Calorimetry in the studies of cement hydration

Setting and hardening of Portland cement–calcium aluminate cement mixtures

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Abstract Calorimetry was applied to an investigation of the early hydration of Portland cement (PC)–calcium aluminate cement (CAC) pastes. The heat evolution measurements were related to the strength tests on small cylindrical samples and standard mortar bars. Different heat-evolution profiles were observed, depending on the calcium aluminate cement/Portland cement ratio. The significant modification of Portland cement heat evolution profile within a few hours after mixing with water was observed generally in pastes containing up to 25% CAC. On the other hand the CAC hydration acceleration effect was also obtained with the 10% and 20% addition of Portland cement. As one could expect the compressive and flexural strength development was more or less changed—reduced in the presence of larger amount of the second component in the mixture, presumably because of the internal cracks generated by expansive calcium sulfoaluminate formation.

Keywords Calcium aluminate cement ·
Heat of hydration · Portland cement · Setting · Strength

Introduction

Hydration and setting of Portland cement mixed with a few percent of high alumina cement (HAC) occurs rapidly and the significant strength development within a few hours is observed [1]. This mixture was utilized in various applications including the sealing of leaks, rapid road pavement repair and waste solidification [2, 3]. The materials for self-levelling floors, applied in thin layers to level the floors before further finishing are composed of a ternary binder system based on Portland cement, calcium aluminate cement and calcium sulfate to provide fast set [4]. It is known that ettringite is the main hydration product of these mixed binder systems and the hydration development at early ages is significant. However the longer term strength development is relatively poor as compared with either pure PC or CAC. The reasons for this reduced strength development remain unclear [5].

Monocalcium aluminate phase $CaO \cdot Al_2O_3$—CA (notation commonly used in cement chemistry: $C = CaO$, $A = Al_2O_3$, $H = H_2O$) is the principal phase in aluminate cements [6]. The compound corresponding to the formula $12CaO \cdot 7Al_2O_3$ is the second aluminate phase. On reaction with water at ambient temperature a setting and hardening of calcium aluminate paste is observed and the hydrated calcium aluminate phases, such as $CaO \cdot Al_2O_3 \cdot 10H_2O$—$CAH_{10}$, $2CaO \cdot Al_2O_3 \cdot 8H_2O$—$C_2AH_8$ (hexagonal hydrates) and aluminium hydroxide (AH_3) are formed [6, 7]. The reaction of calcium aluminate cements with water followed by calorimetry gives two strong peaks with so-called induction period between them; there is a few hours lasting latent period in which a dissolution of initial substance to attain the supersaturation of liquid phase and slow nucleation of less soluble hydration products takes place [6, 7]. Hydration of Portland cement paste is a complex process, however the heat evolution profile is similar to that for CAC; generally the two peaks with the induction period can be observed. The calcium aluminate $3CaO \cdot Al_2O_3$—C_3A from cement reacts with gypsum (set

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controlling agent) to produce the ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$. The progress of hydration and heat of hydration is lower than in case of calcium aluminate cement [8]. In the Portland cement–alumina cement systems the gypsum component from Portland cement is consumed by the CAC phases and the crystallization of ettringite can either accelerate the setting and hardening of the binder or to hamper it as the impermeable ettringite layers on cement grains cut off the access of water. This ettringite phase is unstable and decomposes releasing the sulphate ions to the liquid phase. The delayed or secondary ettringite formation at later age can bring about the reduction of strength [6–9].

In this work the calorimetric method was used to investigate the behaviour of calcium aluminate cement and Portland cement (CAC + PC) mixtures on hydration. This method appears very useful as a tool giving an overall continuous view on hydration process not only at early age but also it is very helpful as the more practical parameters of hardened material are concerned [10–12].

Experimental

Materials and methods

The Portland cement and calcium aluminate cement samples used in this study were supplied by cement plants. Their specific surface was 3,120 and 3,160 cm^2/g (as measured by Blaine method), respectively. The chemical composition is given in Table 1. One should notice that the calcium aluminate component is that with the alumina content lower than in the relevant early reports (not HAC); on the other hand the tricalcium aluminate content in Portland cement and consequently the $C_3A + C_4AF$ is relatively high. Pastes containing various percentages of calcium aluminate cement (ranging from 0% to 100% by mass) were prepared. The following mixtures were taken into account:

(1) 95% PC + 5% CAC
(2) 90% PC + 10% CAC
(3) 85% PC + 15% CAC
(4) 80% PC + 20% CAC
(5) 75% PC + 25% CAC
(6) 20% PC + 80% CAC
(7) 10% PC + 90% CAC

A nonisothermal–nonadiabatic differential BMR microcalorimeter, constructed in the Institute of Physical Chemistry, Polish Academy of Science, was used. Hydrating pastes were prepared by mixing of 5 g samples with 2.5 mL of water (water to solid ratio 0.5); the initial temperature was kept constant at 25 °C. The heat evolved values were

Table 1 Composition of cements

Component	Percentage (wt%)	
	In Portland cement	In calcium aluminate cement
SiO_2	19.21	1.05
Al_2O_3	4.96	40.68
Fe_2O_3	2.86	13.50
CaO	62.09	35.06
MgO	0.94	0.36
SO_3	2.74	0.06
Loss on ignition	3.69	4.15
Insoluble	0.76	1.48
TiO_2	0.36	2.07
Total	97.61	98.41

Table 2 Heat evolved values in hydrated systems

Series of samples (Fig. No)	Composition of mixture	Heat evolved (J/g)	
		24 h	41 h
1, 3	100% PC	264	337
	5% CAC + 95% PC	245	302
	10% CAC + 90% PC	219	291
	15% CAC + 85% PC	218	290
	20% CAC + 80% PC	232	315
	25% CAC + 75% PC	215	277
2	80% CAC + 20% PC	362	Not determined
	90% CAC + 10% PC	359	
	100% CAC	368	

measured with accuracy of ±5 J/g (Table 2). The standard tests including setting time, flexural and compressive strength of materials were carried out according to the procedures given in the EN 196-1 and 196-3 standard series for common and special cements. Because of some discrepancies between the standard requirements for Portland and alumina cements the procedures were modified in some cases (see section "Studies of Portland cement–calcium aluminate cement mixtures hydration by calorimetry" for details).

The phase composition of Portland cement was as follows: C_3S—62.3%; C_2S—5.8%; C_3A—11.3%; C_4AF—8.7%, gypsum—4.7%. The estimated composition of calcium aluminate cement was: $CA + C_{12}A_7 \approx 70\%$; $C_4AF + C_2AS \approx 30\%$.

Studies of Portland cement–calcium aluminate cement mixtures hydration by calorimetry

The heat evolution curves are shown in Figs. 1 and 2; the heat values are listed in Table 2.

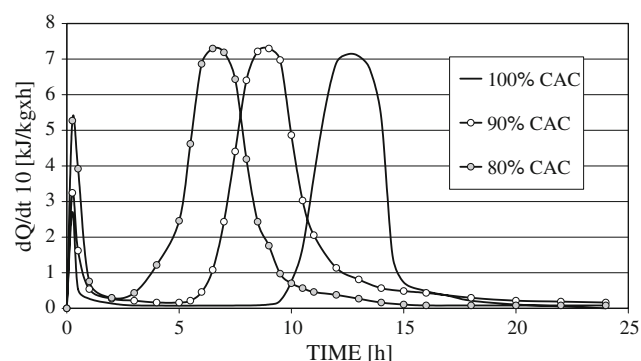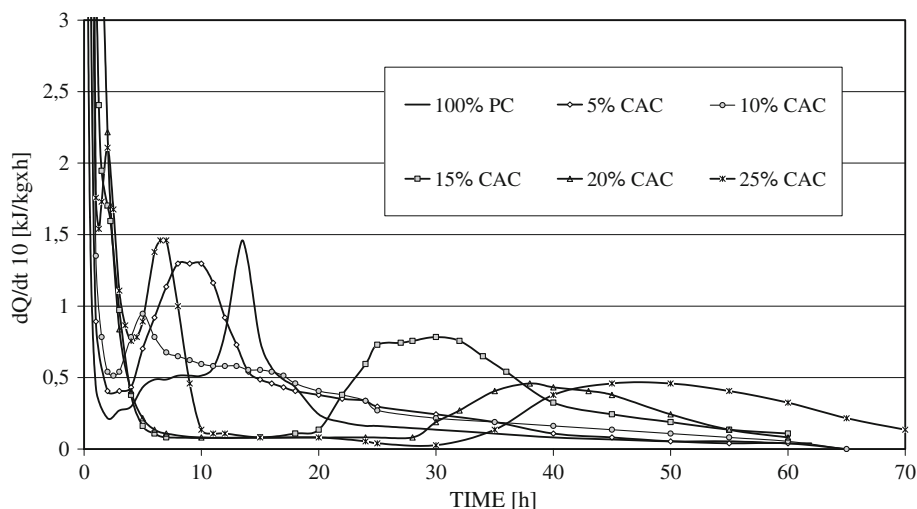**Fig. 1** Heat evolution curves for CAC + PC samples

Fig. 2 Heat evolution curves for rich in calcium aluminate cement CAC + PC samples

Setting and hardening of Portland cement–calcium aluminate cement mixtures

Setting time was measured using the standard Vicat apparatus on the pastes produced at water to solid ratio 0.3. The experiments with higher w/s failed because of segregation (in concrete technology bleeding). The results are visualized as Fig. 4.

The compressive strength of pastes cast in small cylindrical moulds (water to solid ratio = 0.5) was measured after 7, 14, 28, 60 and 90 days maturing in water. The results are presented as Fig. 5. The standard cement–sand mortars (sand to cement ratio = 3; water to cement ratio = 0.5) were also produced and subjected to the

Fig. 3 Heat evolution of CAC + PC samples; enlarged plot for CAC addition to 25%. Description of axes as in Figs. 1 and 2
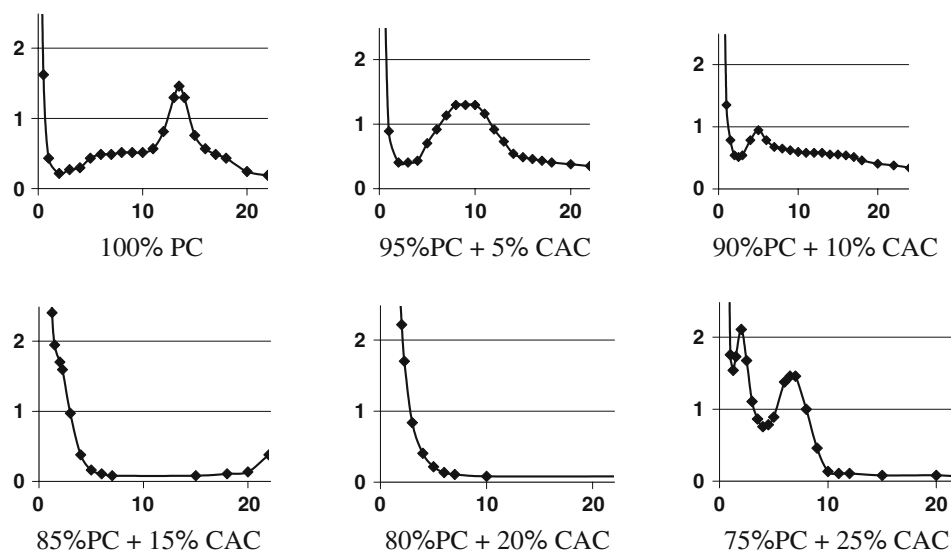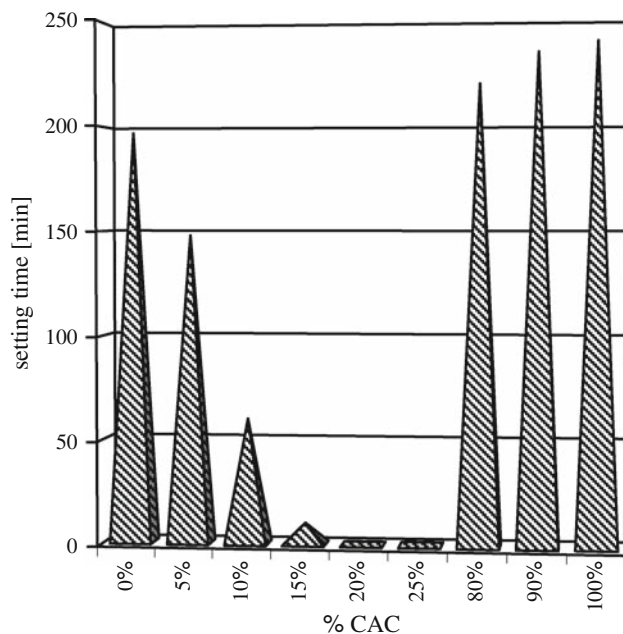
Fig. 4 Initial setting (in minutes) for Portland cement–calcium aluminate cement mixtures; a very fast setting was found for the samples with 15%, 20%, 25% CAC
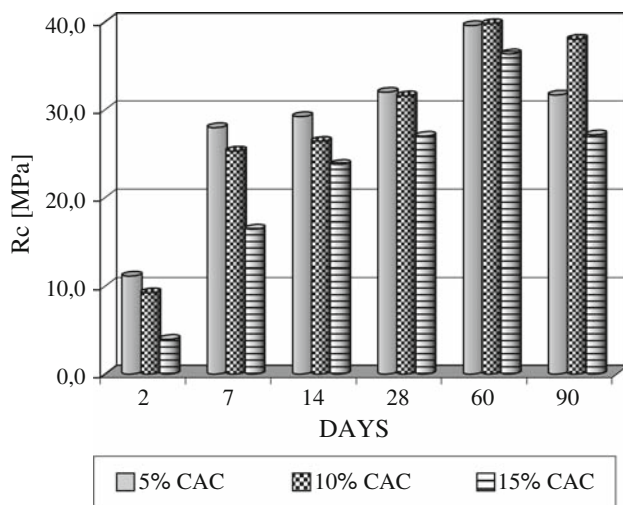

Fig. 5 Compressive strength of Portland cement + alumina cement pastes (not standardized specimens–cements mixed with water only!) versus time

flexural and compressive strength measurements. The results are presented in Fig. 6 and 7.

Discussion

As it can be easily seen in Figs. 1 and 2 the heat evolution process in Portland cement mixed with 5–25% of alumina cement is significantly modified. An enlarged plot of heat

evolution versus time for CAC addition to 25% is also shown in Fig. 3. The curves exhibit an initial exothermic peak within the first hour of hydration, attributed to the complex reactions occurring during the wetting process. As one can see in Figs. 1 and 3 the induction period associated with pure PC paste hydration is about 2 h. This is followed by an exothermic peak attributed to the C_3S and/or C_2S hydration and additional peak corresponding presumably to the excess C_3A hydration. On the calorimetric curve (Fig. 2) of the hydrated CAC there is a initial exothermic peak and the main one, sharp and very high, separated from the first one by a few hours lasting latent period. At 5% CAC addition the second main "silicate" generated peak becomes larger; the separated aluminate effect disappears. Presumably the peaks from aluminate cement and Portland cement interfere. It means that not only the heat evolved by CAC hydration may accelerate PC hydration but also the contribution from CAC to the rate of heat evolution is much larger than that of PC. In the sample corresponding to 10% CAC the peak from aluminate appears again soon after the induction period. It is quite reasonable that gypsum from Portland cement is consumed by the CAC phases during the first hour; the C_3A hydration is marked as a separated peak after short latent period. Further, with growing CAC content, the latent period becomes longer and longer and there is a significant delay in the appearance of the main hydration peak. The impermeable layer of ettringite is responsible for this effect, as it has been suggested by the other authors [1–5]. The formation of ettringite seems to take place "inside" the first thick peak. At 25% CAC (see Fig. 3) the two sharp, not very high "aluminate" peaks, separated from the first one are visible; the main "silicate" peak is broadened and appears after ca. 30 h.

There is a significant, evident similarity of the calorimetric curves for pure CAC (Fig. 2) with other curves for PC/CAC pastes containing not less than 80% CAC, as the total heat evolved is concerned. It means that heat evolution effect is due mainly to CAC hydration, however some Portland cement present in these blends can hydrate at the same time, even though a distinct separated peak cannot be observed. This is because the contribution from CAC to the rate of heat evolution is much larger than that of PC and some ettringite is deposited also on PC grains (however, the delaying effect in respect to the PC rich mixtures is not detected).

The total heat evolved during the 41 h (standard measuring time) is reduced in the mixtures of Portland cement with 5–25% of alumina cement. Therefore the delaying effect of ettringite/calcium aluminate hydrate layer is reflected. However, the changes are not of systematic, monotonic character because of the relatively high heat attributed to the ettringite or the other aluminate phase

formation and the "competition mechanism" between the PC and CAC components hydrating with or without gypsum. The mixtures rich in CAC (doped with up to the 20% PC) exhibit relatively high heat effect, very similar for the pure CAC.

The Portland cement samples doped with 20% and 25% CAC show a so-called flash setting on hydration (stiffening just after mixing with water) as it is illustrated in Fig. 4. This is the consequence of the large amount of ettringite formation. The quick setting is observed at 15% CAC addition. In the CAC + PC mixtures with no more than 10% CAC or no more than 20% PC the standard setting time (between 1 and 4 h) is found.

The Portland cement and calcium aluminate blends (with up to 15% CAC by mass of binder) reveal the compressive strength increase with time as measured throughout the 60 days storage (Fig. 5); this is a "normally predictable" effect. On prolonged storage, that is between 60 and 90 days, there is more or less significant strength decrease observed. However, the compressive strength of Portland
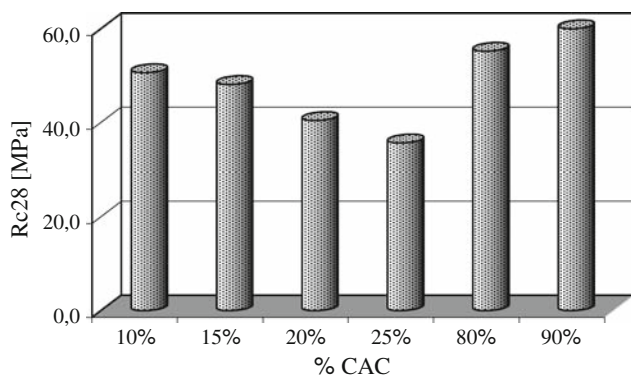
cement pastes with alumina cement addition up to 15% is reduced with growing CAC content in every term on hardening within 60 days. The strength of standard mortars (Fig. 6) lowers (after 28 days) with CAC percentage up to 25% CAC. This may be the consequence of phase transformations (decomposition of calcium aluminates, secondary or delayed ettringite formation) accompanied by structural changes. This may also result from the quick formation of impermeable layer of primary product (see the setting time data, Fig. 4) and hampered further hydration. On the other side the CAC rich mortars show rather stable strength values, though some slight strength decrease is observed with PC percentage. The flexural strength data (Fig. 7) seem to indicate the presence of structural elements strengthening the material on bending. This may be the fibrous ettringite phase. Finally one must find once again that the CAC additions destabilize generally the balance of the reaction of calcium sulfate from PC with C_3A and consequently the heat evolution process, setting and strength development are strongly modified. The CAC hydration is significantly less affected by PC additive.

Fig. 6 Compressive strength of Portland cement + alumina cement mortars (cementitious material mixed with quartz sand and water) after 28 days hardening
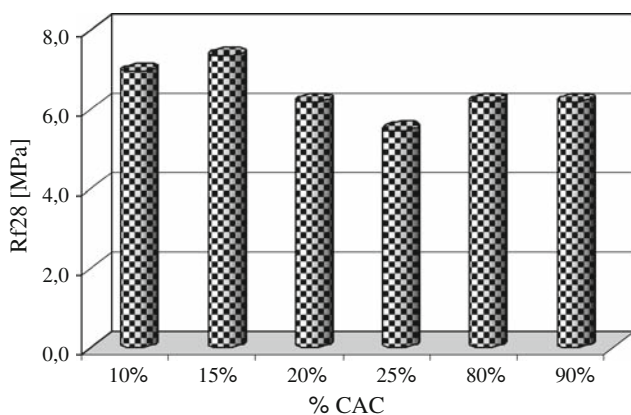

Fig. 7 Flexural strength of Portland cement + alumina cement mortars (cements mixed with quartz sand and water) after 28 days hardening

Conclusions

1. Calorimetry shows very clearly the effect of calcium aluminate cement addition on Portland cement hydration: the separate hydration of aluminate phases from CAC with gypsum from PC, the shortening of initial dormant period at low CAC ratio, the delaying effect attributed to the formation of ettringite on PC grains.
2. Calorimetry shows also the accelerating effect of low Portland cement additive on CAC hydration—the shortening of initial dormant period by the nuclei of PC originated primary products.
3. The Portland cement samples doped with 20% and 25% CAC show flash setting on hydration. The quick setting is observed at 15% CAC addition. In the CAC + PC mixtures with no more than 10% CAC or no more than 20% PC the standard, moderate setting is found.
4. The compressive strength of Portland cement pastes with alumina cement addition up to 15% is reduced with CAC content on hardening within 60 days. For every mixed sample the compressive strength increase with time up to 60 days is observed.
5. The compressive strength of Portland cement mortars with alumina cement addition up to 25% is reduced with CAC content on hardening within 28 days.
6. There is more or less significant strength decrease between 60 and 90 days storage of PC + CAC pastes.
7. The CAC rich mortars show stable strength values after 28 days maturing, though some strength decrease is observed with PC percentage.

8. CAC additions to PC modify strongly the heat evolution process, setting and strength development. The effect of small PC additive to CAC is much less pronounced.

References

1. Gu P, Beaudoin JJ, Quinn EG, Myers RE. Early strength development and hydration of ordinary Portland cement/calcium aluminate cement pastes. Adv Cem Based Mater. 1997;6:53–8.
2. Kinghelman J. Hydration and structure development of ternary binder system as used in self-levelling compounds. PhD Thesis (dir. Scrivener KL), Ecole Polytechnique, Lausanne, Switzerland; 2007.
3. Runova RF, Nosovsky YL. The composite binders based on alumina cement for special building mortars. Weimar: 15. Internationale Baustofftagung; 2003. p. 1-0265–2075.
4. Amathieu L, Bier Th A, Scrivener KL. Mechanism of set acceleration of Portland cement through CAC addition. International conference on calcium aluminate cements. Edinburg; 2001. p. 303–16.
5. Gu P, Beaudoin JJ. A conduction calorimetric study of early hydration of ordinary Portland cement/high alumina cement pastes. J Mater Sci. 1997;32:3875–81.
6. Scrivener KL. Calcium aluminate cements. In: Hewlett, PC, editor. Lea's chemistry of cement and concrete. London: Arnold; 1998. p. 709–78.
7. Scrivener KL. High performance concretes from calcium aluminate cements. Cem Concr Res. 1999;29:1215–23.
8. Taylor HFW. Cement chemistry. London: Thomas Telford; 1997. p. 295.
9. Amathieu L, Estienne F. Impact of the conditions of ettringite formation on the performance of products based on CAC+CS+OPC. Weimar: 15. Internationale Baustofftagung; 2003. p. 1-0253–63.
10. Janotka I, Krajci L. Sulphate resistance and passovation ability of the mortar made from pozzolan cement with zeolite. J Therm Anal Calorim. 2008;94:7–14.
11. Nocuń-Wczelik W. Calorimetry in the studies of cement—Pb compounds interaction. J Therm Anal Calorim. 2007;88:291–4.
12. Pacewska B, Błonkowski G, Wilińska I. Studies on the pozzolanic and hydraulic properties of fly ashes in model systems. J Therm Anal Calorim. 2008;94:469–76.