STUDY ON PROPERTIES OF SULFOALUMINATE CEMENT-BASED MATERIALS MADE FROM MUNICIPAL SOLID WASTE INCINERATION FLY ASH

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Abstract

Municipal Solid Waste Incineration (MSWI) fly ash was used as a major cement raw material in producing sulfoaluminate cement-based materials (SACBM) in laboratory. In this paper, the sintering system and morphology of the sulfoaluminate cement clinker, the properties of the SACBM, including compressive strength, setting time, drying shrinkage resistance, carbonization resistance and sulfate corrosion resistance, were investigated. Results show that sulfoaluminate cement clinker can be sintered properly under the temperature of 1200-1250. Compared with composite Portland cement P.C32.5R (C-I) and commercial sulfoaluminate cement (C-II), the resistance properties of SACBM to drying shrinkage and carbonization are better than that of C-I but lower than that of C-II. The SACBM also have an excellent property of sulfate corrosion resistance and the resistance coefficient increases with the time prolonging.

1. INTRODUCTION

The cement industry, which is a large-scale industry, is a larger consumer of mineral and energy resources. Present researches mainly are focus on resource utilization of wastes in cement industry and exploring new types of saving-energy cement-based materials.

Municipal Solid Waste Incineration (MSWI) fly ash is classified as a special hazardous waste world widely for the presence of leachable heavy metals, Dioxin and high concentrations of soluble salts. The amount of MSWI fly ash increases greatly with more MSWI factories being built in China recently, leading themselves to be a serious environmental problem. Various methods have been used to treat MSWI fly ash such as melting, solidification/stabilization (S/S), acid extraction, vitrification, sintering, and now researchers have been focused on its utilization, especially in preparation of cement-based materials because of, the main composition of MSWI fly ash belongs to CaO-SiO2-Al2O3-SO3 system which is similar to cementitious material.
There are three major application approaches of MSWI fly ash in cement-based material: raw material in producing cement clinker [1, 2], cement or concrete admixture [3, 4] and concrete aggregate [5-7]. Among them, the first application is regarded as the most effective way to eliminate the toxicity of MSWI fly ash since the high temperature (above 1450 °C) in the kiln is propitious to capture most of heavy metals by cement clinker.

Sulfoaluminate cement has drawn great attentions due to its lower energy consumption and higher early strength. The sulfoaluminate cement clinker can be sintered at a lower temperature (1200 °C) compared with the ordinary Portland cement (>1400 °C) [8]. Ragozina[9] has described the formation of a ternary compound in the CaO-Al₂O₃-SO₃ system by the reaction of calcium sulfate with aluminates at 1200 °C. Halstead and Moore have confirmed the formula of the ternary phase as 3CaO·3Al₂O₃·CaSO₄ (C₄A₃S) and reported that C₄A₃S exhibited a body-centered cubic structure with a =18.39Å[10].

In order to explore a new approach for the resource utilization of MSWI fly ash and the development of green cement industry, this paper describes the feasibility of reusing MSWI fly ash as a raw material in producing SACBM. In this paper, parts of the studies are devoted to determining the sintering system of sulfoaluminate cement clinker. The properties of SACBM, including compressive strength, setting time, drying shrinkage resistance, carbonization resistance and sulfate corrosion resistance are evaluated compared with Composite Portland cement (P.C32.5R (C-I)) and commercial sulfoaluminate cement (super-strong 30, C-II). All of the above performances are investigated to evaluate the reuse feasibility of MSWI fly ash in cement production.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Raw materials and preparation

The MSWI fly ash was originated from Suzhou Wastes Incineration Plant in China. The chemical compositions of MSWI fly ash and other raw materials are given in Tables 1 and 2 separately. All materials were ground and sieved through a 200-mesh sieve.

2.2. Experimental methods

Cement raw materials were blended in proportions following the Cement Moduli commonly used by cement industry and previous study [11-14]: alkalinity coefficient \((C_m) =1.05\), alumina–sulfur ratio \((P) =2.5\) and alumina-silica ratio \((N) =3\). All of the raw materials in this work were mixed in proportions as follows: MSWI fly ash 30.89%, limestone 31.83%, aluminite 26.49%, desulfurize gypsum 10.79%. The blends were pressed and moulded into cylindrical moulds of 30mm in diameter and 5mm in height to prepare cylinder samples. Then the prepared samples were calcined in a Nabertherm furnace and sintered for 120 min.

The mineral composition of sulfoaluminate cement clinker (SA) was determined by X-ray diffraction (XRD). The Chemical composition of clinker was determined by X-ray fluorescence spectrometry (XRF). The morphology of clinker was performed by scanning electron microscopy (SEM).

The clinker with CaSO₄·2H₂O was ground to make SACBM. The SACBM were mixed with water with a W/C ratio of 0.3, and the paste was put into the 1cm×1cm×1cm cube moulds, then the specimens were cured in water to 1d, 3d, 7d
and 28d for the measurement of compressive strength. The setting times of SACBM were determined according to Chinese National Standard GB/T 1346-2001 (test methods for water requirement of normal consistency, setting time and soundness of the Portland cement).

Table 1 Chemical composition of MSWI fly ash (wt.% by weight).

<table>
<thead>
<tr>
<th>Composition</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Cl</th>
<th>SO₃</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>36.20</td>
<td>14.83</td>
<td>11.48</td>
<td>6.66</td>
<td>3.94</td>
<td>3.42</td>
<td>3.02</td>
<td>1.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>ZnO</th>
<th>PbO</th>
<th>BaO</th>
<th>CuO</th>
<th>LOSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>1.41</td>
<td>1.08</td>
<td>0.61</td>
<td>0.54</td>
<td>0.23</td>
<td>0.14</td>
<td>0.13</td>
<td>21.73</td>
</tr>
</tbody>
</table>

Table 2 Chemical compositions of raw materials (wt.% by weight).

<table>
<thead>
<tr>
<th>Composition</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>Fe₂O₃</th>
<th>LOSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>54.90</td>
<td>0.70</td>
<td>0.08</td>
<td>1.58</td>
<td>0.03</td>
<td>0.19</td>
<td>42.14</td>
</tr>
<tr>
<td>Aluminite</td>
<td>0.64</td>
<td>6.13</td>
<td>71.00</td>
<td>0.26</td>
<td>0.07</td>
<td>1.22</td>
<td>18.26</td>
</tr>
<tr>
<td>Desulphogypsum</td>
<td>33.4</td>
<td>6.83</td>
<td>3.25</td>
<td>0.76</td>
<td>52.3</td>
<td>1.13</td>
<td>-</td>
</tr>
</tbody>
</table>

The test method of drying shrinkage was prepared in accordance with the Chinese Building Material Industrial Standard JC/T 603-95 (test method of drying shrinkage for cement glue sand). The properties of carbonization resistance were examined in accordance with Chinese National Standard GBJ 82-85 (test methods of long term performance and durability for ordinary concrete). Due to the quantitative limitation of SACBM samples, this work used cement glue grand blocks instead of concrete specimens. The properties of sulfate corrosion resistance were tested according to Chinese National Standard GB/T 749-2008 (test method for determining capability of resisting sulfate corrode of cement) which can be summarized as follows: the specimens with mould are cured in moisture for 1d then demoulded, after that all the specimens are curing in water to 7d and then separated into 2 groups: one is immersed in water; and the other is immersed in 5% NaSO₄ solution. All the specimens are cured to corresponding ages for the measurement of flexural strength.

3. RESULTS AND DISCUSSIONS

3.1. Preparation of sulfoaluminate cement clinker

3.1.1. The XRD analysis of the clinker

The sintering temperatures were selected at 1150 °C, 1200 °C and 1250 °C, while the soaking times were selected to be 30min, 60min and 120 min. The XRD patterns of clinker SA sintered at different temperatures are shown in Figure 1.

Figure 1(a) shows that C₄A₃S is the major phase with minor phases of C₂S, unreacted CaSO₄ and C₃AS in clinker under 1150 °C. The existence of C₃AS reveals that the temperature of 1150 °C was lower since C₃AS is one of transient phases. The mineral of C₃AS disappears when the temperature is increased to 1200°C (Figure 1(b))
and 1250 °C (Figure 1(c)). And the unreacted CaSO₄ was involved in the reaction with the soaking time prolonging in 1200 °C and 1250 °C so that it disappeared in 120min.

From the above experiments, it is shown that the sulfoaluminate clinker can be synthesized between 1200°C and 1250°C. Results show that the soaking time has little effect on the major phase while the longer soaking time can eliminate unreacted CaSO₄. Thus considered the results above and energy-saving, the sintering temperature 1200°C and soaking time 120min are selected as the proper sintering system for preparation of sulfoaluminate cement from MSWI fly ash.

![XRD patterns of clinker SA in different temperatures and soaking times](image)

**Figure 1:** XRD patterns of clinker SA in different temperatures and soaking times

3.1.2. The SEM analysis of the clinker

The SEM photos of clinker SA sintered at 1200°C are shown in Figure 2. The clinker is irregular and high porous so that the clinker may have better grindability. Since C₄A₃S is the major phase in clinker SA, C₄A₃S can be observed identified by Energy Disperse Spectroscopy (EDS) in Figure 2(c). From the Figure 2 and Table 3, it is seen that the real value of composition of C₄A₃S is very close to the theoretic value. Mg is found most possibly as taking place of Ca while Fe was substituted with Al in the phase of C₄A₃S.
Table 3 Atomic proportion of the point A in Figure 2 (b) (at.%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca</th>
<th>Al</th>
<th>S</th>
<th>Mg</th>
<th>Fe</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS value of the point A</td>
<td>36.33</td>
<td>50.14</td>
<td>10.22</td>
<td>1.29</td>
<td>2.02</td>
<td>100.00</td>
</tr>
<tr>
<td>Theoretic value</td>
<td>36.36</td>
<td>54.54</td>
<td>9.09</td>
<td>-</td>
<td>-</td>
<td>99.99</td>
</tr>
</tbody>
</table>

Figure 2: SEM photos and EDS pattern of clinker SA

3.2. Compressive strength

The SACBM were prepared by grinding the clinker with 3% (SA97DG03), 5% (SA95DG05), 7% (SA93DG07) and 10% (SA90DG10) CaSO$_4$$\cdot$2H$_2$O (DG) separately to a fineness of 400 m$^2$/kg (Blaine). The compressive strength of SACBM at different curing ages was tested. The results are illustrated in Figure 3.
As displayed in Figure 3, C-II has the highest compressive strength in all curing ages. The development of 1d compressive strength is sequenced as C-II $>$ SA90DG10 $>$ SA93DG07 $>$ SA95DG05 $>$ SA97DG03 $>$ C-I. Results indicate that all SACBM samples have higher early strength compared with Portland cement but increased slowly at later ages, which is one of characteristics for SAC. As curing age prolongs, the compressive strength of SA97DG03 develops very slowly between 3d and 28d. Thus the addition amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has its appropriate content range, which is 5~10% by weight.

### 3.3. Setting time

The setting times of C-II, SA95DG05 and SA90DG10 are given in Table 4. It can be seen that SACBM samples have shorter setting time compared with Portland cement, which is a significant characteristic for SACBM. The initial setting time of SA95DG05 is not more than 60min while the final setting time is within 80min. SA90DG10 has the shortest setting time, but it may have an adverse influence on the experimental operation. Thus considering all of the above results, the SA95DG05 was involved in the following experiments.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial setting time (min)</th>
<th>Final setting time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA95DG05</td>
<td>41</td>
<td>75</td>
</tr>
<tr>
<td>SA90DG10</td>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>C-II</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>C-I</td>
<td>53</td>
<td>260</td>
</tr>
</tbody>
</table>

### 3.4. Durability

#### 3.4.1. Drying shrinkage

Drying shrinkage ratios of C-I, C-II and SA95DG05 are shown in Figure 4. It can be seen that the ability to resist drying shrinkage of all samples are reduced in the following sequence: C-II$>$SA95DG05$>$C-I, and the SACBM has a better drying shrinkage resistance than that of Portland cement. The drying shrinkage ratio of
SA95DG05 increases rapidly compared with C-II due to its higher content of clinker in cement. It is illustrated that addition amount of admixture can reduce the drying shrinkage ratio effectively. Therefore, optimizing the composition of SACBM and adding appropriate amount of admixture in SACBM, especially investigating the feasibility of using MSWI fly ash as an admixture in SACBM can be the future work.

3.4.2. Carbonization

Carbonization depths of C-I, C-II and SA95DG05 are given in Figure 5. From Figure 5, it is observed that carbonization depths of C-II and SA95DG05 are lower than that of C-I at early age. With the prolongation of curing age, carbonization rate of C-II and SA95DG05 increases rapidly, compared with that of C-I. Due to higher compressive strength and more compact pore structure at the early age, the SACBM is more effective in resisting carbonization than that of C-I. Since the amount of SACBM hydrates Ca(OH)₂ are less than those of Portland cement with the prolongation of curing time, the carbonization resistance ability of SACBM reduces rapidly, compared with C-I.

Carbonization depths of C-II are lower than those of SA95DG05 due to its higher amount of admixture. Parts of those cementitious materials reacted with hydrates, and gained some ettringite (AFt) and gel, then these products filled in the harden cement paste and pores, which could help refine the porosity and obtain a more compact pore structure in sample C-II, leading to a better capability of carbonization resistance.
3.4.3. Sulfate corrosion

Flexural strength and corrosion resistance coefficient of different samples are given in Table 5. And the corrosion resistance coefficient is obtained according to the following formula:

$$K = \frac{R_{\text{solution}}}{R_{\text{water}}}$$

Where $K$ is corrosion resistance coefficient; $R_{\text{solution}}$ and $R_{\text{water}}$ are the flexural strength of samples immersed in 5% $\text{NaSO}_4$ solution and water, respectively.

From Table 5, it can be seen that corrosion resistance coefficients of all samples are greater than 1. Abilities of C-II and SA95DG05 to resist sulfate corrosion increases with immerging, but C-I shows an opposite trend. Therefore, the SACBM can be applied in the project which has a requirement for sulfate corrosion resistance.

In order to investigate the mechanism of SACBM for resisting sulfate corrosion, XRD and SEM analysis of hydrates in the curing age of 60d are given in Figure 6 and Figure 7 separately. The main hydration products of SACBM immersed in different solution are similar, including AFt and unreacted $\text{C}_4\text{A}_3\text{S}$, $\text{C}_2\text{S}$. But the peak intensity of AFt which was immersed in sulfate solution is higher than those immersed in water, which would lead to a higher corrosion resistance coefficient. It can be concluded that the chemical reaction processes are as follows:

$$3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 34\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} + 2(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O})(\text{gel})$$

$$2\text{CaO} \cdot \text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{C-S-H(gel)} + \text{Ca(OH)}_2$$

When there was sufficient sulfate, the hydration reaction carried out is written as:

$$(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O})(\text{gel}) + 3\text{Ca(OH)}_2 + 3\text{CaSO}_4 + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$$

SEM photos (Figure 7) also verify the aforementioned results. From the Figure 7, it can be seen that there are more AFt crystals in cylindrical shape are surrounded by gel.

### Table 5: Flexural strength and corrosion resistance coefficient of samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>30d (MPa)</th>
<th>K</th>
<th>60d (MPa)</th>
<th>K</th>
<th>90d (MPa)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulfate solution</td>
<td>water</td>
<td>Sulfate solution</td>
<td>water</td>
<td>Sulfate solution</td>
<td>water</td>
</tr>
<tr>
<td>SA95DG5</td>
<td>5.75</td>
<td>5.45</td>
<td>1.06</td>
<td>6.17</td>
<td>5.73</td>
<td>1.07</td>
</tr>
<tr>
<td>C-II</td>
<td>6.70</td>
<td>5.90</td>
<td>1.14</td>
<td>7.08</td>
<td>6.17</td>
<td>1.15</td>
</tr>
<tr>
<td>C-I</td>
<td>6.60</td>
<td>6.20</td>
<td>1.06</td>
<td>7.00</td>
<td>6.54</td>
<td>1.05</td>
</tr>
</tbody>
</table>

When there was sufficient sulfate, the hydration reaction carried out is written as:

$$(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O})(\text{gel}) + 3\text{Ca(OH)}_2 + 3\text{CaSO}_4 + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$$
Figure 6: XRD patterns of hydration products. SACBM-W: sample SA95DG05 immersed in water up to 60d; SACBM-S: sample SA95DG05 immersed in 5%NaSO4 solution up to 60d.

Figure 7: SEM photos of hydration products

4. CONCLUSIONS

MSWI fly ash was successfully used as a major raw material in sintering sulfoaluminate cement clinker in laboratory under temperature of 1200-1250°C and sintered time of 30-120min. Considering both the composite of phase and energy consumption, the best sintering system is 1200°C with the soaking time is 120min.

SACBM has a good compressive strength property, especially at the early age. Compared with cement samples C-I and C-II, the resistance properties of SACBM to drying shrinkage and carbonization are better than that of C-I, but lower than that of C-II. SACBM also has an excellent property of resisting sulfate corrosion and the resistance coefficient increases with the corrosion time prolonging.

5. ACKNOWLEDGEMENT

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