EFFECT OF MINERAL ADMIXTURES ON HYDRATION PROCESS OF HIGH C₃S CLINKER

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Abstract

Effect of activated coal gangue and fly ash on hydration process of high C₃S clinker during 360 days at the water/binder ratio of 0.3 was investigated by XRD, isothermal calorimetry, differential scanning calorimetry and strength test. The results showed that during the early period of hydration the effect of coal gangue on acceleration hydration of high C₃S clinker was better than fly ash, but during the late period of hydration the reactivity of fly ash was higher than coal gangue.

Key words: coal gangue; fly ash; high C₃S clinker; hydration

1. INTRODUCTION

Recent years, with the rapid development of national economy and capital construction, the cement demand rises year by year. In 2007, the output of cement in China has exceeded 1.35 billion tons [1]. In order to restrain the rapid increase of clinker output and find the substitute for clinker, the researchers did many experiments and found that [2-4] increasing the C₃S content of clinker to acquire the high performance clinker and then intergrinding activated coal gangue or fly ash with high C₃S clinker to produce blended cements was an effective way to reduce the output of clinker and reuse the coal industry waste in civil engineering. In order to study the hydration mechanism of activated coal gangue or fly ash with the high C₃S clinker, the researchers investigated the hydration process of blended cements from many aspects, such as constituent phases of cement pastes, microstructure, reaction degree of mineral admixtures, Ca(OH)₂ content, mechanics and drying shrinkage properties[3-6], but the reports were mainly focused on the hydration within 90 days. But whether 90 days are long enough to say which one is more active? In this paper in order to investigate whether there were some differences between the activity of the two mineral admixtures during the early period and the late period, the testing ages were extended to 360 days.

2. EXPERIMENTAL
2.1 Materials

In this study, three cements were provided by 973 task group of China Building Materials Academy, i.e., high C₃S Portland cement (C1), coal gangue cement (C2) and fly ash cement (C3). The Portland cement C1 was made by intergrinding the high C₃S clinker with the gypsum, and the Blaine fineness of C1 was controlled at 370 m²/kg. Two blended cements were made by intergrinding 70% high C₃S Portland cement (the Blaine fineness was about 340 m²/kg) with 30% activated coal gangue or activated fly ash for five minutes. The chemical compositions of the raw materials are shown in Table 1. The mineral composition of C1 calculated from the oxide compositions in Table 1 by using the conventional Bogue calculation [7] is shown in Table 2. The density of three cements are 3.16 g/cm³, 2.98 g/cm³, 2.86 g/cm³; and the Blaine fineness are 370 m²/kg, 443 m²/kg, 404 m²/kg, respectively. The particle size distribution of cements were determined by using laser diffraction through a dilute suspension of cement particles in ethanol. The results are plotted in Fig.1.

Table 1 Chemical composition of raw materials w (%)

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>F-CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>high C₃S Portland cement</td>
<td>64.78</td>
<td>20.34</td>
<td>5.02</td>
<td>3.11</td>
<td>2.20</td>
<td>1.09</td>
<td>0.35</td>
<td>0.10</td>
<td>--</td>
<td>0.10</td>
</tr>
<tr>
<td>coal gangue</td>
<td>13.80</td>
<td>55.80</td>
<td>17.70</td>
<td>3.33</td>
<td>0.41</td>
<td>1.17</td>
<td>0.46</td>
<td>0.60</td>
<td>--</td>
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</tr>
<tr>
<td>fly ash</td>
<td>5.33</td>
<td>45.90</td>
<td>37.30</td>
<td>2.84</td>
<td>1.74</td>
<td>1.33</td>
<td>0.61</td>
<td>0.35</td>
<td>1.36</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 2 Mineral composition of high C₃S Portland cement w(%)*

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>64.60</td>
</tr>
<tr>
<td>C₂S</td>
<td>9.56</td>
</tr>
<tr>
<td>C₃A</td>
<td>8.05</td>
</tr>
<tr>
<td>C₄AF</td>
<td>9.45</td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td>4.73</td>
</tr>
</tbody>
</table>

Fig.1: Particle size distribution of the cements

The XRD patterns of raw materials are shown in Fig.2 –Fig. 4, respectively. The main phases of high C₃S Portland cement are C₃S, C₂S, C₃A, C₄AF and CaSO₄·2H₂O; the main crystalline phases of activated coal gangue are quartz(SiO₂), gehlenite(C₃A₂Al₂SiO₇), gismondine (Ca₃Al₂Si₂O₈·4H₂O), C₃A and microcline (KAlSi₃O₈); the main crystalline phases of activated fly ash are mullite (Al₆Si₂O₁₃), CaSO₄·2H₂O, SiO₂, hematite(Fe₂O₃), C₂S and sillimanite (Al₂SiO₅). Moreover, the diffuse peak extending from about 18° to about 38° and from about 15° to about 40° in Fig.3 and Fig.4 respectively indicate there are a great deal of glass existing in activated coal gangue and fly ash.
Fig. 2: XRD powder diffraction pattern of high $C_3S$ Portland cement

Fig. 3: XRD powder diffraction pattern of activated coal gangue

Fig. 4: XRD powder diffraction pattern of activated fly ash
2.2 Specimen preparation and test methods

Cement pastes were prepared with water to binder ratio (w/b ratio) 0.3. The cement powder and necessary mass of water were mixed together by cement paste mixer (NJ-160A), and then specimens 20mm×20mm×20mm were prepared. The specimens were demolded after being cured at 20±2 °C /95%R.H. for 24 hours, and subsequently were kept saturated with 20 °C water. At the ages of 1, 3, 7, 14, 28, 56, 90, 180 and 360 days, the compressive strength of the cement pastes were determined. After the strength test, the core of samples were broken into pieces and stopped hydration with ethanol, and then vacuum-ooven-dried at -0.1MPa /45 °C until constant weight. The powder for X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analysis was obtained by grinding of the dried pieces with FRISCH Puluerisette 7 Planetary Micro Mill.

The mineralogical phase of the raw materials and cement pastes were determined by XRD analysis, using a Rigaku D/max2550 X-ray diffractometer with graphitemono- chromatized CuKα radiation (40kV and 100mA), steps 2°C/min, and 20 values ranging from 5 °C to 75°C.

According to GB2022-80, the heat of hydration was assessed by using a multichambered microcalorimeter (TAM Air 08 Isothermal Calorimeter) at w/b ratio of 0.3 for seven days.

In order to test the portlandite content of cement pastes, the samples were tested using a NETZSCH STA 449C differential scanning calorimeter, heating from 30 °C to 700 °C at an increasing temperature rate of 20 °C / min under a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1 Constituent phases of cement pastes

XRD powder diffraction patterns of three cement pastes, hydrated for 1, 3, 7, 14, 28, 56, 90, 180 and 360 days, are presented in Fig.5-Fig.7, respectively. Fig.5 indicates that the main crystalline phases of cement paste C1 are C3S, C2S, C3A, C4AF, portlandite(Ca(OH)2, CH) and ettringite (3CaO·Al2O3·3CaSO4·32H2O, AFt). In the first 7 days of hydration, the diffraction peaks of C3S, C2S, C3A and C4AF phases diminished rapidly, while the peaks of CH increased rapidly. The peaks of AFt were just apparent in cement paste hydrated for 1 day. Following the hydration process, the peaks of main clinker phases and hydration products changed slowly, and the peaks of monosulphoaluminate (3CaO·Al2O3·CaSO4·12H2O, AFm) became apparent after the age of 180 days.

During the hydration process of blended cements, as shown in Fig.6 and Fig.7, SiO2 and CaAl2Si2O8·4H2O in coal gangue, Al6Si2O13, SiO2, Fe2O3 and Al2SiO5 in fly ash were all inert components which almost did not react in the hydration process. Following the hydration process, the peaks of main clinker phases changed in a similar way to that of pure Portland cement, but CH was different. The peaks of CH just increased evidently in the early age, and then diminished. The active SiO2 and Al2O3 in the activated coal gangue and fly ash could react with portlandite, so the peaks of CH in blended cements decreased due to the pozzolanic reaction at later ages. Moreover, X-ray diffraction confirmed the absence of AFm in the cement paste C2, but the C-A-H (xCaO·Al2O3·nH2O, calcium aluminum oxide hydrate) was detected. In Fig.7, the AFm was detected, while the C-A-H was absent. The detection of C-A-H indicates that the activity of active Al2O3 in coal gangue is higher than in the fly ash, so it is easier to react with portlandite and then form the C-A-H. Yumei Yao [8] also found this phenomenon with the same cements which were prepared with w/b ratio of 0.29 and cured in sealed plastic bag hydrated within 90 days.
Fig. 5: XRD powder diffraction patterns of cement paste C1

Fig. 6: XRD powder diffraction patterns of cement paste C2

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3.2 Heat of hydration

The heat evolution curves of cements are illustrated in Fig.8. As shown in the rate of heat evolution curves, there were five stages in the whole hydration process of three cements. On first contact of cement with water, a series of rapid and highly exothermic reactions started. Within several minutes, the initial heat peak was formed, and then the induction period began. During the induction period, the rate of heat evolution of C1 and C2 were close, while the C3 was lower than them. The length of the induction period of C1 and C2 were similar, while the C3 was longer than them. After about 3 or 4 hours, the acceleration periods of three cements began successively. The acceleration period of C1 began earliest. The rate of heat evolution was maximum of three cements and reached the second heat peak after hydrated for 12.25 hours. During the acceleration period of C2, the rate of heat evolution was close to C1 until about 7 hours, and reached the second heat peak at 11.57 hours. While C3 was the last one to go into the acceleration period. During the acceleration period of C3, the rate of heat evolution was lower than C1 and C2, and reached the second heat peak at 15.92 hours. When the hydration process went into deceleration period, three cements reached the third heat peak at 15, 15.8 and 19.25 hours respectively. During this period, the rate of heat evolution of C1 was always higher than C2, while the C3 was higher than C1 and C2 from about 20 hours to 30 hours. After hydrated for 3 days, the hydration reaction became slow, and the rate of heat evolution changed into C2 > C3 > C1, although the difference was not so obvious. In the whole hydration process, the relationship between the hydration heat of three cement was C1 > C2 > C3, and in the first 12 hours, the values of C1 and C2 were very close.
As soon as the cement contacts water, the clinker phases react very rapidly and exothermically. Comparing with cement C1, because of the reduction of 30% clinker, the heat evolution rate of blended cements are lower than pure Portland cement in the early age. In 7 days, the mineral admixtures have not reacted yet, they just influence the hydration process of the blended system in a physical way. On one hand, they can disperse the cement particles and increase the effective w/c ratio, and on the other hand, they provide much nucleation sites which will be favorable for the formation and growth of hydration products. In a conclusion, the intergrinding of the mineral admixtures with Portland cement will promote the hydration of the clinker. The morphology of fly ash is glassy sphere, but the microstructure of coal gangue is full of micropore, so the morphology of coal gangue is more favorable for formation and growth of hydration products. At the early age, the acceleration function of coal gangue on hydration is better than fly ash. In general, the formation of the third heat peak is because of the conversion of AFt to AFm [7], so the difference between the second heat peak and the third heat peak in every cement indicates that the conversion of AFt to AFm in cement C1 and C3 is more than C2.

### 3.3 Ca(OH)₂ content

![Graph showing Ca(OH)₂ content of three cement pastes](image)
The measured Ca(OH)\(_2\) content for three cement pastes by DSC analysis are provided in Fig.9. The Ca(OH)\(_2\) content of pure Portland cement C1 increased rapidly at early ages and slowly at later ages, and was always higher than the other two blended cements. But in the blended systems, the Ca(OH)\(_2\) content increased rapidly at early ages, and then decreased at later ages. For the cement paste C2, the Ca(OH)\(_2\) content increased up to 7 days, 6.41\%, 8.16\%, 8.33\%, and then the values went down. From 7 days to 56 days, the decrease of the Ca(OH)\(_2\) content was obvious, but after 56 days, the variation was very small. For the cement paste C3, the Ca(OH)\(_2\) content increased up to 14 days, 6.17\%, 7.84\%, 9.36\%, 9.57\%, and then the values went down. From 14 days to 56 days and after 180 days, the decrease of the Ca(OH)\(_2\) content was greater.

At early ages, the mineral admixtures have not reacted yet, so the Ca(OH)\(_2\) content increases with the hydration of the clinker. In 3 days, the morphology of coal gangue with a great deal of micropore is favorable for the formation and growth of hydration products, so the acceleration of the cement hydration by coal gangue is greater than fly ash, and then the Ca(OH)\(_2\) content of cement paste C2 is higher than C3.

Following the hydration, the Ca(OH)\(_2\) content of blended systems decreases due to the pozzolanic reaction at later ages. According to the report [9], when the activated coal gangue was calcined at high temperature, the coal gangue expanded and some components evaporated. It may be discovered that much micropore, broken bond and active SiO\(_2\) and Al\(_2\)O\(_3\) appear in the microstructure of coal gangue with high energy. The pozzolanic reaction of coal gangue can begin in a system with lower alkali. But the glass of fly ash is very stable and the surface of fly ash is very dense [7], so the pozzolanic reaction of fly ash will begin in a system with higher alkali.

At later ages, such as after 180 days, when the Ca(OH)\(_2\) content of coal gangue has become stable, the Ca(OH)\(_2\) content of fly ash can still decrease obviously. The results indicate that at early ages the active components of activated coal gangue is easier to begin pozzolanic reaction, but at later ages, when the glassy surface structure of fly ash has been etched, the inner part of the fly ash becomes easier to react with portlandite. Two coauthors of this article had investigated the same cements at w/b ratio of 0.3 and cured under sealed condition hydrated for one year, the same phenomenon had been founded. The time of the Ca(OH)\(_2\) content of fly ash cement system beginning to decrease was later than coal gangue cement system, but the decrease of the Ca(OH)\(_2\) content was greater at later ages [10].

### 3.4 Compressive Strength

The compressive strength of three cements are plotted in Fig.10. It can be seen that the compressive strength of pure Portland cement C1 is always the highest one. The strength of blended cements is lower than pure cement because of the replacement of cement by mineral admixtures. But comparing cement C2 with C3, it can be found that during 7 days the difference between the strength of two blended cements is very small, while after 7 days, the strength of C2 begins to be higher than C3. At early ages, the coal gangue and the fly ash contribute to the hydration process in a physical way, so the difference between them is not great. In this period, the contribution of coal gangue is mainly due to the large number of micropore in the microstructure which is favorable for the hydration products to grow. While the contribution of fly ash is mainly due to the large number of small particles (as shown in Fig.1) which are good fillers. But after 7 days, with the proceeding of the pozzolanic reaction, the activity of coal gangue is higher than fly ash, so in the cement paste C2, there
will be more hydration products, such as C-S-H gel and C-A-H gel to provide strength. For cement paste C3, the spherical fly ash particles are not easy to hydration, so at early ages, they mainly act as the inert fillers, and the strength of C3 is lower than C2 during the period of 28 days to 90 days. At later ages, with the pozzolanic reaction of the fly ash, the active of fly ash is released, and then the difference between C3 and C2 is reduced.

![Graph showing Compressive Strength of three cement pastes at different ages](image)

**Fig. 10 Compressive strength of three cement pastes at different ages**

4. CONCLUSIONS

1. When the blended cements hydrated at the w/b ratio of 0.3 and cured in saturated condition, the inert compositions of mineral admixtures almost did not react during the hydration process. The content of main clinker phase in three cements changed in a similar way, but the Ca(OH)₂ content varies in a different way. The C-A-H was detected in coal gangue cement, while the conversion of AFt to AFm was more obvious in fly ash cement.

2. During the hydration process of high C₃S Portland cement, the rate of heat evolution is high and the heat of hydration is large. Replacing the cement with 30% mineral admixture can reduce them effectively. Comparing with the fly ash, the coal gangue can slow and decrease the total heat evolution, but do not influence the hydration greatly.

3. At early ages, the active components of coal gangue are easier to begin pozzolanic reaction, but at later ages, the pozzolanic activity of fly ash is higher than coal gangue.

4. During the hydration process of blended cements, the development of compressive strength in coal gangue cement is better than fly ash cement.

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REFERENCES


