STRÄTLINGITE AND CALCIUM HEMICARBOALUMINATE HYDRATE IN BELITE-CALCIUM SULPHOALUMINATE CEMENT

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Belite-calcium sulfoaluminate (BCSA) cement is a promising low-CO₂ alternative to ordinary Portland cement. With high water cement ratio, phase compositions of the BCSA pastes at different curing ages were investigated via X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Large amounts of water accelerated the hydration reaction significantly and substantial ettringite (C₆Å₃·H₃₂) was generated in the early stages. With the carbonation of AFt in the later stages, lots of strätlingite (C₂Å₈) and calcium hemicarboaluminate hydrate (C₄Å₃·H₁₂) formed after curing age of 28 days. The microstructure of C₂Å₈ and H₄ in the BCSA pastes were observed and confirmed via a scanning electron microscope (SEM) and an energy dispersive X-ray spectrometer (EDS). The results indicated that C₂Å₈ was thick hexagonal plate product and H₄ was thin sheet-like product. C₂Å₈ and H₄ would stack together respectively in the later stages of hydration. In addition, spherical aluminum hydroxide (AH₃) and rod-like AFt were also observed.

INTRODUCTION

Calcium sulfoaluminate (CSA) cement is manufactured by sintering mixtures of limestone, bauxite and gypsum (CŠ·2H) at a temperature of about 1250°C [1, 2]. It has good performance of rapid hardening, high strength, low alkali and so on [3, 4]. However, the compression strength of CSA cement decreases in the later age [5]. Bauxite as one of the main raw materials is too expensive. Therefore, high-performance belite-calcium sulfoaluminate (BCSA) cement is developed. The long-term strength and durability of concrete made from BCSA cement can potentially exceed those of other cements [6, 7]. Manufacturing BCSA cement produces less CO₂ than ordinary Portland cement and fully utilizes industrial by-products, such as fly sah, steelmaking slags, scrubber sludge and so on [8-12].

The main minerals in the BCSA cement are belite (C₅S) and yeelimite (C₄A₃Š). It may also contain other minor phases such as ferrite, maynite and excess anhydrite (CŠ) [13]. The main hydration products of BCSA cement are similar to that of the CSA cement. The hydrates are ettringite (C₆Å₃·H₃₂, AFt), monosulfate (C₄Å₃·H₁₂, AFm), hydrated calcium silicate (C–S–H), amorphous aluminum hydroxide (AH₃) and so forth [5, 14, 15].

Strätlingite (C₂Å₈) is an important hydration product of cement in the later stages [16, 17]. C₂Å₈ is also known as “hydrated gehlenite” [18]. C₂Å₈ might be responsible for the strength recovery in high-alumina cement (HAC) [19, 20]. To promote C₂Å₈ formation, zeolites or silica fume was added to HAC cement and plate-like C₂Å₈ was observed in HAC pastes [20, 21].

Calcium hemicarboaluminate hydrate (C₄Å₃·H₁₂·H₂) can form when the calcite (CČ) is low or absent in cement pastes but the H₄ microstructure has not been reported [16, 22]. In fact, H₄ belongs to AFm systems whose anion can be replaced by hydroxy, sulfate, carbonate and so on [23]. Especially, C₂Å₈ is also a variant of AFm systems [24].

C₂Å₈ and H₄ have been also detected by many researchers in BCSA pastes but the microstructure has not been examined in detail. In this paper, to accelerate the hydration reaction, massive water was added to BCSA cement. C₂Å₈ and H₄ microstructure were examined. Such research data are necessary to understand C₂Å₈ and H₄.

Cement nomenclature will be used, i.e.; C = CaO, S = SiO₂, Š = SO₃, A = Al₂O₃, Č = CO₂, H = H₂O
EXPERIMENTAL

Materials and methods

BCSA cement prepared as an industrial trial but not commercially available was studied. The chemical compositions of the BCSA cement were obtained by X-ray fluorescence spectrometry as shown in Table 1.

Table 1. Chemical compositions of the BCSA cement (wt. %).

<table>
<thead>
<tr>
<th>Comp.</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>SO₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>48.24</td>
<td>24.56</td>
<td>6.98</td>
<td>16.43</td>
<td>0.56</td>
<td>0.60</td>
<td>2.22</td>
<td>0.41</td>
</tr>
</tbody>
</table>

The BCSA cement was milled to a Blaine fineness between 400 and 500 m²/kg. The BCSA pastes were prepared using a water/cement ratio of 2.0. The BCSA cement blended with proper water was cast into a beaker and stored in a curing chamber at a temperature of 20°C ± 1°C and relative humidity was 95 % ± 5 %. After curing for 1, 3, 7 and 28 days, the BCSA pastes which had been filtered were respectively stopped by soaking in an excess of ethanol for 24 h and dried in a vacuum desiccator. Finally, part of the samples was ground for various tests.

Characterization

The X-ray diffraction patterns for the BCSA cement and pastes were obtained using an X-ray diffractometer (XRD, Smartlab-3kw, Rigaku Ltd, Japan) using Cu Ka radiation (λ = 0.15405 nm) running in a reflection geometry (θ/θ) at room temperature. A scanning speed of 5° min⁻¹ with a step size of 0.02° was used to examine the samples. The acquisition range was from 5° to 45° 2θ. The X-ray tube was operated at 40 kV and 30 mA.

A thermal analysis was performed via differential scanning calorimetry (DSC, DSC 204, NETZSCH Co., Germany). The temperature was varied under N₂ atmosphere from 50°C to 300°C at a heating rate of 10° min⁻¹.

A scanning electron microscope (SEM, JSM-6510, JEOL Ltd, Japan) equipped with a W-filament and operated under an accelerating voltage of 15 kV was used to observe the samples microstructure. The samples were coated with a very thin layer of gold to increase their electrical conductivity.

The elemental compositions of hydration products with the characteristic morphologies were acquired using an energy dispersive X-ray spectrometer (EDS, NS7, Thermo Fisher Scientific Co., America).

RESULTS AND DISCUSSION

Phase compositions and microstructure of the BCSA cement

The XRD pattern for the BCSA cement is shown in Figure 1. The main phases of the BCSA cement are C₄A₃sembling and C₂S. C₄A₃sembling has an orthorhombic structure. The crystal structures for C₂S are in the β and α′ forms. Both C₄A₃sembling and C₂S possess good crystallinity. Moreover, the BCSA cement also contains small amounts of CŠ.

Figure 2 shows the SEM images and EDS patterns of the BCSA cement. There are many polygonal particles with a diameter around 2 μm as shown in Figure 2a. The EDS pattern (Figure 2b) indicated that the elemental compositions of polygonal particle (P 1) were Al, O, S and Ca. The Au signal arose from the sample surface coating used to elevate the electrical conductivity. Therefore, the polygonal particle was C₄A₃sembling. From Figure 2c, spherical substance with a diameter of 1 ~6 μm was detected. The EDS pattern (Figure 2d) indicated that the elemental compositions of the spherical substance (P 2) were significant Si, O, Ca and a little Al. Therefore, the spherical substance was C₂S and it was doped with a little Al₂O₃. The grain size of main phases in BCSA cement was small.

Phase compositions of the BCSA pastes

The XRD patterns for the BCSA pastes with water/cement ratio of 2.0 at different curing ages are given in Figure 3. After curing age of 1 day, CŠ was completely dissolved and small amounts of unreacted CŠ·2H which was the hydration product of CŠ was found in the BCSA pastes. AFt formed in large scale according to Equation 1 but there was still small amounts of unreacted C₄A₃sembling in the pastes [16]. Massive water significantly accelerated the hydration reaction. Furthermore, AFm and AH₃ was also present according to Equation 2 [25, 26].

\[
C₄A₃sembling + 2CŠ + 38H \rightarrow AFt + 2AH₃ \quad (1)
\]
Small amount of hydrated calcium aluminate (CAH$_{10}$) was present in the BCSA pastes after curing age of 3 days and it was the hydration product of calcium aluminate (CA). Crystallinity of a little CA may be poor so it can not be detected by XRD. Both C$_4$A$_3$Š and CŠ·2H were fully reacted after curing age of 3 days. Especially, due to the existence of carbon dioxide in the air and water, small amounts of H$_c$ was found in the BCSA paste after curing age of 3 days.

After curing age of 7 days, small amounts of C$_2$ASH$_8$ formed according to Equation 3 [22]. Quantity of AFm and H$_c$ increased slightly. Small amounts of CS·2H was found again because the AFt carbonation reaction started as shown in Equation 4 [14, 27].

$$C_4A_3Š + 18H \rightarrow AFm + 2AH_3 \quad (2)$$

$$C_2S + AH_3 + 5H \rightarrow C_2ASH_8 \quad (3)$$

$$AFt + 3\hat{C} \rightarrow 3CC + 3CŠ·2H + AH_3 + 23H \quad (4)$$

Due to the continuous decomposition of AFt, a significant reduction of AFt was found after curing age of 28 days. It revealed that massive water significantly

![Figure 2. SEM images and EDS patterns of the BCSA cement: a), c) SEM images of the BCSA cement, b), d) EDS patterns for P1 and P2 respectively.](image)

![Figure 3. XRD patterns for the BCSA pastes with water cement ratio of 2.0 at different curing ages. (A – C$_4$A$_3$Š; B – β-C$_2$S; C – α'-C$_2$S; E – AFt; F – AFm; G – AH$_3$; H – CAH$_{10}$; I – C$_2$ASH$_8$; J – H$_c$; K – CS·2H).](image)
accelerated the AFt carbonation reaction. The main carbonation product of AFt, CČ was not detected by XRD but lots of Hč was generated. This can be explained by the fact that CČ benefits the formation of Hč [16]. With the existence of CŚ·2H, AHš reacted with calcium hydroxide (CH) which was the hydration products of CšŚ illustrated in Equation 5 [16]. Therefore, small amounts of CŚ·2H disappeared again after curing age of 28 days. CšŚ reacted further with AHš according to Equation 3 so the intensity of the main peaks of CšŚ decreased apparently and great deal of CšASHšš formed after curing age of 28 days.

\[
\text{AH}_š + 3\text{CH} + 3\text{CŚ·2H} + 20\text{H} \rightarrow \text{AFt} \quad (5)
\]

A broad band between 20° and 21° indicative of AHš revealed that AHš was amorphous or micro-crystalline after curing age of 1, 3 and 7 days. For curing 28 days, AHš band overlapped with the CšASHšš band. In this case, the presence of AHš in the BCSA pastes could not be determined requiring further testing via thermal analysis.

Thermal analysis of the BCSA pastes

The XRD results are also verified by the DSC data (Figure 4). The endothermic peak near 100°C belongs to dehydration of AFt and CAHšš [28]. From the XRD analysis, the CAHšš content was relatively small. Therefore, absorbing heat which increased and then decreased at the temperature around 100°C was mainly caused by the dehydration of AFt. It revealed that the amount of AFt increased in the first 3 days but from the seventh day to the twenty eighth day, the amount decreased because of the carbonation reaction. Meanwhile, AHš (about 260°C) followed the same rule. AHš was generated after curing age of 1 day and it achieved significant growth after curing age of 3 days according to Equation 1, 2. After curing age of 7 days, the amount of AHš decreased slightly. After curing age of 28 days, the amount of AHš decreased significantly according to Equation 3 but AHš did not vanish in the BCSA pastes.

Absorbing heat quantity increased with ongoing hydration at 150 - 200°C because various hydration products were generated, for example AFm, Hč and CšASHšš [17, 22, 29]. Especially, after curing age of 28 days, lots of Hč (about 150°C) and CšASHšš (about 170°C) were produced [18, 22].

\[
\text{C}_2\text{ASH}_8 + \text{H}_č \rightarrow \text{AFm} \quad (6)
\]

Microstructure of CšASHšš and Hč in the BCSA pastes

From XRD results, after curing age of 7 and 28 days, CšASHšš and Hč formed intensively so the microstructure of these curing age pastes were examined via SEM and EDS. Several typical morphologies of CšASHšš and Hč were observed and confirmed as shown in Figure 5.

Figure 5a shows thick hexagonal plate-like substance precipitates together with rod-like AFt and villous spherical AHš (confirmed by EDS) after curing age of 7 days. Figure 5b indicated that the elemental compositions of plate-like substance (P 3) were Al, Si, O and Ca, so the plate-like substance was CšASHšš. The result is similar to that of F. Puertas [30].

From Figure 5c, thin sheet-like product surrounded by rod-like AFt and gel was observed after curing age of 7 days. The elemental compositions of the thin sheet-like product (P 4) were C, Al, O and Ca (Figure 5d), so the thin sheet-like product was Hč.

After curing age of 28 days, accumulated thick plate-like product covered by gel is detected as shown in Figure 5e. EDS pattern (Figure 5f) indicated that the elemental compositions of P 5 were Al, Si, O and Ca, so accumulated plate-like product was CšASHšš. It revealed that CšASHšš would stack together in the later stages.

After curing age of 28d, lamellar structure substance covered by gel which is a mixture of C-S-H and AHš (confirmed by EDS) is observed (Figure 5g). Figure 5h indicated that the elemental compositions of P 6 were C, Al, O and Ca. The lamellar structure substance was Hč. It is speculated that the thin sheet-like Hč stacks together with each other forming the lamellar structure in the early stages and the lamellar Hč will also gather together in the later stages.

Although CšASHšš and Hč belong to AFm systems or a variant of AFm systems, they have different morphologies. CšASHšš and Hč gather together in the later stages of hydration and they are always surrounded by various hydrates.
Figure 5. SEM images and EDS patterns of the BCSA pastes: a), c) SEM images of the paste after curing age of 7 days; b), d) EDS patterns for P 3 and P 4 respectively; e), g) SEM images of the paste after curing age of 28 days; f), h) EDS patterns for P 5, P 6.
CONCLUSIONS

- $\text{C}_4\text{A}_3\text{S}$ and $\text{C}_2\text{S}$ in BCSA cement possess good crystallinity and have polygonal and spherical morphologies respectively.
- Large amounts of water significantly accelerates the hydration and carbonation reaction. Especially, it promotes the formation of $\text{C}_2\text{ASH}_8$ and $\text{H}_c$ in the later stages.
- $\text{C}_2\text{ASH}_8$ is thick hexagonal plate product and $\text{H}_c$ is thin sheet-like product in the early stages. Massive thick plates gather together in the later stages. Meanwhile, thin sheet-like $\text{H}_c$ stacks together forming the lamellar structure and lamellar structure $\text{H}_c$ will also gather together.
- $\text{C}_2\text{ASH}_8$ and $\text{H}_c$ are always surrounded by AFt or gel which may be a mixture of AH$_3$ and C–S–H.

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REFERENCES