Preparation of bittern-resisting cement used by fly ash

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Abstract

Based on compound cementitious system of clinker containing C4A3S phase, ground fly ash, and granulated blast-furnace slag, a new kind of cement, the Bittern-resisting Cement, is studied for high-bittern environment in the northwest of China. This new material uses class III fly ash as raw material to produce BRC clinker containing C3S and C4A3S phase, and class II fly ash as high-activity cement admixture. Experiments show that the setting time of BRC is relatively shorter but the later strength is higher, and the resistance to chemical attack of brines is more excellent than ordinary Portland cement, which is more suitable for engineering construction in saline lakes. By means of XRD, TG-DTA and SEM, the clinker phases and the hydrated products of BRC are studied and the mechanism of corrosion resistance to chemical attack in brines also is examined.

Keywords: fly ash; compound cementitious system; bittern-resisting cement; chemical attack

1. Introduction

Recently, there has been a growing trend for using supplementary cementitious materials, whether natural, waste, or by-products, in the production of composite cements because of ecological, economical or diversified product quality reasons [1].

Fly ash is a by-product during coal power generation and consists mainly of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and CaO. According to GB/T 1596-2005, fly ash is divided into three types. Generally, Class III fly ash is not suitable for use as a construction material due to its high carbon content and large particle size. This kind of fly ash is mainly used for backfilling, roading and so on. The other two kinds of fly ash, Class I fly ash and Class II fly ash, exhibits excellent pozzolanic properties and has been widely used as mixed materials of cement or admixture of concrete to improve performances such as higher later strength, good durability and chemical stability. In China, about 100 million tons of fly ash is discharged annually from coal-burning electric-generating plant, but only about a fourth of it is utilized [2]. This is due to the fact that fly ash has lower hydration activation, higher requirement water and poor resistance carbonation; so it has become important to improve utilization ratio of fly ashes, especially that of Class III fly ash.

Saline lakes, especially those in Qinghai province in the northwest of China, are rich in corrosive ions such as Cl$^-$.
, $\text{Mg}^{2+}$ and $\text{SO}_4^{2-}$. The cement-based material exposed to high-bittern environment can be subjected to various kinds of physical and chemical attacks; thereby there has been a lot of increasing interest in the durability of cement-based material in saline lakes and salinized soil areas in recent years [3-6]. However, from the long-term point of view, the most effective way to solve the durability problem of cement-based material in high-bittern environment is to research and develop special bittern-resisting cement [7]. In this work, a new kind of cement, Bittern-resisting Cement (BRC), is prepared for high-bittern environment, which use Class III fly ash as raw material to burn BRC cement clinker containing the mineral Alite ($\text{C}_3\text{S}$) and calcium sulfoaluminate ($\text{C}_4\text{A}_3\text{S}$), and use Class II fly ash as high-activity cement admixture to produce blended cement. The performance and mechanism of corrosion resistance to chemical attack of brines is also investigated.

2. Materials and experimental methods

2.1. Raw materials

Three types of industrial waste materials, including granulated blast furnace slag (GBFS), Class II fly ash (designated “FAII”) and Class III fly ash (designated “FAIII”), were used for the experiments. The other raw materials are limestone and gypsum. The chemical compositions of those raw materials are listed in Table 1.

Table 1. Chemical compositions of main raw materials (wt. %)

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Chemical compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Loss</td>
</tr>
<tr>
<td>Limestone</td>
<td>41.82</td>
</tr>
<tr>
<td>Gypsum</td>
<td>17.52</td>
</tr>
<tr>
<td>GBFS</td>
<td>0.52</td>
</tr>
<tr>
<td>FAII</td>
<td>6.92</td>
</tr>
<tr>
<td>FAIII</td>
<td>15.58</td>
</tr>
</tbody>
</table>

2.2. Clinker burning and cement manufacturing

The raw materials such as limestone, gypsum and Class III fly ash were dried in an oven at about 105~110 °C for 4h and ground to pass a 75 mesh sieve. After thorough homogenization in proportion with the addition 0.5 % CaF$_2$, those raw materials including adequate quantities of Class III fly ash (about 12%~18% in weight by mass) were mixed with 8%~10% water and nodulized to the size of approximately 10 mm diameter each. Nodules were burned to clinker in an electric furnace with silicon molybdenum bars heating elements at 1250 °C, 1280 °C, 1320 °C, 1360 °C and 1400 °C, respectively for 60 min, then removed from the furnace at 1200 °C and cooled rapidly in air.

Bittern-resisting Cement was made by inter-grinding clinker and gypsum in laboratory ball mill firstly, then mixed with 40% high-fineness mineral admixtures composed of blast furnace slag and Class II fly ash (Blaine specific surface area up to 480~550 m$^2$/kg, half and half respectively), and also with 1.0%~1.3% compound additive prepared in advance, until the cementitious material being mixed homogeneously.

2.3. Experimental methods

The standard consistency water requirement and setting time of Bittern-resisting Cement are examined by the method of GB/T 1346-2001 (the state Standards of the P.R. China for Standard Test Method for Water Requirement of Normal Consistency, Setting Time and Soundness of Portland Cement). The mortar strength is tested according to GB/T 17671-1999 (Method of testing cements-Determination of strength, the state Standards of the P.R. China). The prisms size is 40 mm×40 mm×160 mm.

The paste specimens of Bittern-resisting Cement (the ratio of water to cement at normal consistency was 0.26~0.28) were cured to 3 days, 7 days and 28 days respectively, then were taken out from fresh water and washed by the anhydrous ethanol and acetone to stop their hydration and dried at the temperature of 100±5 °C for 4 h.
Matter phase analysis of clinker and hydrated products was analyzed by method of X-ray diffraction analysis (XRD), TG-DTA analysis and Scanning Electron Microscope (SEM).

Bittern corrosion test was carried out in order to assess the corrosion resistant performance of Bittern-resisting Cement in high-bittern environment. According to GB/T 17671-1999, BRC mortar prisms were molded into 40 mm× 40 mm×160 mm in dimensions. After being moist-cured for 28 days, those prisms were taken out from curing room and were oven-dried at 80 °C for 16 h in response to the literature [8]. When be cooled to room temperature, some of those prisms were whole-immersed or half-immersed into high concentration brine and stored in sealed plastic vessel at 20±3 °C for 3 months, 6 months and 18 months respectively, others are immersed into the fresh water as the control ones [9]. There are three kinds of aggressive solution whose compositions are given in Table 2 [3, 8].

<table>
<thead>
<tr>
<th>No.</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.96</td>
<td>18.47</td>
<td>68.34</td>
<td>4.18</td>
<td>241.50</td>
<td>6.23</td>
<td>1.17</td>
<td>356.7</td>
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<td>2</td>
<td>35.51</td>
<td>7.04</td>
<td>55.05</td>
<td>0.88</td>
<td>220.50</td>
<td>4.20</td>
<td>0.18</td>
<td>323.4</td>
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<tr>
<td>3</td>
<td>20.80</td>
<td>0.83</td>
<td>6.50</td>
<td>0.97</td>
<td>168.50</td>
<td>11.10</td>
<td>—</td>
<td>208.7</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Clinker mineral formation

The loss on ignition of Class III fly ash in the experiment is up to 15%, so it is used as raw material to burn Bittern-resisting Cement clinker containing the mineral Alite and calcium sulfoaluminate. The XRD patterns of Bittern-resisting Cement clinkers burned at different temperatures are shown in Fig. 1.

By XRD analysis, the main mineralogical phases in Bittern-resisting Cement clinker are Ca₃SiO₅ (C₃S), Ca₂SiO₄ (C₂S), 3CaO·3Al₂O₃·CaSO₄ (C₃A₃S) and 4CaO·Al₂O₃·Fe₂O₃ (C₄AF). When burning temperature gets to 1250 °C, the C₄A₃S phase begins to form and coexists with C₃S phase, but the f-CaO content is more than 2.85% by mass. With the burning temperature increasing, the f-CaO content in clinker goes on decreasing, but if the burning temperature exceeds 1380 °C, the mineral phase C₄A₃S begins to decompose, so the range of temperatures for clinker formation is 1300~1380 °C.

From the results, it is also concluded that although its higher carbon content will has an adverse effect on durability of cement-based material if used as mixed materials of cement or admixture of concrete, Class III fly ash can be used as a raw material instead of bauxite clay for the manufacture of Bittern-resisting Cement clinker.

3.2. Physical properties of BRC

The grindabilities of clinker and mineral materials are different. If intergrinding cement clinker with slag, it is not possible to exercise an independent control on the degree of fineness of the constituents, so the harder component slag tends to accumulate in coarse-size fractions which results in less participation of slag in the hydration reactions and thus reduction in the strength. Normally, the volume of fly ash in cement or concrete is low due to its slow pozzolanic reaction. To address this issue, studies are focused on such methods to accelerate the pozzolanic reactivity of fly ash as increasing its fineness or the use of chemical activators [10]. BRC is to grind clinker and mineral materials including slag and fly ash separately and mix them in appropriate proportions according to performance requirements.

The results of physical properties of Bittern-resisting Cement are shown in Table 3. The setting time of Bittern-resisting Cement is relative shorter and the volume of hardened mortar keeps its body in shape or expands slightly. This is because that the clinker of Bittern-resisting Cement contains about 10%~15% C₄A₃S, which has the property of rapid hardening and hydration expansion. The compressive and flexural strength of Bittern-resisting Cement in early stage, are only 18.8 MPa and 4.7 MPa respectively, but the later strength develops very quickly, which have relation to the pozzolanic activities of finely ground Class II fly ash and granulated blast furnace slag.
Table 3. Physical properties of bittern-resisting cement

<table>
<thead>
<tr>
<th>Blaine (m²/kg)</th>
<th>Water of Consistency (%)</th>
<th>Setting time (minutes)</th>
<th>Compressive strength (MPa)</th>
<th>Flexural strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>3 days</td>
</tr>
<tr>
<td>416</td>
<td>25.9</td>
<td>52</td>
<td>97</td>
<td>18.8</td>
</tr>
</tbody>
</table>

3.3. Analysis of hydration products

The hydration products of Bittern-resisting Cement (BRC) pastes for 28 days, which is the same as those of ordinary Portland cement (OP), can be seen in Fig. 2. The dehydration peaks of C-S-H gel and AFt (at 128 °C) in the paste of BRC are higher, and the endothermic peak of Ca(OH)₂ is much lower, implying more C-S-H gel, AFt and less Ca(OH)₂ produced in Bittern-resisting Cement than those in ordinary Portland cement. Undoubtedly, few content of Ca(OH)₂ but more C-S-H gel in cement paste will help to improve the durability of cement-based material to resistance chemical attack. The calcium carbonate is also formed (at 750~760 °C) by the reaction between the Ca(OH)₂ and CO₂ in atmosphere, leading to the endothermic peaks.

3.4. Bittern corrosion test

The results of the mortar prisms cured in three kind of high concentration brine after 28 days of curing in plain water are given in Fig. 3. The experimental results indicate that there is no significant change in flexural strength of BRC samples at 3 months and 18 months of curing in different brine. Only the compressive strength in Brine 1# goes on decreasing but the corrosion coefficient of Kc and Kf of BRC are all much more than 0.96 [7] which means that Bittern-resisting Cement has excellent performance to resist the chemical attack in high-bittern environment.

The SEM micrograph of Bittern-resisting Cement paste stored in aggressive solution is presented in Fig. 4. After cured in No.3 brine for 18 months, the microstructure of Bittern-resisting Cement paste still appears to highly integrate with a network of needle-column ettringite and floccular C-S-H gel and no visible corrosion products form. As the literature stated [11], Bittern-resisting Cement can improve the corrosion resistance of cement-based material in brines from four aspects: (1) making full use of dominant complementation effect of mineral materials such as fly
ash and slag; ② diminishing hydrated products easy to be attacked; ③ densifying microstructure of harden cement paste; ④ degrading chemical attacks of corrosive ions.

Fig. 3. Strength development of BRC mortar exposed to high concentration brine; Fig. 4. SEM morphology of BRC paste stored in No.3 brine for 18 months

4. Conclusions

The following conclusions may be drawn from the above results:

(1) Class III fly ash can be used as a raw material instead of bauxite clay for the manufacture of Bittern-resisting Cement clinker.

(2) Class II fly ash exhibit pozzolanic properties and is used as activated admixture of Bittern-resisting Cement to improve its performance such as higher later strength, good durability and chemical stability.

(3) The combination of highly ground fly ash and blast-furnace slag in Bittern-resisting Cement results in an effect of mutual complement of superiority supplement which can help to improve its corrosion-resisting ability.

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References


