

Investigations of anhydrite in CFBC fly ash as cement retarders

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HIGHLIGHTS

- ▶ Anhydrite in CFBC ash is used as a setting retarder.
- ▶ The overall SO₃ content is controlled in blended cement.
- ▶ Anhydrite in CFBC ash is a suitable setting retarder.
- ▶ Mechanical properties decreased by replacing gypsum with anhydrite in CFBC ash.

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ABSTRACT

Circulating fluidized bed combustion (CFBC) ashes are different from conventional coal ashes for good pozzolanic and hydraulic properties. However, the ashes are undesirable as cement admixture due to excessively high SO₃ content. The aim of this paper is to investigate the possible displacement of natural gypsum in cement with anhydrite in CFBC ash in terms of setting time, strength development, volume stability and hydration process. Experimental results indicated that anhydrite in CFBC ash can be used as an efficient setting retarder but lead to lower mortar strength. The effect is harmless to volume stability of cement paste with appropriate anhydrite addition. Compared with natural gypsum, anhydrite in CFBC ash makes ettringite formation slower and more transformable.

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1. Introduction

Circulating fluidized bed combustion (CFBC) is a very promising coal combustion technology for cleaning flue gases. The CFBC technology is more efficient and advanced than pulverized coal combustion (PCC) due to large reductions of SO₂ and NO_x emissions in flue gases [1]. In CFBC boiler, powdered coal is burnt in the presence of ground limestone which is used as a sorbent of SO₂ at 850–900 °C, below the temperature of PCC about 1200–1400 °C. And in order to increase the efficiency of SO₂ removal, typical Ca/S molar ratios are often increased to 2–2.5 [2,3]. Both fine fly ash and coarse bottom ash are produced in the combustion process. Mainly due to the relatively lower combustion temperature, the CFBC ash differs distinctly from the PCC ash in chemical and mineral composition. Besides the pozzolanic components from the burnt coal, CFBC ash is richer in anhydrite as well as free lime. Previous studies have shown that CFBC ash has better pozzolanic activity, and higher contents of anhydrite and free lime contribute to higher self-cementing property than PCC ash [4].

Today, approximately 50 million tons of CFBC ashes are generated annually in China [5], which poses a challenge for ash disposal. However, large quantities of CFBC ashes are usually discharged directly to waste dumps or stockpiled landfills, leading to large land occupation and environment pollution. Thus, further insight into the potential use of CFBC ash in construction should be made extensively. Many attempts to use CFBC ash as cement or concrete admixture have been reported due to good pozzolanic activity and self-cementing property [6,7]. Nevertheless, the utilization of CFBC ash remains limited in cement and concrete in which the PCC ash is widely utilized because the CFBC ash is outside of the specification for pozzolans. For an admixture used in cement and concrete, its parameters are specified in the standards of many countries. Most importantly, the SO₃ content should be kept within limits to provide protection against severe expansion and cracking of hardened cement mixtures. Chinese specification GB1596-2005 limits the SO₃ content of PCC ash to 3.5% while the upper limitation of ASTM C618-00 is 5.0%. However, the average SO₃ content of CFBC ashes usually exceeds 5%, which does not meet the specified requirements to qualify as PCC ash. Many studies have indicated that the great expansion may easily occur in cement and concrete containing CFBC ash [3,8,9]. Consequently,

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to avoid the adverse effect of high SO₃ content of CFBC ash, the strategy of ash utilization should be changed accordingly.

In Portland cement, usually natural gypsum is added to act as an effective retarder controlling the hydration of the C₃A phase [10]. Tzouvalas et al. have investigated the replacement of natural gypsum with natural anhydrite and by-product gypsum [11,12]. They found that natural anhydrite and FGD gypsum can be suitable alternatives to gypsum based on the setting and strength results. The work of Hou, Yang and Guo Shouming also showed that the addition of calcined gypsum which is prepared by calcining gypsum at about 800 °C, instead of natural gypsum, has no significant effect on cement setting and can improve the mechanical properties of cement [13,14]. On the basis of these investigations, high content of anhydrite in CFBC ash formed at 850–900 °C is used to replace natural gypsum to act as a retarder in this work, but the addition of anhydrite in CFBC ash should be adjusted to keep the overall SO₃ content in the final cement within limits.

The aim of this work is to develop an understanding of the potential for anhydrite in CFBC ash to serve as a cement retarder. The effect of anhydrite in CFBC ash on cement properties was studied in terms of setting and hardening, with particular focus on the difference between anhydrite in CFBC ash and natural gypsum.

2. Experimental

2.1. Materials

Two CFBC fly ashes, a Portland cement clinker and two kinds of gypsum were used in this work to make blended cements. The chemical compositions of the CFBC fly ashes, the Portland cement clinker and the natural gypsum are listed in Table 1. The amount of (SiO₂ + Al₂O₃)_{act} in CFBC fly ash was determined by boiling circumfluence. The alternative gypsum used in this work is calcined gypsum, which is prepared by calcining the natural gypsum at 850 °C for 2 h. The calcined gypsum is used to simulate anhydrite in CFBC fly ash because it is difficult to extract the anhydrite from CFBC ash. As cement retarders, the two kinds of gypsum can be used for comparison with anhydrite in CFBC fly ash. The mineral composition of the CFBC fly ashes were determined by XRD and the result is presented in Fig. 1. It shows that the dominant mineral phases of CFBC ash are anhydrite, quartz and hematite. Calcite and free lime can only be found in HF, and both the chemical and mineral compositions of the CFBC fly ashes demonstrate that HF has higher contents of CaSO₄ and f-CaO than LF. The sand used to prepare mortars was graded natural siliceous sand.

2.2. Cement preparation

Four different blended cements were prepared with clinker, CFBC ash and gypsum. The mix proportions are shown in Table 2. The clinker proportion was kept constant in the four cements. Cement A was prepared with clinker and HF while LF was used instead of HF in cement D. Cement B and C were prepared with clinker, LF and gypsum. In order to study the effects of anhydrite of CFBC fly ash, cement A, B and C have a constant SO₃ content of 3.5%. The clinker, CFBC ash and gypsum mixed in the proportions were interground in a laboratory ball mill, and the specific surface obtained was in the range of 3400–3500 cm²/g. These cements were used to prepare both the paste and mortar mixtures.

2.3. Test procedures

Dissolution rate in water was used to evaluate the reactivity of calcium sulfate in blended cements. The procedure to test the dissolution rate of sulfates was as follows. 10 g cement mixture was mixed with 100 ml of distilled water. The mix-

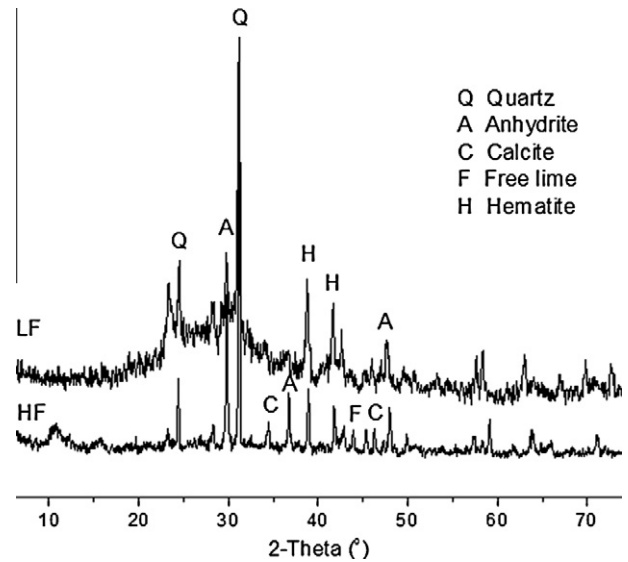


Fig. 1. XRD patterns of two CFBC fly ashes.

Table 2

The proportions of cement mixtures (%).

Cements	Clinker	HF	LF	GM	CG	SO ₃ (%)
A	76.6	23.4				3.50
B	76.6		17.6	5.8		3.50
C	76.6		18.8		4.6	3.50
D	76.6		23.4			1.25

Note: CG: calcined gypsum.

ture was then kept at 20 °C for different ages. After that, the solution was filtrated and the sulfate content in the filtrate was determined by precipitation with barium chloride.

The water requirement ratio and setting time of cement pastes were determined using a Vicat apparatus according to ASTM C187 and ASTM C191 respectively.

Mortar strengths were measured on 40 mm × 40 mm × 160 mm prism specimens. Mortars were cast at a sand-to-cement ratio of 3, and water-to-cement ratio was determined to bring the mortars to a flow of 180–190 mm. After 24 h of moist curing at 23 °C, the specimens were demolded and cured again at 23 °C and 100% relative humidity. The flexural and compressive strengths were measured at ages of 3, 7, 28 and 56 days. The strength value was the average of the test specimens.

Volume stability was determined by measuring length changes of 25 mm × 25 mm × 280 mm prisms. Pastes specimens were cast with water requirement for normal consistency. After 24 h of moist curing at 23 °C, the specimens were demolded and the initial lengths were measured. The specimens were subsequently placed in air and lime-saturated water respectively for long-term storage at 23 °C. Lengths measurements were taken periodically and expansion/shrinkage was determined as the average change in length of three prisms relative to the initial lengths measured at 1 day.

Cement pastes for studies of hydration products were prepared with water requirement for normal consistency. The pastes were sealed in a plastic container and cured at 23 °C from 1 to 28 days. At the set time, the hardened paste specimens were crushed into small pieces and soaked in acetone to stop further hydration. Then the samples were dried in a vacuum desiccator and ground to pass through

Table 1

Chemical compositions of raw materials (%).

Samples	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	(SiO ₂ + Al ₂ O ₃) _{act} ^d	TiO ₂	CaO	MgO	SO ₃	f-CaO	LOI
HF ^a	39.80	9.77	14.89	18.50	–	17.13	1.08	10.67	2.56	5.01
LF ^b	42.00	6.58	28.22	9.59	1.06	1.40	0.64	1.26	0.05	16.60
Clinker	22.43	2.73	4.00	–	0.32	64.30	1.56	1.25	–	1.23
GM ^c	4.30	0.65	1.74	–	–	31.50	1.30	40.20	–	–

^a HF: CFBC fly ash with high SO₃ content.

^b LF: CFBC fly ash with low SO₃ content.

^c GM: natural gypsum.

^d (SiO₂ + Al₂O₃)_{act}: soluble SiO₂ and soluble Al₂O₃ in saturated lime solution.

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