J Therm Anal Calorim (2009) 98:737–742
DOI 10.1007/s10973-009-0107-3

Calorimetric study of calcium aluminate cement blended with flue gas desulfurization gypsum

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Received: 15 November 2008 / Accepted: 17 February 2009 / Published online: 19 June 2009

Abstract The use of by-product gypsum is an important alternative in concrete design. In present experiment, conduction calorimetry was applied to investigate the early hydration of calcium aluminate cement (CAC)/flue gas desulfurization (FGD) gypsum paste, supplemented with the determination of setting times and analysis of hydrates by X-ray diffraction (XRD). It was found that different profiles of heat evolution rate were presented depending on the CAC/FGD gypsum ratio. Two distinct exothermic peaks, associating with CAC hydration and ettringite formation respectively, appeared when the FGD gypsum content was less than 20%. Hydrate barrier mechanism was introduced to explain the difference in induction periods of the pastes with or without FGD gypsum. It is concluded that the blending of FGD gypsum accelerates the hydration of CAC for the quick formation of ettringite and generates greater hydration heat from per gram of pure CAC for the high exothermic effect of ettringite formation. The dissolution and diffusion of gypsum plays an important role of reacting controller during the hydrations of the pastes with FGD gypsum. The modified hydration process and mechanism in this case is well visualized by means of calorimetry.

Keywords Calcium aluminate cement · Calorimetry · Ettringite · FGD gypsum · Hydration

Introduction

Flue gas desulfurization (FGD) gypsum is a by-product generated from lime–gypsum wet flue gas desulfurization, which dominates the technologies of SO_2 emission control in coal-fired power plants. Two effective ways to utilize FGD gypsum in Europe and the United States are in plasterboard manufacture and in Portland cement production as a retarder [1]. Generally, the plaster-based products cannot be applied in exterior situation because gypsum is relatively soluble in water. In Portland cement production, the disadvantage is that only 3–5% FGD gypsum can be mixed in the clinker [2, 3]. A preferably hydraulic binder with large proportion of FGD gypsum would be an optimum for the utilizations of FGD gypsum.

Calcium aluminate cement (CAC) is an important construction material for its resistance to chemical attack and high temperatures. Different hydrates are created, i.e., CAH_{10}, C_2AH_8 and C_3AH_6 (notation commonly used in cement chemistry: $C = \mathrm{CaO}$, $A = \mathrm{Al_2O_3}$, $H = \mathrm{H_2O}$, $S = \mathrm{SiO_2}$, $\hat{S} = \mathrm{SO_3}$), depending on the temperature at which the hydration process take place [4]. The conversion of hexagonal phases (CAH_{10} or C_2AH_8) to C_3AH_6 and AH_3 in the hydration of CAC under certain temperature conditions has been a problem, limiting its use as a structural material [4, 5]. The following benefits are achieved when gypsum is added as CAC cement replacement in concrete: reducing the cement content (reducing costs), reducing shrinkage, increasing early strength, preventing strength declining at later ages, improving sulphate corrosion resistance [6]. Natural gypsum has been used for this purpose for a long time, until the by-product gypsum appeared. The processes of hardening and new phases' formation in such CAC/gypsum materials have been well investigated, but the characteristics of heat release, which are of great

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importance in the studies of hydration mechanism, need more investigations. The differences of chemical composition and particle size distribution between natural and FGD gypsum may also affect the hydration process and micro-structural development of such materials.

In this study, the calorimetric measurement, a well-establish method to study the kinetics and mechanism of hydration in cementitious materials in situ [7–17], was used to investigate the effect of different FGD gypsum contents on the hydration process in CAC/FGD gypsum admixture. The study followed by other standard measurements, allowed to elucidate the scale of FGD gypsum utilization in cement, an important task from waste utilization point of view.

Experimental

Materials

The FGD gypsum used here comes from Ban Shan Power Plant, a local coal-fired power plant in Hangzhou, China. Its main chemical compositions are given in Table 1. The mass percentage of calcium sulfate dihydrate is up to 94.3% and the main impurities are quartz and unreacted limestone. Other impurities including some hazardous elements are also presented in this table. The FGD gypsum is not ground, and its particle size distribution is shown in Fig. 1. The maximum particle size of the FGD gypsum is less than 250 μm and its mean particle size of the FGD gypsum is 40.5 μm.

The chemical compositions of a commercial CAC are also shown in Table 1. Its XRD patterns indicate that gehlenite (C_2AS) rather than monocalcium aluminate (CA) is the major mineral. The CAC's surface area is 3,000 m^2 kg^{-1} (BET).

Preparation of sample and test method

The binders were prepared with different FGD gypsum proportions (5–60%) and the pure CAC was set as reference (Table 2). An isothermal heat flow microcalorimeter-TAM Air, manufactured by Thermal Analysis Co. (U.S.A.), was employed for calorimetric measurement. Distilled water (2.50 mL) was added into 5.00 g binder giving a w/c ratio of 0.5, and then the sample was mixed and put into the calorimeter's chamber where it was submerged in an air bath maintained at 20.0 °C.

A w/c ratio of 0.35 was adopted in the pastes prepared for setting time determination and XRD analysis. Setting time was measured by a Vicat test apparatus according to the procedure described in ISO 9597: 1989. At giving hydration time, small pieces of the pastes were soaked in alcohol for 24 h to stop hydrating. Then, they were ground

Table 1 Chemical composition of FGD gypsum and CAC

Oxides/elements	Chemical compositions (wt.%)	
	FGD gypsum	CAC-50
CaO	31.76	34.0
SO_3	43.87	–
SiO_2	2.00	8.0
CO_2	0.82	–
Al_2O_3	0.25	51.0
Fe_2O_3	0.10	1.9
MgO	0.03	1.2
K_2O	0.03	–
Na_2O	<0.01	–
TiO_2	–	2.6
B	18×10^{-4}	–
Pb	$<10 \times 10^{-4}$	–
Ni	$<10 \times 10^{-4}$	–
Cr	7.1×10^{-4}	–
As	1.17×10^{-4}	–
Cd	$<1.0 \times 10^{-4}$	–
Hg	0.441×10^{-4}	–
IL	20.10	–
Total	98.96	98.7

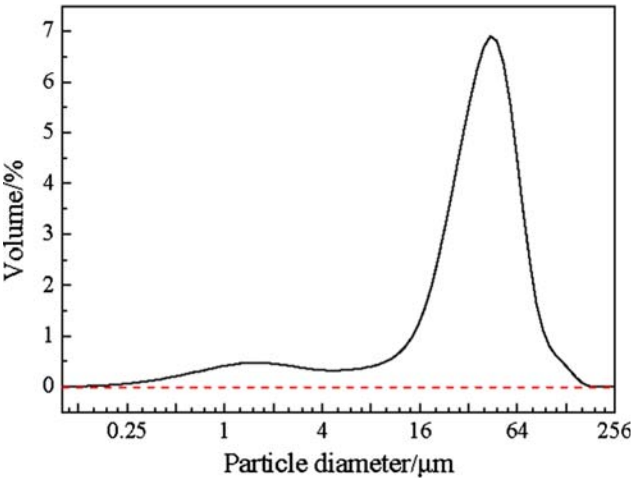

Fig. 1 Particle size distribution of FGD gypsum

Table 2 Compositions of CAC/FGD gypsum binders

Component	Percentage (wt.%) in binder								
	1	2	3	4	5	6	7	8	9
CAC	100	95	90	85	80	70	60	50	40
FGD gypsum (FG)	0	5	10	15	20	30	40	50	60

in alcohol with an agate mortar and filtrated. The ground samples for XRD analysis were dried in a vacuum oven at 45 °C for 48 h. X-ray diffraction was carried out with RIGAKU D/MAX 2550/PC diffractometer in the range of 5° 2θ to 60° 2θ, with step of 0.02°/2 s.

Results

Calorimetric analysis

The curves of heat release rate versus hydration time up to 24 h of pure CAC paste and pastes containing various percentage of FGD gypsum are illustrated in Fig. 2. The curves exhibit an initial exotherm in preliminary minutes of hydration, and then present low and steady heat release rate in several hours, which is usually called as induction period. The induction period of pure CAC hydration is about 5.9 h followed by an exothermic broad hump. The maximum heat evolution rate of pure CAC paste is 5.13 W kg^{-1} at 8.9 h. Comparing with the pure CAC, a shorter induction time of 2 h around is observed in the pastes containing 5–40% FGD gypsum. A little longer induction period is observed for pastes containing 50% and 60% FGD gypsum, i.e. 2.5 h.

Two exothermic peaks are observed for pastes containing 5–15% FGD gypsum. The first peaks in pastes with 5%, 10% and 15% FGD gypsum appears at 3.4, 3.5 and 3.1 h respectively, and the corresponding heat release rates are 5.69, 5.56 and 4.86 W kg^{-1}. The second ones appear at 4.1, 6.2 and 10.5 h respectively, and the corresponding heat release rates are 7.74, 5.48 and 4.31 W kg^{-1}. It presents such tendency that the first peaks appear closely regardless of different amount of FGD gypsum, while the second peaks shift to later ages with the increase of FGD content. Not an obvious second peak but a “shoulder” is found at around 12 h when the FGD gypsum content reaches 20%. All pastes with exceeding 20% FGD gypsum present similar heat evolution profiles: the heat evolution rate declines gradually after an exothermic peak. The maximum heat release rates of pastes with 20%, 30% and 40% FGD gypsum are 4.77, 4.26, 4.06 W kg^{-1} respectively, and the corresponding times are all at 3.6 h around. The maximum heat release rates of pates with 50% and 60% FGD gypsum are 3.06 and 2.83 W kg^{-1} respectively, and the corresponding times are both at about 4.2 h.

Plots of cumulative heat evolution versus time are given in Fig. 3. The pastes with FGD gypsum have much bigger cumulative heat release than the pure CAC paste in preliminary hours, so an obvious acceleration effect is observed in the pastes with FGD gypsum. The pure CAC has a very small cumulative heat in the first 6 h, and then start to increase quickly. After 24 h hydration, the pure CAC paste and the pastes with 5–20% FGD gypsum have similar cumulative heat release. However, the total heat

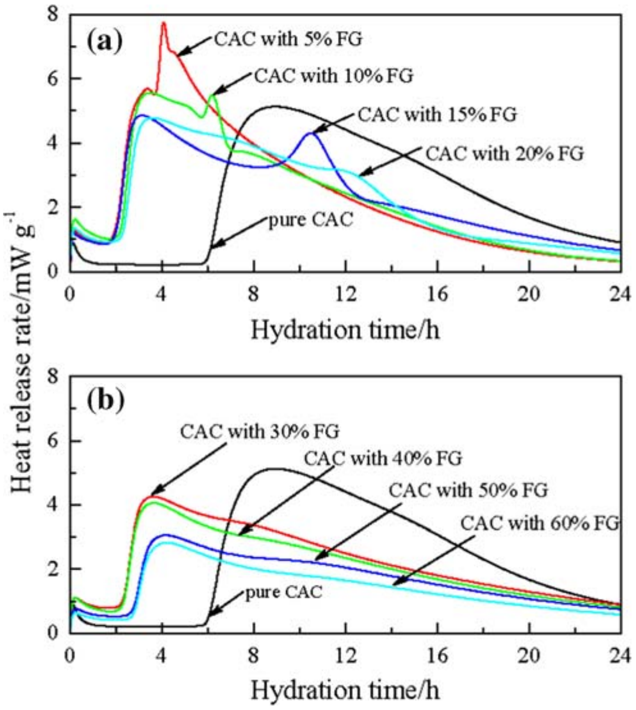

Fig. 2 Heat evolutions on binders of pure CAC and CAC/FGD gypsum

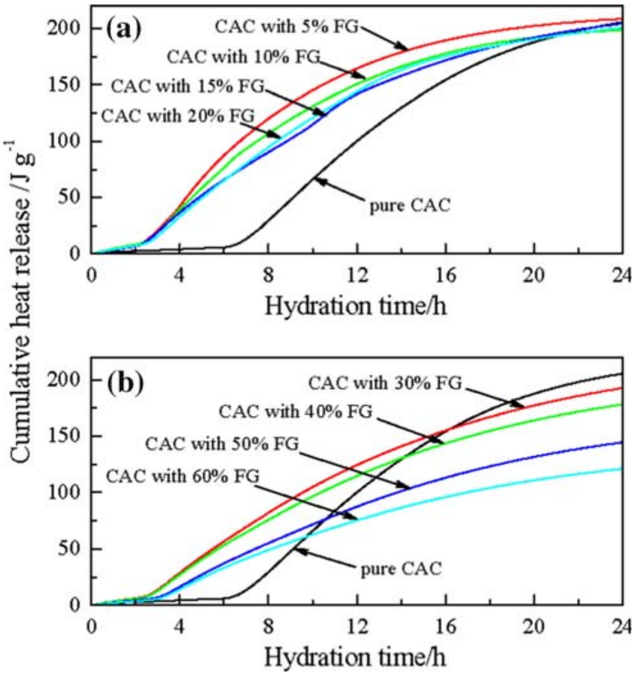

Fig. 3 Cumulative heat releases on binders of pure CAC and CAC/FGD gypsum

releases of pastes decrease gradually with the increase of FGD gypsum content (30–60%).

The percentages of total heat of hydration released from per gram of CAC are shown in Fig. 4. The data is calculated by the results of cumulative heat release in 24 h (Fig. 3). More heat releases from per gram of CAC in the pastes with FGD gypsum. It shows an ascending profile until FGD gypsum reached 40% in the paste.

Setting times and hydrates analysis

The initial and final setting times of the pastes are shown in Fig. 5. Comparing with the pure CAC paste, the setting times of pastes with FGD gypsum shorten remarkably and increase regularly as FGD gypsum exceeding 20%. The initial setting times of the pastes with different amount of FGD gypsum are from 105 to 220 min and the final setting times are from 145 to 280 min, while the initial and final setting time of the pure CAC paste are 350 and 460 min respectively.

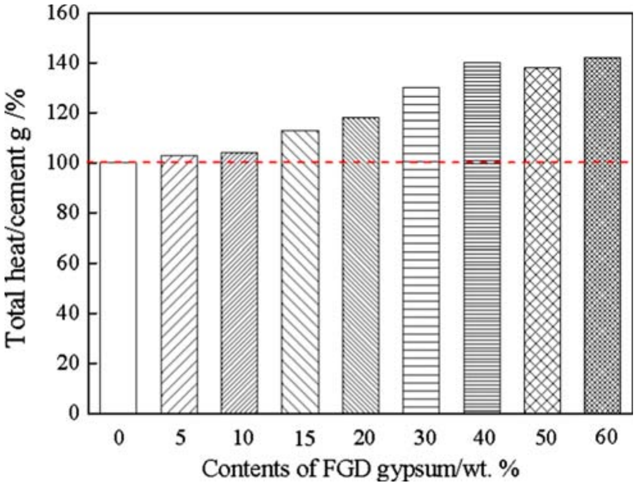

Fig. 4 Heat release from per gram of CAC for CAC/FGD gypsum binders

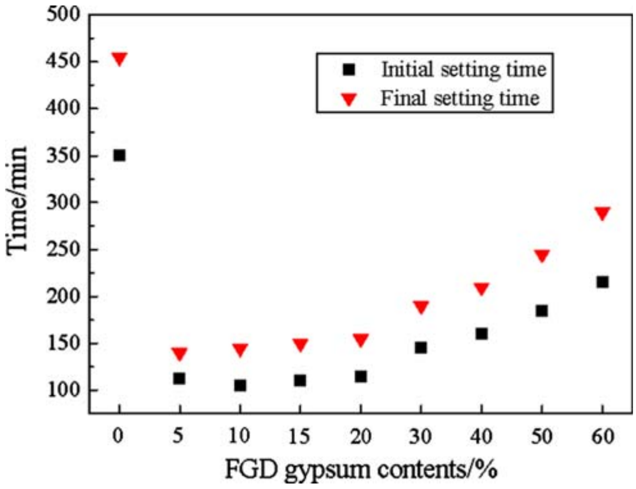

Fig. 5 Setting times of the pastes of pure CAC and CAC/FGD gypsum

The XRD patterns of pure CAC paste at three different hydration times are shown in Fig. 6. There is no clear indication of a CAH_{10} peak at 2 and 5 h, but the characteristic peaks appears at 24 h. No characteristic peaks of C_2AH_8 appear during the whole hydration time of 24 h. The intensity of CA peaks has no obvious decreasing at 5 h but at 24 h. The XRD patterns of the paste with 10% FGD gypsum at three different hydration times are shown in Fig. 7. The characteristic peaks of gypsum are still very strong after 2 h hydration, and decrease remarkably after 5 h and disappear after 24 h. The characteristic peaks of ettringite appear until 5 h of hydration, and enhance remarkably at 24 h. It indicates clearly that all of the

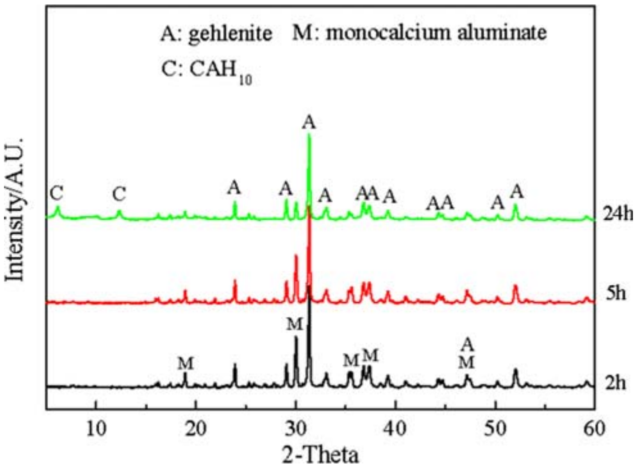

Fig. 6 XRD patterns of pure CAC paste at different curing times

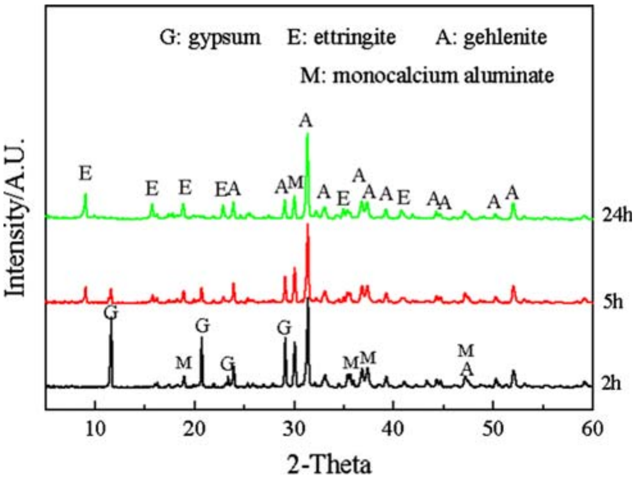

Fig. 7 XRD patterns of CAC with 10% FGD gypsum paste at different curing times

gypsum in this paste has been depleted in 24 h for the quick formation of ettringite. Peaks of CAH_{10} vanish in the pastes with FGD gypsum because aluminates prefer to form ettringite in the cementitious system with gypsum. Gehlenite peaks appear in both pastes and keep nearly the same intensity at different hydration times (Figs. 6, 7).

Discussion

Hydration mechanism of CAC with or without gypsum

Basically, hexagonal phase of CAH_{10} is generated when CAC is blended with water at 20.0 °C at early hydration age [4, 5], as Eq. 1 and 2 show.

$$\mathrm{CA} + 10\mathrm{H} \rightarrow \mathrm{CAH_{10}} \tag{1}$$

$$\mathrm{CA_2} + 13\mathrm{H} \rightarrow \mathrm{CAH_{10}} + \mathrm{AH_3} \tag{2}$$

However, Ettringite is directly produced when gypsum exists according to the following reactions:

$$3\mathrm{CA} + 3\mathrm{C}\widehat{\mathrm{S}}\mathrm{H_2} + 32\mathrm{H} \rightarrow \mathrm{C_6A}\widehat{\mathrm{S}}_3\mathrm{H_{32}} + 2\mathrm{AH_3} \tag{3}$$

$$3\mathrm{CA_2} + 3\mathrm{C}\widehat{\mathrm{S}}\mathrm{H_2} + 41\mathrm{H} \rightarrow \mathrm{C_6A}\widehat{\mathrm{S}}_3\mathrm{H_{32}} + 5\mathrm{AH_3} \tag{4}$$

Ettringite can precipitate in a few minutes and has a very low solubility of 1.1×10^{-40} mol L^{-1} [18, 19].

Soon, hydrates of ettringite and AH_3 gel cover the surface of CAC particle in the pastes with FGD gypsum, while hydrates of CAH_{10} and AH_3 gel cover the surface of CAC particle in the pure CAC paste. Then, the hydration process is inhibited and little heat is released (Fig. 2). Such period known as induction period can be explained by hypothesis mechanism of hydrate barrier [20, 21]. It supposes that a thin layer of hydration products rapidly covers the entire unhydrated grain when cement reacts with water and a physical barrier impedes further contact between water and the inner cement particles and the hydration reaction then becomes diffusion controlled.

It seems that the AH_3 gel layer integrated with ettringite crystal is much more permeable by water and easier broken by over crystallization than the layer of AH_3 gel together with poor crystal CAH_{10}. So the pastes with FGD gypsum have bigger heat release rate during the induction period and much shorter induction period than the pure CAC paste (Fig. 2).

Hydrates of CAH_{10} and ettringite are believed to generate as the pastes contact with water. However, their characteristic peaks do not appear in the pastes within the induction time (Figs. 6, 7). It may attribute to the low concentration of such hydrates at that time.

It is noticed that gehlenite peaks nearly keep the same intensity at different hydration time in the pastes with or without FGD gypsum. The reason may be linked to its low hydraulic activities and the conditions in which gehlenite hydrate could be formed [22–25]. Theoretically, gehlenite's hydrate can be formed by hydration reaction of C_2AS:

$$\mathrm{C_2AS} + 8\mathrm{H} \rightarrow \mathrm{C_2ASH_8} \tag{5}$$

Association of heat release with hydration

The initial exotherm in preliminary minutes of hydration is attributed to complex reaction during the wetting process. These reactions include hydration of CA and CA_2, dissolution of gypsum and formation of ettringite. Then the hydration proceeds in induction period and low heat releases as mentioned above.

With process of hydration, large mounts of heat are released during that process. For the pastes with 5–15% FGD gypsum, the first exothermic peaks appear at close time associating with ettringite formation, and the second ones present ascribing to CAC hydration when the gypsum is depleted. So the second peaks delay as the content of FGD gypsum increases (Fig. 2a).

For the pastes with 20% or more FGD gypsum, no obvious second exothermic peak appears (Fig. 2). It means that the whole hydration process is controlled by the reaction of ettringite formation. However, maximum heat released from per gram of CAC achieved only as exceeding 40% FGD gypsum is blended in the paste (Fig. 4). It means that the dissolution and diffusion of gypsum is a key process for hydrates of CAC turning to ettringite in the pastes with FGD gypsum, especially in the pastes with 20% and 30% FGD gypsum. It also indicates that more heat could release when aluminates react with gypsum and water to generate ettringite for its big synthetic heat. The gradual decline of heat release rate and cumulative heat release in the pastes with exceeding 20% FGD gypsum is mainly caused by the dilution effect of CAC with excessive gypsum.

The sampled CAC in which gehlenite dominates the mineral phases generates lower heat evolution than ordinary CAC where CA is usually the main mineral.

Association of heat release with setting time

Setting time is intrinsic reflections of the hydrating processes and the matrix structure formations in different pastes. As hypothesis mechanism of hydrate barrier, the paste does not set until the breakdown of this barrier by nucleation of CAC hydrates and ettringite. The initial setting times of the pastes coincide well with the heat evolution regulation, that is, the initial setting time is close with the ending of induction time for each paste (Figs. 2, 5). The quick setting of pastes with FGD gypsum is beneficial for early strength development of the pastes, so it is favorable in some building construction such as self-leveling floor screed.

Conclusion

Based on the experiment results, it could conclude that:

- It is evident that the CAC/FGD gypsum ratio has a significant influence on the hydration behavior of the cementitious system, so the pastes with different CAC/FGD gypsum ratio present different heat release regulation.
- Generally, the blending of FGD gypsum accelerates the hydration of CAC paste because of the quick formation of ettringite. For the pastes with 5–15% FGD gypsum, two dominative hydration processes, the ettringite formation and the hydration of CAC, control the hydration process successively. The whole hydration process is controlled by the reaction of ettringite formation in the pastes with exceeding 20% FGD gypsum. The dissolution and diffusion of gypsum plays an important role of react controller in the blended pastes, especially with 20–30% FGD gypsum.
- It seems that different hydrates and conformation of the initial hydration layer cause the difference of induction period between the pastes with or without FGD gypsum. It is ready to be explained by the simple hydrate barrier effect.
- The quick formation of ettringite and remarkable shortened induction period of pastes with FGD gypsum make the pastes have short setting times, and it is favorable in some building construction such as self-leveling floor screed.

Acknowledgements The authors acknowledge greatly the financial support of this work by the fund of Science and Technology Plan of Zhejiang Province, China (Project No. 2007C23055), Chinese National Programs for High Technology Research and Development (Project No. 2006AA03Z385) and New Century Excellent Scholar Program of Ministry of Education of China (NCET-04-0549).

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