INVESTIGATIONS OF ANHYDRITE IN CIRCULATING FLUIDIZED BED COMBUSTION ASH AS CEMENT RETARDERS

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Abstract: CFBC ashes are different from most conventional coal ashes for good pozzolanic and hydraulic properties, but the ashes with high SO$_3$ content are undesirable for active admixture for cement due to some harmful effects. This study has investigated if anhydrite in CFBC ashes can replace natural gypsum to act as a setting retarder by means of setting time, strength development, volume stability, hydration rate and hydration products. Experimental results have indicated that anhydrite in CFBC ashes can be an efficient retarder of the setting of cement but lead to lower mortar strength. The effect is not harmful to volume stability of cement paste in the case of appropriate anhydrite addition. Compared with natural gypsum, anhydrite in CFBC ashes makes ettringite formation slower and more transformable. Additionally, the long-term behavior of anhydrite in CFBC ashes in the hardening process of cement also remains to be studied. Consequently, this paper has raised some future work on this topic.

Key words: CFBC ash; Anhydrite; Gypsum; Setting; Cement hydration

1 Introduction

Circulating fluidized bed combustion (CFBC) ashes produced at a significantly lower temperature (850 ~ 900°C) than pulverized fly ashes (1200 ~ 1400°C) are by-products of coal burning in the circulating fluidized bed boiler by injecting calcium-based sorbent. They are different from most conventional coal ashes for good pozzolanic/hydraulic properties. Besides disordered alumina and silica containing substance, coming from inorganic components of coal, CFBC ashes are high in free lime as well as anhydrite since an excess of limestone must be used to achieve satisfactory desulphurization levels [1]. Thus the multi-component CFBC ashes can be potentially used as both pozzolanic admixture and set controlling to cement.

In view of natural environment protection and economic benefit, its utilization as an admixture in cement and concrete has attracted extensive attention. However, there were only a few investigations of the use of CFBC ash in cement as an admixture or as a setting retarder replacing gypsum [2]. Many studies have shown that the form of anhydrite in CFBC ashes is Ï•-anhydrous gypsum( Ï•-CaSO$_4$), and the high content of anhydrite may easily tend to have a great volume expansion of gel system which has negative impact on the volume stability [3,4].

In order to provide ample protection against the abnormal expansion that might
result from the use of excess of SO$_3$, it has been the custom from the beginning to place a limit on the SO$_3$ content of Portland cement and mineral admixtures in standard specifications in different countries [5]. According to GB specification, the upper limitation of SO$_3$ for standard cements is 3.5% [6] while the standard specifications for eight types of Portland cement adopted by the ASTM limit the SO$_3$ content to 3.0%, 3.5%, 2.3% respectively [7] and generally, the SO$_3$ content of mineral admixture as a cementitious component, such as fly ash, should not be more than 3.5% on Chinese specification GB1596-2005 while the upper limitation on ASTM C618-00 is 5% for fly ash. Consequently, CFBC ashes with SO$_3$ content more than 5% are undesirable for admixture in cement and concrete because there may be some harmful effects to cement or concrete, especially with respect to the property of volume stability.

In the cement industry, usually calcium sulfate in form of gypsum or anhydrite are added during grinding of Portland cement to act as set controlling admixture reacting with C$_3$A from cement clinker giving calcium sulfooaluminate phase known as ettringite, instead of rapidly crystallized calcium aluminate hydrates, thus regulating cement setting properties [8-10]. The natural sulfate materials have been used for this purpose for a long term and there are also some investigations of the use of CFBC ashes in cement as a setting retarder replacing natural gypsum or anhydrite by means of calorimetric studies of cement hydration kinetics and standard properties of cements [10-12]. Therefore, whether anhydrite in CFBC ashes can partially or even entirely replace natural gypsum in the utilization of cement to be used as setting retarder for purpose of ash disposal has attracted significant scientific interest in this paper. In other words, this will require reducing the consumption of gypsum, or eliminating the addition of gypsum altogether, but care has to be taken to keep the overall SO$_3$ content in the final cement within limits considering safety in terms of volume stability. However, the fact that anhydrite in CFBC ashes is different from natural gypsum states out how important it is to study if anhydrite in CFBC ashes can show at least similar to gypsum behavior to meet demands of cement properties.

In this paper, the effect of anhydrite in fluidized bed combustion ashes on the performance and hydration of cement was studied not only from the setting and hardening point of view, but also in terms of durability. The aim of this research was to investigate if anhydrite in CFBC ashes can replace natural gypsum to act as a setting retarder in cement, and to find a new way to make full use of this high calcium high sulfate ashes to achieve the goal of changing waste into treasure.

2 Experimental
2.1 Materials

Two different CFBC fly ashes (CFBCF) used in this study were obtained from different CFBC boilers in China. The chemical composition of the tested CFBC fly ashes obtained by chemical analysis is given in Table 1. The differences of chemical composition between the two ashes lie in the fact that CFBCF1 (HF) has a higher content of CaO, f-CaO and SO$_3$ than CFBCF2 (LF). The mineralogical compositions of the two ashes are detected by X-ray diffraction.

The clinker used in this experiment was commercially available ordinary Portland cement clinker in Chongqing, China. The residue on a 0.08mm sieve of the ground clinker is 2.9%. Its chemical composition is given in Table 2.
Table 1: Chemical composition of CFBC fly ashes (mass%)

<table>
<thead>
<tr>
<th>samples</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>Mg</th>
<th>SO₃</th>
<th>f-Ca</th>
<th>L.O.</th>
<th>I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFBCF1(H)</td>
<td>39.8</td>
<td>8.77</td>
<td>14.7</td>
<td>-</td>
<td>17.1</td>
<td>1.08</td>
<td>10.6</td>
<td>2.56</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td>CFBCF1(L)</td>
<td>42.0</td>
<td>6.58</td>
<td>28.2</td>
<td>1.06</td>
<td>1.40</td>
<td>0.64</td>
<td>1.26</td>
<td>0.05</td>
<td>16.6</td>
<td></td>
</tr>
</tbody>
</table>

Note: CFBC ashes with high SO₃ (HF) and ashes with low SO₃ (LF)

Table 2: Chemical composition of clinker (mass%)

<table>
<thead>
<tr>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>56.78</td>
<td>20.32</td>
<td>7.21</td>
<td>4.69</td>
<td>2.31</td>
<td>1.25</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Two calcium sulfate-bearing materials, natural gypsum and calcined gypsum were used as reference materials. The natural gypsum (GM) used in this investigation was from Chongqing, and the calcined gypsum (CG) was obtained from natural gypsum calcined at 850°C for two hours to simulate the anhydrite in CFBC ashes.

2.2 Methods

To assess the role of anhydrite in CFBC ashes in cement, different mixtures are prepared from CFBC fly ashes, ground clinker and some gypsum. The composition of cementitious mixtures are listed in Table 3. Sample 1, 2 and 3 are designed to study the effect of anhydrite in CFBC ashes, natural gypsum and calcined gypsum on the hydration of cement with a constant SO₃ content while the sample 1 and 4 are used to study the influence of content of anhydrite in CFBC ashes on cement hydration.

Table 3: Components of cements with CFBC fly ash admixtures

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage [mass%] in sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Clinker</td>
<td>76.6</td>
</tr>
<tr>
<td></td>
<td>76.6</td>
</tr>
<tr>
<td>Gypsum</td>
<td></td>
</tr>
<tr>
<td>Calcined gypsum</td>
<td></td>
</tr>
<tr>
<td>CFBCF1</td>
<td>23.4</td>
</tr>
<tr>
<td>CFBCF2</td>
<td>17.6</td>
</tr>
<tr>
<td>SO₃ content</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Dissolution test

The procedure adopted to estimate the rate of solution in water was as follows: 10g cementitious mixtures was accurately weighed and then placed in a beaker with 100mL distilled water and magnetically stirred at room temperature. After each stirring period, stirring was stopped. The suspensions were then filtered quickly to measure sulfate concentrations.

Physical test

The tests of setting time were measured by a Vicat apparatus with the percentage of mixing water required for normal consistency (ASTM C 187) according to the ASTM...
The preparation and testing of mortar samples were conformed to the ASTM C 109/C 109M by using 40mm×40mm ×160mm prism specimens with a sand to cement ratio of 3 and cement-water ratio was adjusted to produce a flow of 180~190mm. After specimens were cured in a fog room at 20±2°C till 20~24h, they were demolded and kept in the fog room for continued curing. At each testing age, three prisms were taken out for flexural test first, and then compression tests were conducted on the six pieces of broken prisms.

The length change measurements were performed according to the ASTM C490. Paste specimens were cast as 25 by 25 by 280mm prisms in line with normal consistency. The lengths of paste specimens at 24h after casting were measured prior to air storage or water storage at 20°C. To date, length measurements have been made in the short term. Measurements will continue on a monthly basis for a total duration of at least one year.

Chemical test

Cement pastes for hydration rate and hydration products tests were prepared according to normal consistency, and then cured under 20 ± 1°C. At each testing age, the samples were broken into 3~5mm pieces, and their process was interrupted by submerging the hydrating paste in ethanol for 24h. After treatment of the samples in vacuum, the samples were ground to attain a Blain fineness of 300m²/Kg.

LOI analysis was employed to measure the chemically combined water content as that quantity removed from the specimens between 105°C and 1000°C, corrected for the LOI of the initial cement powder.

Hydration products of the stopped samples were identified by X-ray diffractometer (D/MAX-III) with Co kα radiation and infrared spectrometer (IR-75). Step scan was performed with stepping interval of 0.2° and scanning rate 4.00 deg/min during XRD pattern of samples analyzed. Infrared absorption measurements were conducted in 1000 ~ 400 cm⁻¹ wave number ranges, using KBr pellets preparation.

3 Results and Discussion

3.1 Characterization of CFBC fly ashes

![Fig.1 XRD patterns of HF and LF](image)

Table 1 indicates that neither of the two CFBC ashes can meet the Chinese standard
GB/T1596-2005 because L.O.I., SO$_3$ and f-CaO are all beyond the limits defined in the standard.

Major mineralogical compositions of the two CFBC ashes are presented in Fig.1 and it can be seen that the difference between the two ashes is calcite and free lime which are not present in CFBCF2.

3.2 Dissolution rate

![Fig.2 Dissolution rate of three cement samples](image)

The results are plotted in Fig.2. A general feature of the three cement samples is that the first four hours indicate considerable dissolution, but subsequently, the rapid decrease in dissolution is remarkable as time goes on. At the first four hours, clinker-LF-GM system exhibits much higher dissolution than the other two systems which show similar dissolution rate. After four hours, the curve of clinker-LF-GM system shows a tendency to decrease much more sharply compared with the other two samples, indicating that more sulfate in pore solutions took part in cement hydration within 24h but less available sulfate was left in cement paste in clinker-LF-GM system at later ages.

3.3 Setting time

![Fig.3 Setting time and water requirement for normal consistency of four mixtures](image)

As it is extracted from Fig.3, the content of anhydrite in CFBC ashes has a profound regulatory effect on the setting performance of the cement, especially on initial setting time, such as the initial setting time of clinker-HF system being 122min,
twice higher than clinker-LF system. And the results indicate that cement with anhydrite in CFBC ashes set faster than that with natural gypsum, but slightly slower than that with calcined gypsum.

The mechanism of gypsum retarding the hydration of cement suggests that sufficient gypsum can afford a large amount of SO\textsubscript{4}\textsuperscript{2-} and Ca\textsuperscript{2+} in the liquid phase of the cement and the supply of SO\textsubscript{4}\textsuperscript{2-} and Ca\textsuperscript{2+} is not only dependent on their concentration, but also on their physical and chemical nature [13]. A number of researchers [14-17] confirm that different types of gypsum (natural gypsum, anhydrous gypsum and calcined gypsum) have different retarding effects on the minerals of cement, which is attributed to the different solubility of each form of CaSO\textsubscript{4} and consequently to the different quantities of soluble sulfate that exist in cement after its mixture with water and react with C\textsubscript{3}A retarding its hydration [18-21]. It is interesting in this context to note that these conclusions are in good agreement with what are shown in Fig.2.

Anhydrite in CFBC ashes is always present in the form of \textit{\textsuperscript{I\textsubscript{I}}}-CaSO\textsubscript{4} and usually, distinct amounts of anhydrite will remain in unhydrated form even after long curing time though some of it will eventually hydrate to gypsum in a reaction that may also contribute to setting and hardening [11]. In the direction of accomplishing the best setting behavior, the availability of sulfates should be controlled in such a way that sulfates combine exclusively with the hydrating portion of C\textsubscript{3}A to give ettringite [22]. With an equivalent SO\textsubscript{3} content, more soluble sulfate during the early stage of hydration in clinker-LF-GM system is available for ettringite formation than that in clinker-HF system and clinker-LF-CG system, and consequently, the higher setting times are obtained. This must be ascribed to the fact that natural gypsum is more soluble than anhydrite in CFBC ashes and calcined gypsum and can be an explanation for the faster setting of clinker-HF system.

3.4 Strength development

![Fig.4 Flexural strength and compressive strength of four mixtures](image)

The addition of anhydrite in CFBC ashes also affects the strength growth of mortars made from cements with CFBC fly ashes as it is shown from Fig.4. Anhydrite in CFBC ashes has a significant improvement on the strength of cement system, which shows similar behavior to that of natural gypsum in the range of the appropriate SO\textsubscript{3} addition.

Comparing clinker-HF system with clinker-LF system, it is shown that anhydrite in CFBC ashes, with the appropriate addition, gives notable improvement on the strength development of cement. It has been confirmed that anhydrite can activate the potential activity of coal ashes [23-24], and self-cementitious properties of CFBC ashes are also beneficial for the strength development [25].
Compressive strength of mixtures with natural gypsum is higher than that of mixtures with anhydrite in CFBC ashes and lower than calcined gypsum. This must be related to different properties of gypsum. Calcined gypsum, used as reactivity activator, can accelerate the hydration of clinker phases and the forming of hydration products and make some acceleration of forming of ettringite phase with high degree of crystallinity and good stability. Therefore, the rate of conversions towards monosulphoaluminate is slower and hydrated calcium silicate arises faster, which contributes to a denser structure formation and higher strength [26].

3.5 Volume stability

The variations in the volume stability of four systems are presented in Fig.5. Anhydrite in CFBC ashes has a notable influence on the differentiation of the volume expansion (shrinkage) of cement system. When cured in water, the volume expansion ratio of clinker-HF system is higher than clinker-LF system. Compared with natural gypsum, anhydrite in CFBC ashes causes more expansion after 14d of hydration. While cured in air, clinker-HF system shows similar shrinkage behavior to clinker-LF-GM system.

In this investigation, SO$_3$ content in all of the systems with CFBC ashes are confined to 3.5%. At high pH, in the presence of Ca(OH)$_2$, coal ash components can enter into reaction with CaSO$_4$ to form ettringite [27,28], which effectively binds water and contributes to setting, and its crystallization is also associated with expansion of the set mass [29], which usually follows the conversion of anhydrite to gypsum when water is sufficient. Direct correlation between expansion and anhydrite content is readily apparent through 150 days of testing. More ettringite and gypsum formation in clinker-HF system exhibit higher volume expansion after 14d of hydration compared with clinker-LF-GM system when cured in water. Though anhydrite present in the hydrating cement-CFBC ash mixture may be the source of “delayed ettringite formation” [30], the current results in this investigation indicate that anhydrite in CFBC ash used in the cement as a retarder is not harmful to the volume stability of the cement in the case of appropriate anhydrite content.

3.6 Hydration rate and hydration products
Fig. 6 Chemically combined water content of four systems

Degrees of hydration of the cement pastes, defined as the mass fraction of the original cement that has participated in hydration reactions, are assessed by measuring the chemically combined water content produced at different ages. The results are presented in Fig. 6. It is seen that the system with anhydrite in CFBC ashes has slightly less chemically combined water content than natural gypsum and calcined gypsum in the first day of hydration. After 1 day of hydration, only minor differences are detected among the three systems. The amount of combined water can be significantly reduced as content of anhydrite in CFBC ashes decreases. On one hand, lower sulfate concentration results in the forming of hydration products with lowly combined water (C₄AH₁₃) in clinker-LF system, while more sulfate ions are produced to form the hydration products with highly combined water (C₃A·3CaSO₄·32H) in clinker-HF system, on the other hand, the reaction of anhydrite in CFBC ashes with active silica and active alumina can form more hydration products.

Fig. 7 XRD patterns for two hydrated samples by the age

(a) clinker-HF system  (b) clinker-LF-GM system
The X-ray diffraction patterns of clinker-HF and clinker-LF-GM hydrated system are shown in Fig.7. It is apparent that the addition of CFBC ashes modifies substantially the course of hydration process, particularly in relation to the ettringite phase. In clinker-LF-GM system, the ettringite appears just after 3h from processing with water and the intensity is highest after 1d of hydration beyond which this peak reduces in intensity gradually, while the ettringite peak is not apparent all the time in clinker-HF system possibly due to the poor crystal structure of ettringite formation. Though the diffraction peak at 10 degrees of diffraction angle in clinker-HF system
appears to be similar to the ettringite peak in clinker-LF-GM system, the ettringite peak is still not obvious in clinker-HF system due to the diffraction peak of CFBCF1 at the similar angle and unapparent top three peaks. In Fig.8, significant calcium hydroxide peak is detected in clinker-LF-CG system after three hours, while weak calcium hydroxide peak can be seen in clinker-LF-GM system.

The IR characteristic spectra of ettringite consists of three parts, namely band of OH⁻ (3635 cm⁻¹), bands of crystal water (3420 cm⁻¹, 1640 cm⁻¹, 1625 cm⁻¹) and bands of sulfate ions (1120 cm⁻¹, 620 cm⁻¹, 420 cm⁻¹) and bands of Al-O (550 cm⁻¹, 870 cm⁻¹) [31,32]. It is noted that the formation process and formation rate of ettringite can be investigated according to transformations of bands of water molecules at 3420 cm⁻¹ and SO₄²⁻ vibration at 1120 cm⁻¹ [33,34]. During ettringite formation, a triple band of gypsum at range of 1100~1150 cm⁻¹ will gradually transform into a single band. The results of IR investigations of the above systems in time periods up to 3 days of hydration are presented in Fig.9. There are visible bands characteristic for ettringite (3635 cm⁻¹, 1635 cm⁻¹, 1120 cm⁻¹) in clinker-HF system and clinker-LF-GM system. The triple band of sulfate is apparent after 3h, 6h and 1d of hydration in clinker-HF system and after 3d of hydration the triple band transforms into a single band, indicating the slower rate of anhydrite consumption, while the triple band of sulfate is evident after 3h and 6h of hydration and the band transforms into a single band after 1d of hydration in clinker-LF-GM system. Therefore, it is confirmed that the rate of sulfate consumption and ettringite formation in clinker-LF-GM system is much faster than that in clinker-HF system. In Fig.10, transformation of band of water molecules from 3420 cm⁻¹ to 3440 cm⁻¹ in clinker-HF system indicates that monosulphoaluminate (AFm) is being formed, while there is no transformation of bands at 3420 cm⁻¹ in clinker-LF-GM system due to more stable ettringite formation.

Both the XRD patterns (Fig.7, Fig.8) and the IR curves (Fig.9) indicate that ettringite formation is more apparent in clinker-LF-GM system. Ettringite formation depends on the concentration of [Ca²⁺], [SO₄²⁻], [OH⁻] and [AlO₂⁻] for the void of cement paste [35], and the stability of ettringite was dependent, to a great extent, on the concentration of [SO₄²⁻] [36]. Consequently, the different rate of sulfate consumption and the stability of ettringite formation are linked to different dissolution rate of natural gypsum, calcined gypsum and anhydrite in CFBC ashes in the four systems. Because [SO₄²⁻] concentration is up to saturation at early ages in clinker-LF-GM system, stable ettringite is formed after a short hydration, while there is no stable ettringite formation due to the lower [SO₄²⁻] concentration during hydration in clinker-HF system.

4 Conclusions
a) The anhydrite in CFBC ashes is a suitable alternative to gypsum to act as an efficient retarder of the setting of cement based on the setting results but lead to lower strength of the hardened mortar compared with natural gypsum.

b) The effect of anhydrite in CFBC ash is not harmful to volume stability of cement paste in the case of appropriate anhydrite content.

c) Compared with natural gypsum, anhydrite in CFBC ash makes ettringite formation slower and more transformable.

d) From this investigation, it is noticeable that CFBC ashes, though not in compliance with some specifications, can still be efficiently used as constituents of cement as long as the proportions are properly designed.
The hydration process in cement with CFBC ashes is very complex and depends on many factors. Therefore, some future work on this topic may involve laboratory investigation as follows: the long-term behavior of anhydrite in CFBC ashes in clinker-CFBC ashes-water systems, including long-term strength, volume stability, hydration products, and durability performance, remains to be further studied. Especially, special attention should be paid to the volume stability in terms of delayed ettringite formation which may be accompanied by expansion of paste leading to durability decrease due to the presence of sulfate in the form of anhydrite in CFBC ashes in further investigations.

References