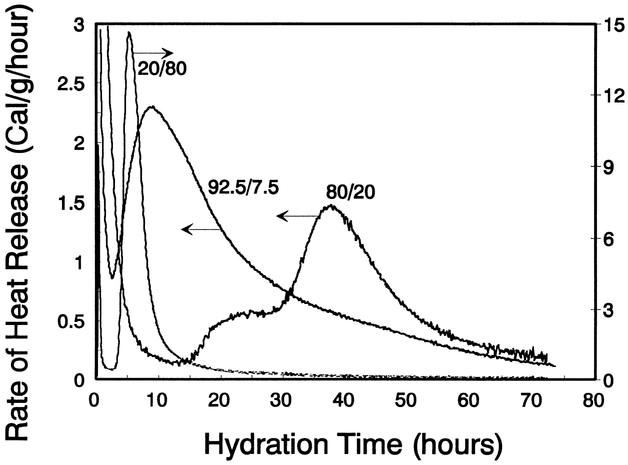

FIGURE 1. Plot of rate of heat development versus hydration time up to 72 hours for OPC/CAC pastes prepared at mass ratios of 92.5/7.5, 80/20, and 20/80. The w/c ratio = 0.40.

Cambridge Stereoscan S250 and Rigaku X-ray equipment were used to obtain SEM micrographs and crystallographic data. X-ray diffraction was not used for any quantitative estimation of phases since use of an internal standard is not effective when using wet cement paste.

Results

Early Compressive Strength

Compressive strength for the three pastes was determined from the first hour to 72 hours. Results are listed in Table 1. Strength was not measured for the 92.5/7.5 paste during the first 4 hours hydration. A value of 0.71 MPa was obtained at 8 hours. The strength then continuously increased to 23.5 MPa at 72 hours. A strength of 0.7 MPa was obtained at 1 hour for the 80/20 paste, and the strength slowly increased to a value of about 2.6 MPa at 48 hours. The strength at 72 hours increased significantly to a value of 10.7 MPa. Strength was not measured for the 20/80 paste during the first 2 hours, but a value of 3.54 MPa was obtained at 4 hours. The early strength development of 92.5/7.5 and 20/80 pastes is very similar to that for pure OPC and CAC cement pastes [2]. The final set values of these two pastes are 6 and 4 hours, respectively. The 80/20 paste has the earliest strength among the three, and it appears to have unique strength development behavior. Conduction calorimetry, X-ray diffraction, and SEM measurements were conducted to assess the factors that attribute to the early strength of these pastes. The results are presented in the following sections.

Conduction Calorimetry

The rates of heat evolution versus hydration time up to 72 hours for the three binary pastes are provided in Figure 1. Curves for the 92.5/7.5 and 20/80 pastes exhibit a heat evolution profile similar to that of pure OPC and CAC pastes [7]. A peak with a maximum value of rate of heat evolution is observed at about 9 hours for 92.5/7.5 and at about 5 hours for 20/80, respectively. These exothermic peaks are attributed to hydration of C_3S and C_2S (92.5/7.5) and mainly CA (20/80), respectively. For the 80/20 paste, the curve exhibits a larger initial exotherm within the first few hours of hydration than that of 92.7/7.5 or 20/80. (Only part of the exothermic peak was recorded in Figure 1 due to the time requirement for the pre-mixing procedure outside the calorimeter.) A long period of slow but continuous heat evolution of about 10 hours and a significant delay in the appearance of the main hydration peak were observed. The rate increases at about 10 hours and exhibits a "shoulder" peak at 15–30 hours. A peak with a maximum value occurs at about 39 hours. The total heat evolution curves for these three OPC/CAC pastes are also given in Figure 2. The curve for the 80/20 paste reveals two stages of heat evolution, one in the first few hours and another beyond 20 hours, whereas curves for the 92.5/7.5 and 20/80 pastes are continuous and do not appear to have two distinct regions.

X-Ray Diffraction

The X-ray diffraction analyses were conducted on the three pastes at 0.5, 4, 8, 24, and 48 hours. Peaks corresponding to ettringite, gypsum, $Ca(OH)_2$, monosulphoaluminate, and CAH_{10}/C_2AH_8 were identified. A summary is provided in Table 2. For the 92.5/7.5 paste, ettringite peaks were observed at 4 hours and later. The $Ca(OH)_2$ peak started to appear at 8 hours and increased in intensity with time. Ettringite peaks were also observed in the 80/20 paste as early as 30 minutes, and the monosulphoaluminate peak appears at 24 and 48 hours. The gypsum peak was observed at 30 minutes and disappeared at 24 hours. No clear peaks

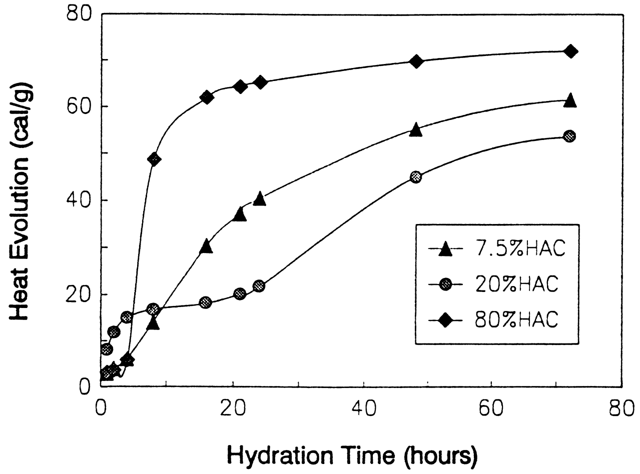

FIGURE 2. Plot of total heat evolution versus hydration time up to 72 hours for OPC/CAC pastes prepared at mass ratios of 92.5/7.5, 80/20, and 20/80. The w/c ratio = 0.40.

for ettringite, gypsum, $Ca(OH)_2$, and monosulphoaluminate hydrate were observed in the 20/80 paste. The CAH_{10}/C_2AH_8 peaks are, however, detected at 8 hours.

Discussion

Factors Affecting Early Strength Development in OPC/CAC Pastes

Many factors influence the strength development of OPC/CAC systems. It is apparent that the OPC/CAC ratio is critical to the hydration mechanism. The effect of reactions including formation of ettringite, C-S-H, $Ca(OH)_2$, monosulphoaluminate hydrate, and CAH_{10}/C_2AH_8 on the strength development in the system is discussed as follows.

ETTRINGITE FORMATION. Ettringite is a well-known hydration product of OPC produced primarily as a result of the C_3A/gypsum reaction. In the OPC/CAC binary cement pastes, ettringite can be formed in the first few minutes of the hydration mainly through the following reactions:

$$CA + 3C\bar{S}H_2 + 2C + 26H \Rightarrow C_6A\bar{S}_3H_{32} \qquad (1)$$

$$C_3A + 3C\bar{S}H_2 + 26H \Rightarrow C_6A\bar{S}_3H_{32}. \qquad (2)$$

The early strength of the binary paste systems is attributed to these reactions [8]. The OPC normally provides the sulphate and the CAC is the primary source of aluminates. The amount of ettringite formed depends on the available amount of sulphate and aluminates. In the 92.5/7.5 paste, the small amount of ettringite formed is evident in both the SEM (Figure 3a) and X-ray study (Table 2). However, it does not contribute significantly to the strength of the paste (Table 1). It is apparent that the aluminates are the limiting reactants. An estimate of the $CAC/C\bar{S}$ ratio is 0.78 (assuming a 4% gypsum content in OPC and 40% aluminate content in CAC in the calculation), which is much smaller than the value of 1.43 suggested as required to develop early strength [8].

In the 80/20 paste, the $CAC/C\bar{S}$ ratio is about 2.50. Rapid formation of a large amount of needle-like ettringite crystals is evident in both the SEM (Figure 3b) and X-ray study (Table 2). This ettringite formation contributes to the quick-set. The early strength is usually less than a few MPa (Table 1). It is much lower than that contributed by C_3S, C_2S, and CA hydration. It was also suggested by Bensted [9] that the fast formation of CAH_{10}/C_2AH_8 due to the CA/C_3A hydration may also contribute to the early strength of the binary paste system. The observations in this study do not seem to support Bensted's suggestion. Significant early strength development in the pure CAC paste or even in the 20/80 paste system does not occur in spite of fast formation of CAH_{10}/C_2AH_8.

In the 20/80 paste, appreciable strength is developed at 4 hours hydration (Table 1). SEM examination at a 30 minutes hydration failed to identify ettringite crystals (Figure 3c). X-ray diffraction also failed to detect early ettringite formation (Table 2). There is apparently not enough sulphate available, and the hydration and strength development behavior of this system are similar to that for pure CAC paste [7].

MONOSULPHOALUMINATE HYDRATE. The strength development of the 80/20 paste is unique. The paste shows very early strength (0.7 MPa at 1 hour); however, the mag-

TABLE 2. Summary of the compounds identified by X-ray diffraction analysis of OPC/CAC at early hydration times

OPC/CAC Paste	30 Minutes	4 Hours	8 Hours	24 Hours	48 Hours
92.5/7.5	Gypsum	Ettringite, gypsum	Ettringite, $Ca(OH)_2$	Ettringite, $Ca(OH)_2$	Ettringite, $Ca(OH)_2$
80/20	Ettringite, gypsum	Ettringite, gypsum	Ettringite, gypsum	Ettringite, monosulphoaluminate	Ettringite, monosulphoaluminate, $Ca(OH)_2$
20/80	—	—	CAH_{10}/C_2AH_8	CAH_{10}/C_2AH_8	CAH_{10}/C_2AH_8

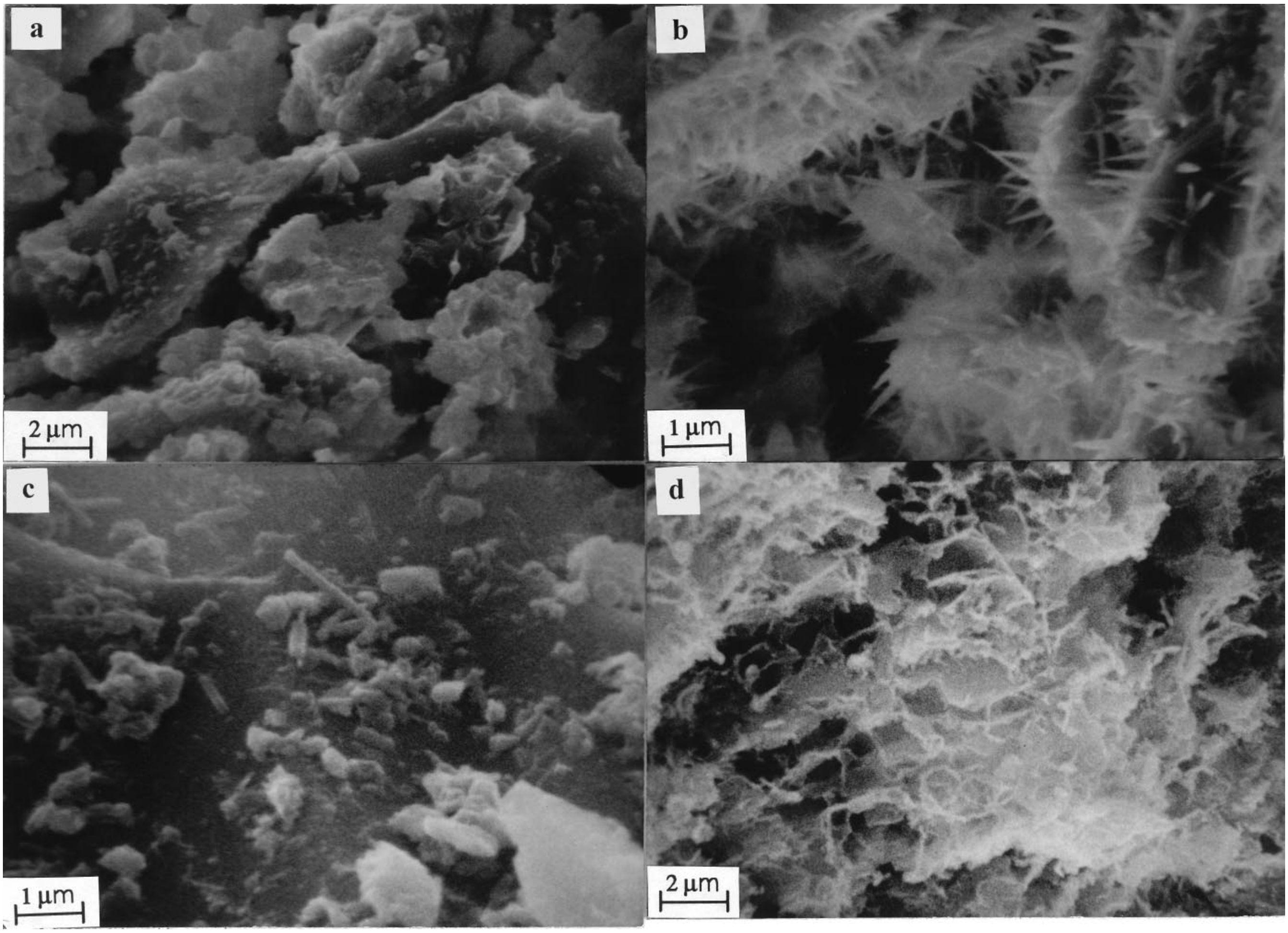

FIGURE 3. SEM micrographs (×5000) taken from (a) 92.5/7.5 OPC/CAC paste at 30 minutes, (b) 80/20 paste at 30 minutes, (c) 20/80 paste at 30 minutes, and (d) 80/20 paste at 8 hours. The w/c ratio = 0.50.

nitude of the strength developed in the first 48 hours is low (2.6 MPa). The heat evolution curves (Figure 1) clearly reveal that the paste system undergoes a relatively long period prior to the onset of the major hydration peaks, but SEM studies at 0.5 and 8 hours hydration (Figure 3b and 3d) show clearly a morphology change of the paste during this period. Many small needle-like or prismatic shaped crystals, about 0.3 mm (length), were observed at 30 minutes (Figure 3b). These crystals were identified as ettringite using energy dispersive X-ray analysis (EDXA) [10]. Some of these crystals were morphologically transformed at 8 hours (Figure 3d). It has been suggested that a slow conversion process of ettringite to monosulphoaluminate hydrate may take place during this period [7]. Conversion of ettringite to monosulphoaluminate hydrate is evident at 24 hours hydration time as indicated by the X-ray study (Table 2).

It is not clear whether the "shoulder" peak at 15–30 hours in the heat evolution curve (Figure 1) is solely related to the ettringite-monosulphoaluminate conversion process. The conversion of CAC hydration products may also be involved. Figure 4 contains the heat evolution-time curves for the 80%C$_3$S-20%CA and 80%C$_3$S-20%CAC pastes (the curve for 80/20 paste is also plotted for comparison). Peaks a1 and a2, and b1 and b2 are attributed to the CA hydration and possible conversion of its reaction products since there was no Ca(OH)$_2$ formation confirmed by X-ray diffraction at the corresponding hydration time. It would appear that the peak c2 has the same origins as a2 and b2. It is suggested that peaks a2 and b2 may appear as the result of the conversion of the hydration products formed in peaks a1 and b1. In the 80/20 paste system, the conversion reaction may also contribute to the "shoulder" peak at 15–30 hours due to the presence of a small amount of CA. If so, it must be insignificant since the ettringite formation consumes most of the CA. It is apparent that whatever mechanism is operative, it has little effect on the OPC/CAC strength development (Table 1). For example, a value of 2.75 MPa

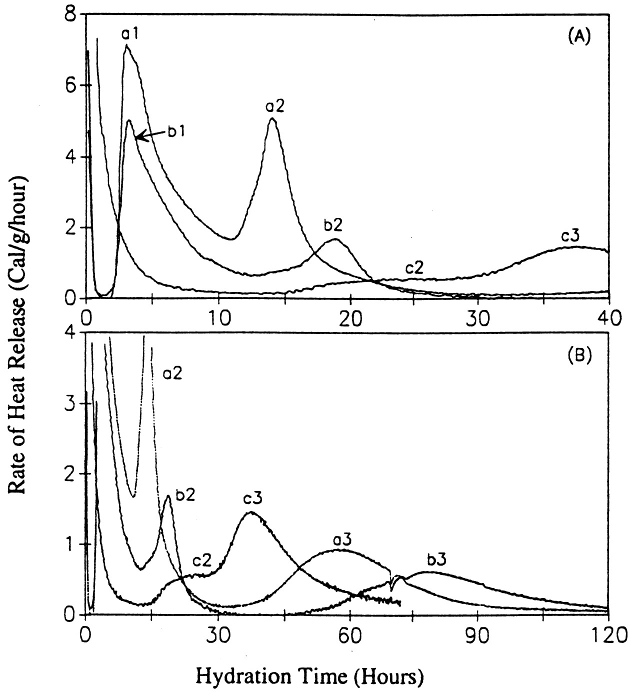

FIGURE 4. Plot of rate of heat development versus hydration time up to (A) 40 hours and (B) 120 hours for pastes: (a) 80%C_3S-20%CA, (b) 80%C_3S-20%CAC, and (c) 80%OPC-20%CAC. The w/c ratio = 0.40.

was recorded at 16 hours and 2.57 MPa at 48 hours. The change of the morphology may lead to a more porous matrix, which could explain the slight decrease in the strength.

DELAYED OPC HYDRATION. The strength of the 80/20 paste rapidly increases during 48–72 hours hydration, which corresponds to the heat evolution during the time period (Figure 1). The observation of a $Ca(OH)_2$ peak at 48 hours by X-ray diffraction analysis (Table 2) suggests that the slow strength development in the 80/20 paste may be due to a delay in hydration of C_3S, as indicated by its heat evolution curve. This delay in hydration of C_3S was also observed in both the 80%C_3S-20%CA and the 80%C_3S-20%CAC paste systems as shown in Figure 4, and the corresponding C_3S hydration peaks a3 and b3 appear at about 55 and 80 hours, respectively. It would appear that peaks a3, b3, and c3 have similar origins and are all related to the delay in hydration of C_3S. The observation that C_3S remains unhydrated until the conversion is completed suggests an incompatibility between the OPC and CAC hydration products.

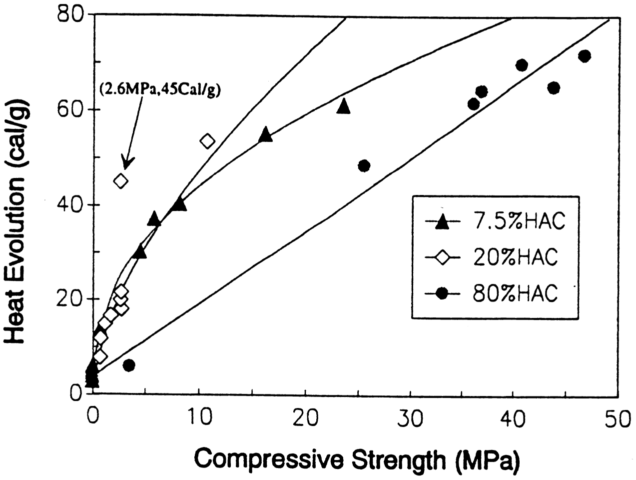

FIGURE 5. Plot of total heat evolution versus compressive strength for OPC/CAC pastes prepared at mass ratios of 92.5/7.5, 80/20, and 20/80. The w/c ratio = 0.40.

Total Heat Evolution and Strength

It is evident that the strength development of the paste is a result of chemical reactions that are accompanied by heat release. The shape of the strength development curves are similar to those of the corresponding heat evolution curves. However, there is no simple correspondence between heat evolution and compressive strength for all systems. Figure 5 is a plot of heat evolution versus compressive strength. It can be seen that an approximate "linear" relationship was obtained between compressive strength and heat evolution for the 20/80 paste. Logarithmic behavior for the 92.5/7.5 and 80/20 pastes was observed. It appears that a higher strength for the same amount of heat evolved was observed in the 20/80 paste. It is noted that one point (for the 80/20 paste) appears to be an outlier from the regression curve as marked in the figure. If the outlier was ignored, the two OPC-rich samples would fall on a single curve. This point is possibly due to the ettringite-monosulphoaluminate hydrate conversion, a process that does not appear to contribute to strength development.

Conclusions

(1) The early strength development of OPC/CAC pastes depends on the OPC/CAC ratio. Rapid formation of a large amount of needle-like ettringite crystals in the 80/20 paste appears to account for the quick-set and early compressive strength development of the system. The delay in hydration of C_3S causes the slow strength development of the binary cement system. (2) Similarity between heat evolution and strength development profiles was obtained for the three OPC/CAC pastes investigated. A linear behavior was obtained between the compressive strength and the heat evolution for the 20/80 paste and logarithmic behavior for the 92.5/7.5 and 80/20 pastes. The 20/80 paste has the highest compressive strength for an equivalent amount of heat evolved.

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