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Effect of Calcium Aluminate Cement Variety on the Hydration of Portland Cement in Blended System

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Abstract: Two kinds of CACs with different monocalcium aluminate (CA) contents were used in the PC/CAC (PAC) mixtures. Effects of CA and CACs on the properties of PAC were analyzed by setting times and the compressive strength tests, and also by means of calorimetry, XRD, DTA-TG and ESEM. The experimental results show that the compressive strength of the PAC mortars decreases with increasing content of CAC while it declines sharply with a higher content of CA in CAC. Compared with neat PC paste, the content of calcium hydroxide in hydrates of PAC paste decreases significantly, and the hydration time of PC is prominently prolonged. Additionally, the higher the content of CA in CAC, the more obviously the hydration of PC is delayed, confirming that the CA phase in CAC plays an important role in the delay of PC hydration.

Key words: calcium aluminate cement; Portland cement; hydration; delay; monocalcium aluminate(CA)

1 Introduction

CAC is well known as an indispensable material in the construction field for its high early strength even at low temperature and resistance to chemical attack^[1], which makes it usually use in special applications where the performance of PC is insufficient. But the usage of CAC is greatly limited for its phase transition at higher temperature, which results in the decline of later strength^[2,3]. The annual production of CAC is very small compared with PC, and CAC can not directly replace PC in daily applications. Therefore, it is widely used in combination with PC and calcium sulfate^[4-15]. In those formulations, CAC mainly contributes to a wide range of properties such as rapid setting and hardening, controlled expansion and shrinkage compensation.

Although it is well known that CAC is added

into PC to accelerate setting and hardening^[2,6,7,12,16], the replacement of PC with CAC has been found to be detrimental to the compressive strength especially at later age^[7,10,17], which becomes a barrier for the application of PAC mixtures. The addition of CAC delayed the hydration of PC^[7,12], which may result from the film-like hydration products which surrounded anhydrate granules at early age, however, with no clear evidence to prove it. Therefore, it is of prime importance to explore the underlying hydration mechanism of the PAC mixtures. Additionally, the commercial variety of CAC is totally different, especially on the content of the main phase CA, which results from the difference in production technology (melting method or calcination method) and the grade of raw material, so the choice of CAC in application becomes another key issue. According to literatures, there is an obvious lack of concerning investigations, so the hydration of PAC was further investigated and two kinds of CACs with different content of CA were compared in the present paper.

The calorimetric measurement is a well established method to study the kinetics and mechanism of hydration in cementitious materials^[18] since it shows great versatility in studying the hydration

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Table 1 Chemical compositions of the cements determined by XRF/wt%

| Cement | SiO ₂ | CaO | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | SO ₃ | K ₂ O | Na ₂ O | TiO ₂ |
|--------|------------------|-------|--------------------------------|--------------------------------|------|-----------------|------------------|-------------------|------------------|
| PC | 21.50 | 65.20 | 4.14 | 2.40 | 2.57 | 2.89 | 0.84 | 0.67 | 0.32 |
| A | 4.43 | 38.90 | 39.40 | 13.70 | 0.60 | 0.10 | 0.13 | - | 1.82 |
| B | 0.34 | 31.20 | 67.10 | 0.10 | - | 0.06 | - | 0.34 | - |

kinetics of cementitious systems and helps to monitor cement-admixture combinations with respect to the hydration process^[9, 19-23]. In addition, compared with widely used SEM, the sample preparation of ESEM has no destruction on the original microstructure, so it enables the more reliable observation of microstructure. Therefore, the calorimetry and ESEM, supplemented by other standard measurements such as XRD and DTA-TG, were used to investigate the effect of CAC variety on the hydration process of PAC mixtures.

2 Experimental

2.1 Cement

Portland cement (PC) (CEM I 42.5) and two varieties of CACs (hereafter named A and B separately) used were obtained from Lafarge Cement Co. and Kerneos cement Co., respectively. The chemical composition of the cements was determined by X-ray fluorescence (XRF), as listed in Table 1.

2.2 Mix proportions

| Table 2 Mix proportions/wt% | | | | | |
|-----------------------------|----|----|----|----|----|
| | PC | A | PC | B | |
| A1 | 97 | 3 | B1 | 97 | 3 |
| A2 | 94 | 6 | B2 | 94 | 6 |
| A3 | 91 | 9 | B3 | 91 | 9 |
| A4 | 88 | 12 | B4 | 88 | 12 |
| A5 | 85 | 15 | B5 | 85 | 15 |

As shown in Table 2, the PAC pastes were prepared by mixing two kinds of CACs in amounts of 3%, 6%, 9%, 12% and 15% by mass of PC respectively, and S0 refers to the pure PC. The water to cement ratio was 0.5 by mass. Mortar prisms (40 mm× 40 mm× 160 mm) were prepared according to GB/T 17671-1999 using 1350 g ISO standard quartz aggregate per 450 g cement.

2.3 Curing and testing

The setting time of PAC pastes was determined according to ASTM C191 using a Vicat apparatus at 20 °C. The specimens were demoulded after 24 hours curing at 20±1 °C with a relative humidity of 60%±10%. And the mechanical tests were performed at certain curing ages (3 and 28 days). Compressive

strength of mortars was measured according to GB/T 17671-1999. The standard deviation less than 15% with respect to the mean was applied in the analysis.

An isothermal heat-conduction calorimeter (TAM air C80, Thermometric, Sweden) was used to measure the hydration heat evolution of the binders. The water to binders ratio was 0.5 and the experimental temperature was 20±0.1 °C. Binders and water were tempered for several hours before mixing, then the water was injected into the reaction vessel and the samples were stirred in the calorimeter for several minutes. This procedure allowed monitoring the heat evolution from the very beginning when water was added to the binders. Data logging was continued up to 7 days.

Freshly fractured surfaces were examined by ESEM (FEI, QUANTA 200) using the low vacuum mode (at 1 Torr H₂O). The polished samples were prepared by epoxy resin impregnating, polishing and carbon coating. BSE images of the polished samples were used to estimate the porosity based on image analysis using the different grey levels under high vacuum mode (at 1E-5 Torr H₂O). The solid fractions of the blended cement pastes were crushed and ground in acetone, dried at curing temperature and then used for XRD and DTA-TG analyses. The XRD data were recorded using a Rigaku-D/max2550VB3+ instrument. Scanning was performed between 5° and 75° with a 2θ increment of 2°/min, and a Cu Kα radiation (λ= 1.54 Å). In addition, an accelerating voltage of 40 kV and a current of 100 mA were selected. DTA-TG analyses were performed with a simultaneous thermal analyzer (NETSCH, STA 449 C Jupiter), where about 10 mg of hydrated sample was placed in an open vessel in N₂ atmosphere, and investigated at a heating rate of 10 °C/min up to 1 050 °C.

3 Results and discussion

3.1 Setting time

The setting time of PAC is given as the function of the dosage of CAC in Fig.1. Both initial and final setting time of PAC are shortened with increasing dosage of CAC. The CAC content at a replacement

level below 6% has little effect on the initial and final setting time; while both initial and final setting time decreases sharply when the CAC content is higher than 6%, and rapid setting even occurs in the A5 and B5 pastes.

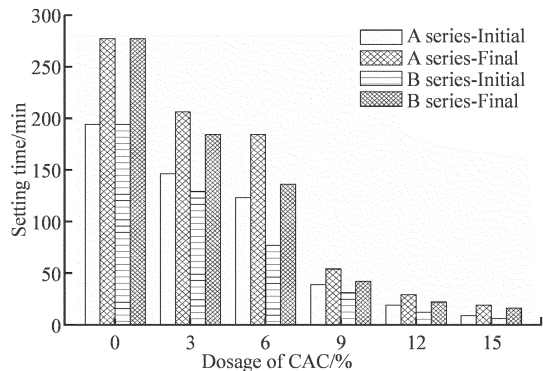


Fig. 1 Relationships between setting times of PAC and dosage of CAC

It also can be observed that both initial and final setting time of the PAC with higher content of CA (B series) are shorter than that of A series. The microstructure of B series paste develops very quickly once in contact with water, which may result from the quick formation of ettringite, alumina gel and hydrated calcium aluminate. But Gu *et al* indicated that the rapid setting of PAC only resulted from the quick formation of ettringite^[7,9]. In addition, Scrivener *et al* demonstrated that hydrates of PC were mainly deposited around unhydrated cement grains, while those of CAC were evenly distributed throughout space^[24]. When they were blended, the main phases in CAC such as CA reacted with water rapidly and thus alumina gel and pellicle-like hydrated calcium aluminate formed, so the connectivity of the paste decreased quickly. As a result, both initial and final setting time was shortened, and the PAC with higher CA set more rapidly.

3.2 Strength development

Fig. 2 shows the relationship between compressive strength of the PAC mortars and the dosage of CAC obtained after 3 days and 28 days. In general, the compressive strength of the PAC mortars is less than that of PC mortar. For instance, the 28-day strength of B3 mortar is only 62% of that of S0. Additionally, it firstly increases slightly and then decreases greatly with increasing CAC content, reaching a maximum value at a CAC content of 6%. As hydration time increases, the effect of CAC content on the compressive strength of PAC mortars diminishes, especially when the CAC content is higher than 6%.

After 3 days of hydration, the compressive

strengths of the A series mortars are much higher than that of B series. However, this situation does not prevail as hydration time increases. The compressive strengths of the A series mortars improve little from 3 days to 28 days, while that of B series mortars grows gradually and even exceeds that of A series after 28 days when the CAC dosage is 3% and 6%, indicating that the increasing content of CA phase in PAC mixtures declines the early strength of cement mortar significantly, but has less effect on the later strength.

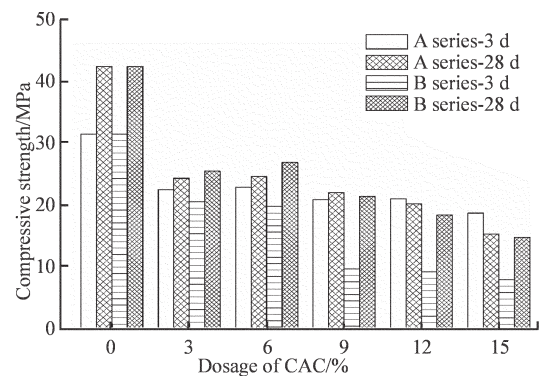


Fig. 2 Relationships between compressive strength of PAC mortars and dosage of CAC

3.3 Hydration

3.3.1 Rate of heat evolution

The curves for the rate of heat evolution of A5 and B5 exhibit a heat evolution profile similar to that of neat PC paste (Fig. 3). According to the Taylor's theory on cement chemistry^[2], the first exothermic peak in the heat evolution curve of PC results from complex reactions during the wetting process. The second exothermic peak can be attributed to the C_3S and/or C_2S hydration. In addition, the third exothermic peak (if present) results from the transition from ettringite to monosulfate. Compared with the curve of PC (S0), there is a significant delay in the appearance of the second peak for the curve of A5 and B5. The so-called induction period associated with S0 paste is about 2 h. However, it is much longer for A5 and B5. The maximum values of the heat evolution rate for S0, A5 and B5 pastes are 2.71, 1.77 and 1.54 $mW \cdot g^{-1}$, and the corresponding time is 13.08, 54.40 and 62.34 h, respectively. It means that the hydration of PC is significantly delayed with CAC addition. This finding is consistent with the findings of Gu *et al*^[7,9] and Gawlicki *et al*^[25] who stated that this long dormant period may result from a surface coverage of the clinker grains by early hydration of CAC.

Moreover, it can also be concluded from Fig. 3 that the hydration of PC is more obviously delayed

by B series than A series, which indicates that the hydration of PAC is sensitive to CA content. A higher content of CA slows down the hydration of PC more seriously. As a result, the 3-days compressive strength of B series is much lower than that of A series, which is consistent with the results obtained from Fig.2.

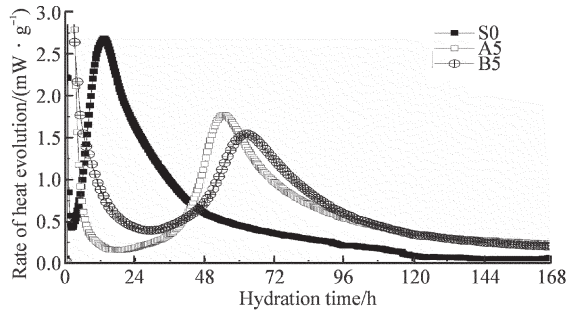


Fig. 3 Rate of heat evolution of the pure S0, A5 and B5 pastes

3.3.2 Phase composition

From the XRD patterns of PAC pastes obtained after 3 days of hydration (Fig.4), both calcium hydroxide (CH) and ettringite formed in the hydrates. Notably, the amount of CH in A5 hydrates was much lower than that of S0. Additionally, a small peak around 10° in the pattern of A5 indicates that calcium aluminate hydrate formed.

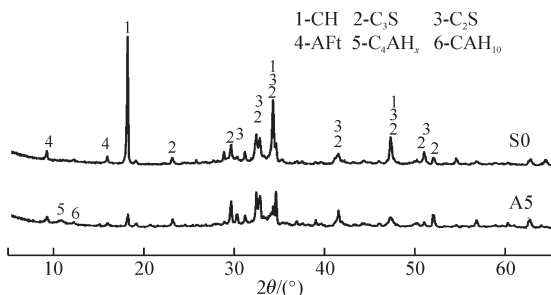


Fig. 4 XRD patterns of S0 and A5 pastes hydrated after 3 days

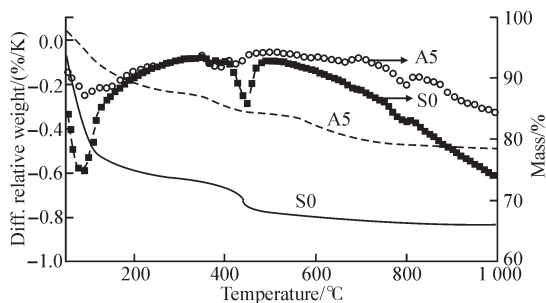


Fig. 5 DTA-TG curves of S0 and A5 pastes hydrated after 3 days

CH is one major phase of PC hydrates, and the amount of CH reflects the overall hydration degree of clinker. The DTA-TG data (Fig.5) indicate that the CH content in hydrates of S0 and A5 pastes after 3 days is 14.1% and 3.7%, respectively. It means that the PC in PAC has a much lower degree of hydration,

which is confirmed by the XRD patterns shown in Fig.4. Additionally, the CH content in hydrates is not consistent with the weight ratio of PC in PAC. The PC content in the unhydrated A5 paste is 85% of that in the unhydrated S0, but the CH amount in the A5 paste is only 26% of that in the S0 paste after 3 days of hydration. This further suggests that the hydration of PC is delayed by CAC, which is in agreement with the findings of Gu *et al*^[7].

3.3.3 Morphology

The ESEM images show clearly that film-like hydrates cover the unhydrated granules of A5 and B5 paste hydrated after 3 days (Fig.6(b) and Fig.6(c)), which is more obvious in the B5 paste at higher magnification factor in Fig.6(d). However, instead of such film-like hydrates, only ettringite and C-S-H gel are clearly observed in the S0 paste (Fig.6(a)). Additionally, comparing Fig.6(b) with Fig.6(c), it can also be concluded that a higher content of CA in paste contributes to an obvious increase in the formation of film-like hydrates.

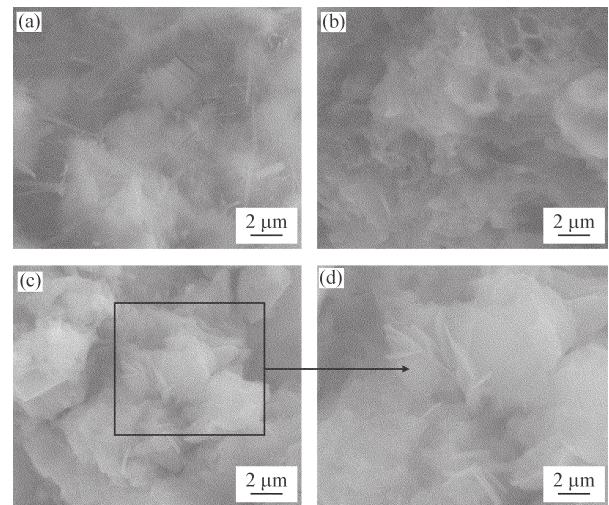


Fig. 6 ESEM images of pastes after 3 days: (a) S0 paste; (b) A5 paste; (c) B5 paste; (d) B5 paste

The protective layer hypothesis has been widely accepted by many researchers, who postulates that a hydrate forms fitting closely on the surface of C3S and hydration restarts when this hydrated layer is removed or converted, but no evidence has been given up to now. The ESEM is used in this paper to avoid the destruction on the sample during sample preparation. As can be seen from Fig.6, the layer which forms in the hydrates of PAC may delay further hydration of PC, and directly leads to the reduction of compressive strength (Fig.2) and the delay in heat evolution of PAC (Fig.3). The film-like hydrates in B5 paste are more

pronounced than those in A5 paste, so the hydration is delayed more seriously.

To characterize the chemical composition of the membrane, energy dispersive spectroscopy (EDS) was also applied. However, because the film-like hydrates are very thin and irregular, it is difficult to determine them even at low acceleration voltage, so further study is necessary. But the deduction, which the delay of PC hydration only results from the formation of ettringite crystals which surround the anhydrate granules at early age, is not universal. Palou MT^[26] found that Al^{3+} delayed the hydration of PC, which may result from the formation of alumina gel. Such semi-permeable membrane broke until the concentration of Ca^{2+} and OH^- was higher enough and then the hydrates such as ettringite and CH precipitated, which seems more reasonable.

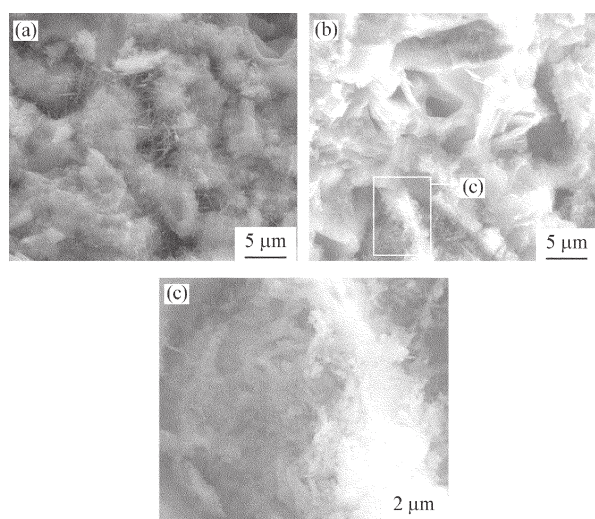


Fig.7 ESEM images of pastes after 28 days: (a) S0 paste; (b) A5 paste; (c) A5 paste

After 28 days of hydration, the hydrates such as C-S-H gel, CH and ettringite fill the granules and voids in S0 paste (Fig.7(a)) and form a spatial network with unhydrated grains. Instead, many coarse pores are generated (Fig.7(b)) and the calcium alumina hydrates such as C_3AH_6 form in A5 paste (Fig.7 (c)). Therefore, the strength of PAC mortar decreases compared with that of PC mortar.

3.4 Discussion

When PC is blended with CAC, the mechanical strength of the binary system mortar (especially the 3-day strength) is significantly reduced, which is mainly caused by the following three aspects: on the one hand, PAC sets rapidly for these with higher content of CAC, so the hydration products generate

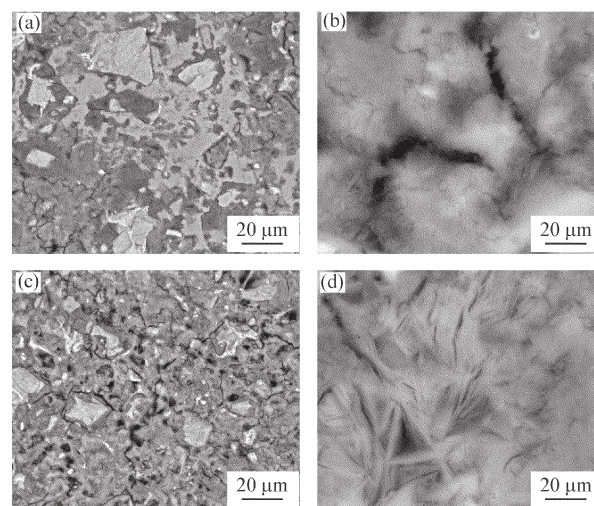


Fig.8 BSE images of pastes for 28 d: (a) S0; (b) A5

with no time for even dispersion, as a consequence, hydration product deposits on the surface of the unhydrated particles with low filling in pores, which has obviously adverse effects on later hydration; on the other hand, from the aspect of hydration process, the incorporation of CAC significantly leads to longer induction period, thus delays the early hydration of PC; additionally, from the aspect of microstructure of hydration products, a large amount of flake-like hydrated calcium aluminate generates and ettringite transfers to monosulfate because of the lack of sulfate in PAC. As shown in Fig.8(b), those flake-like hydration products between the laps are very loose, so they are vulnerable to crack. In addition, according to the cement chemistry theory^[3], solid volume increases by 164% when ettringite generates, while it increases by 79.2% when monosulfate generates (the density of ettringite is 1.73 g/cm^3 and the density of monosulfate is 1.80 g/cm^3), so if ettringite transfers into monosulfate, the solid volume decreases and porosity increases prominently. Therefore, under the combined effects of the above factors, the 3-day strength of binary system mortar is significantly lower than PC mortar, and the higher the CAC content, the lower the strength, accompanied with greater drying shrinkage at the same time.

4 Conclusions

Based on the aforementioned results, the variety of CACs with different CA contents exert a significant influence on the hydration properties of PAC blends. The following conclusions can be drawn from the present work:

a)The compressive strength of PAC mortars

decreases with increasing content of CAC. Additionally, even with the same dosage of CAC, the higher the content of CA in CAC, the lower the compressive strength.

b) Compared with PC paste, the content of CH in hydrates of PAC paste decreases significantly and the appearance of heat evolution from PC is obviously prolonged, which confirms that the hydration of PC is delayed by the addition of CAC.

c) The CA phase in CAC plays an important role in the delay of PC hydration. The higher the content of CA in CAC, the more obviously the hydration of PC is delayed.

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