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Cement and Concrete Research 34 (2004) 2009–2013

CEMENT AND CONCRETE RESEARCH

Study on the hydration of Ba-bearing calcium sulphoaluminate in the presence of gypsum

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Received 2 July 2002; accepted 23 February 2004

Abstract

A new series of Ba-bearing calcium sulphoaluminate minerals are synthesized by a different equivalent of Ba^{2+}, replacing Ca^{2+} in the $C_4A_3\bar{S}$. By means of XRD, IR, SEM, etc, we studied the hydration of minerals in the presence of a certain amount of gypsum. The hydrates are AFt, $BaSO_4$, and $Al(OH)_3$ gel. This paper gives the reason for early strength and rapid hardening of Ba-bearing calcium sulphoaluminate cement.

Keywords: Ba-bearing sulphoaluminate cement; Curing; Hydration; SEM

1. Introduction

$C_4A_3\bar{S}$ is one of the minerals in sulphoaluminate cement with high cementing properties. Its derivatives, $3CaO\cdot 3Al_2O_3\cdot BaSO_4$ and $3CaO\cdot 3Al_2O_3\cdot SrSO_4$, are more preferable over $C_4\,A_3\bar{S}$ in performance [1]. Feng Xiuji studied the minerals [2]; Cheng Xin synthesized the single crystal of $3CaO\cdot 3Al_2O_3\cdot SrSO_4$ [3]; and P. Yan studied the hydration mechanism of the minerals [4]. A series of Ba-bearing calcium sulphoaluminate minerals are made by Chang Jun [5]. In this paper, a series of a new type of Ba-bearing sulphoaluminate single minerals is synthesized, and the hydration mechanisms in the presence of gypsum are studied.

2. Experimental

2.1. Preparation of $(4-x)CaO\cdot xBaO\cdot 3Al_2O_3\cdot SO_3$ (Abbr. $C_{(4-x)}B_xA_3\bar{S}$)

All raw materials used in the experiment, such as $CaCO_3$, Al_2O_3, $BaSO_4$, and $CaSO_4\cdot 2H_2O$, are pure analytical reagents. According to the stoichiometry molar ratio of $C_{(4-x)}B_xA_3\bar{S}$, each agent is weighed accurately in proportion as $x = 0.5$, 0.75, 1.00, and 1.25 (identified as A, B, C, and D, respectively), using 0.01% analytical balance, after which the reagents are blended and ground to pass a 200-mesh sieve. They are then watered and transformed into cakes. After being dried for 1 h at 105 °C, the cakes are put into a high-temperature furnace and heated to 1350 °C for 140 min with a speed of 5 °C/min. Finally, the cakes are taken out and air-cooled. After grinding, f-CaO in all sintered products is determined to be zero by the ethyleneglycol extraction method.

2.2. Moulding and hydration

According to the water–cement ratio ($w/c = 0.3$), we mixed the clinker with 8% $CaSO_4\cdot 2H_2O$ and put the paste into a 2 × 2 × 2-cm mould by vibration. The specimens are unmoulded after being cured in more than 90% moist air at 20 °C for 1d; then the specimens are cured in water at 20 °C for measurement of the compressive strength of 1d, 3d, 7d, and 28d. The broken samples are studied using DTA, IR, and SEM for hydration mechanisms.

3. Results and discussion

3.1. The result of strength

The compressive strength of A, B, C, and D with gypsum is listed in Table 1. We can see that the compressive strength increases with the increase of x value.

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0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2004.02.021

Table 1
The compressive strength of cements (MPa)

Number	1d	3d	7d	28d
A	53.0	64.8	69.3	73.9
B	40.4	56.3	67.2	75.7
C	68.6	57.0	69.1	70.0
D	80.2	78.4	84.2	89.4

3.2. XRD analysis

XRD patterns (Fig. 1) of clinkers show that the mineral is Ba-bearing calcium sulphoaluminate [6,7].

Fig. 2 shows the XRD patterns of D hydrated sample at each age. We can see that the hydration rate is fast. Two minerals are formed in 1d hydrated product, $BaSO_4$ ($d = 3.45$, 3.10, 2.12 Å) and AFt ($d = 9.8$, 5.70, 2.79 Å). After 3d and 7d, a little of AFm is produced but disappeared after 28d, leaving only AFt, $BaSO_4$ and unhydrated clinker minerals. We did not find any diffraction peaks of C_2AH_8 and C_3AH_6 in XRD patterns, but they are formed when gypsum is not present [7]. The reason for this is that when gypsum reacts with Ca^{2+}, Al^{3+} and sulphoaluminate is formed. This also accounts for the variation of hydration products with and without gypsum.

3.3. IR analysis

Fig. 3 shows the IR analysis of specimen D. The infrared spectrum of Ba-bearing calcium sulphoaluminate moves to the high band (1200.56, 1102.71, 860.362, 688.559, 642.583, and 410.893 cm^{-1}) compared to that of the $C_4A_3\bar{S}$ (1190, 1098, 882, 690, 641, and 410 cm^{-1}) [7] because of the substitution of Ba^{2+} for Ca^{2+}. The vibration rate of $C_{(4-x)}BA_3\bar{S}$ radical falls at 1250–400 cm^{-1}.

In IR patterns of cement paste at different ages, the formation process and rate of hydration of samples can be judged from the variation of absorption band of [OH] at 3635 cm^{-1} and [SO_4] at 1111cm^{-1} [8]. From Fig. 3, we can see that after 1d hydration, there are obvious peaks at the 3439-cm^{-1} band and strong absorption peaks at 1116 cm^{-1}, which means that considerable amount of AFt is formed and that its forming speed is fast. The little difference between bands results from the substitution of Ba^{2+}. The presence of AH_3 at 1020-cm^{-1} bands is obvious, which proved that AH_3 and AFt are formed at the same time and are in large amount. The diagnostic value of $C_{2.75}B_{1.25}A_3\bar{S}$ at 688, 642, and 614 (cm^{-1}) did not completely disappear after 28d hydration, which proves that clinker minerals still exist. This result is consistent with that of the XRD patterns.

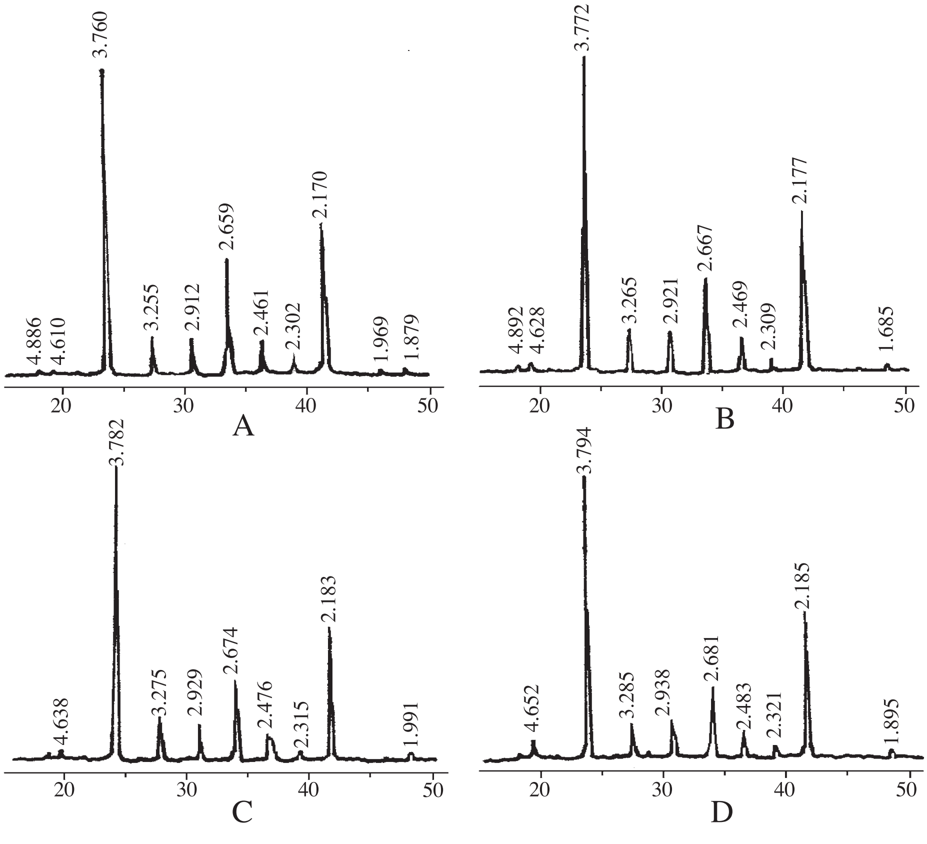

Fig. 1. XRD patterns of clinker minerals.

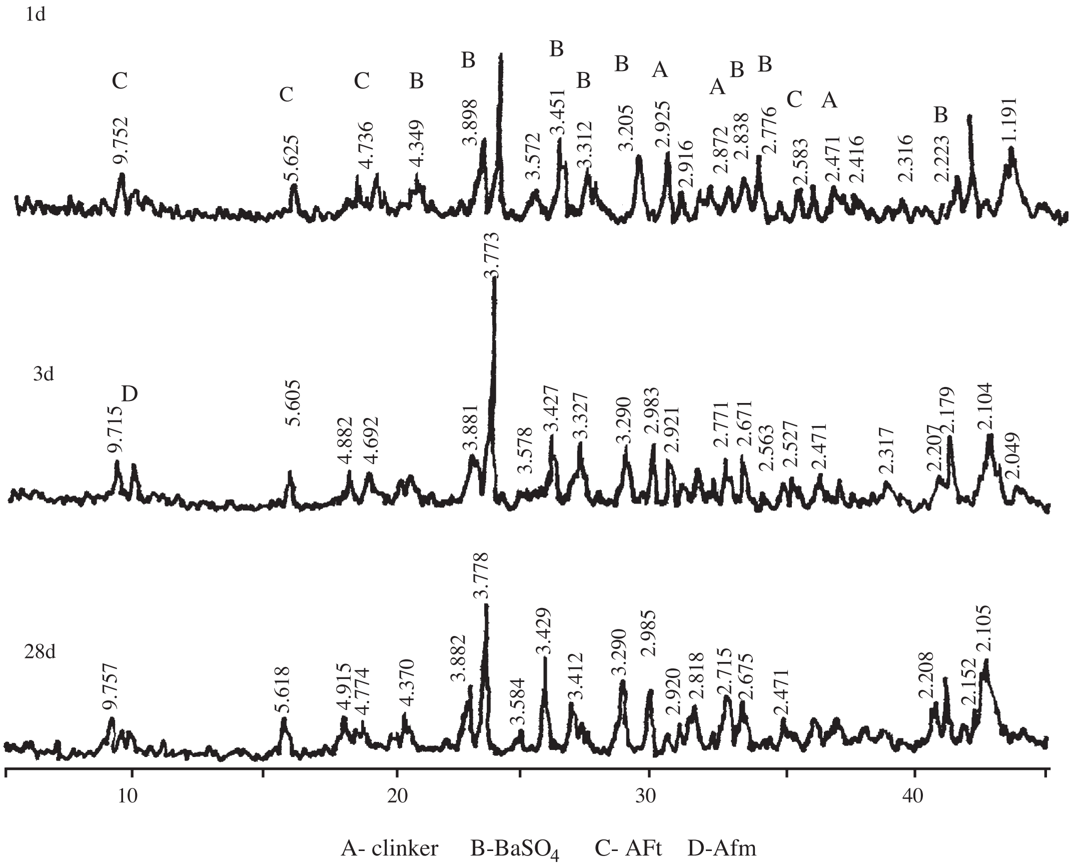

Fig. 2. The XRD patterns of D hydrated product. A—clinker; B—$BaSO_4$; C—AFt; D—AFm.

3.4. SEM analysis

From the SEM photos (Fig. 4) of the hydration of Sample D with gypsum at 1d, 3d, and 28d, we can see that the rate of the hydration of the minerals is fast. After 1d hydration, a large amount of unhydrated clubbed gypsum is present, but after 3d, the clubbed gypsum disappeared and granular $BaSO_4$ and AH_3 gel are formed, mainly accounting for the early strength of the cement. AFt then continues to grow thick, while AFm can hardly be figured out in the picture. Only after 3d hydration that we can see a small amount of sheet in a hexagonal shape. This result is consistent with the XRD analysis. The hydrates of 28d hydration are surrounded by AH_3 and C–S–H gels.

4. Conclusions

1. The compressive strength of Ba-bearing calcium sulphoaluminate with gypsum increases with the content of Ba ions.
2. From the beginning of the hydration of Ba-bearing calcium sulphoaluminate, $BaSO_4$ is formed and filled in the hole, while calcium aluminate reacts with gypsum to form AFt and AH_3 gel.
3. From the hydration process of $C_{(4-x)}B_xA_3\bar{S}$, the hydrates at 1d include AFm, $BaSO_4$, and AH_3 gel. AH_3 gel fills in the gaps between the clubbed AFm and granular $BaSO_4$ to form a compact structure, which leads to the early strength of this cement.

Acknowledgements

This work was financed by the Projects of Development Plan of the State Key Fundamental Research of China (2001CB610700), National Natural Science Foundation of China (59972018, 50272024), and Natural Science Foundation of Shandong Province (Q2002F03, Z99B01 and Y98F04085).

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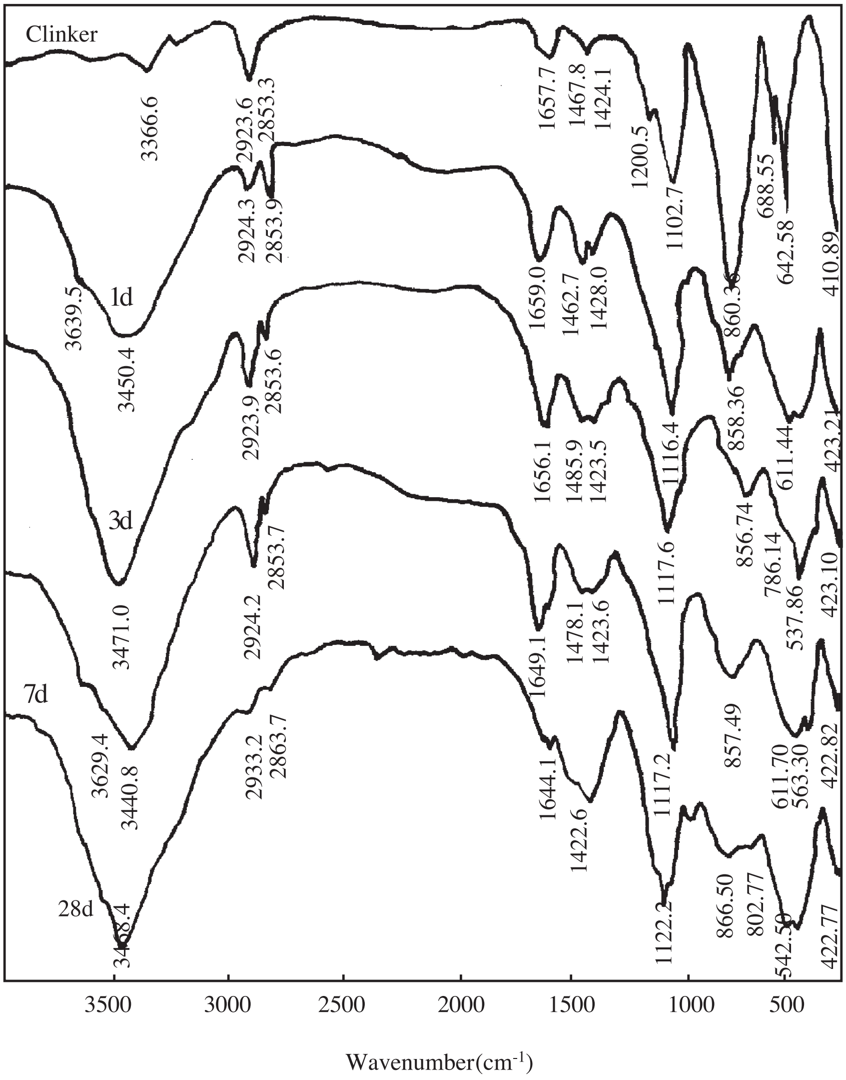
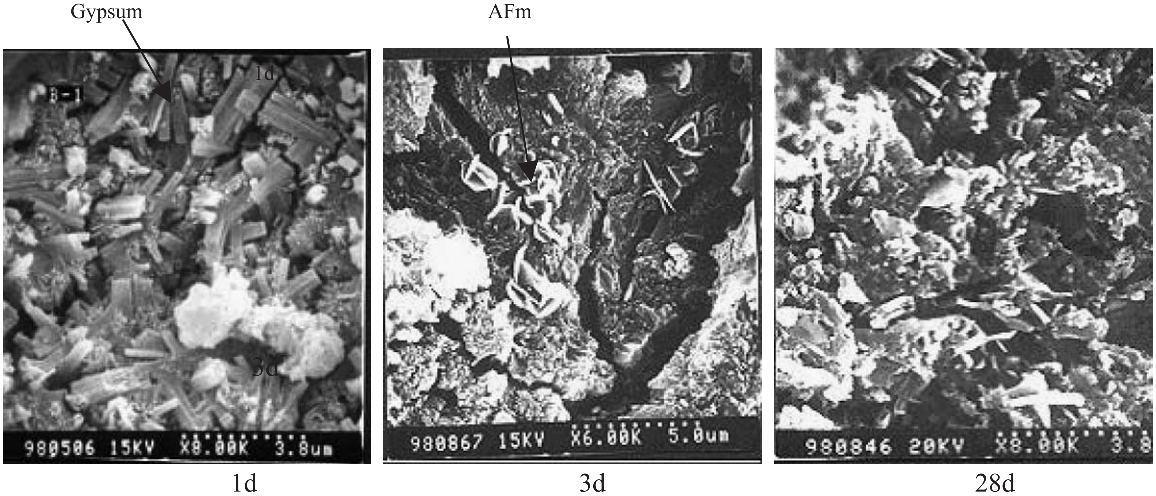


Fig. 3. The IR patterns of Sample D.



1d 3d 28d

Fig. 4. The SEM photos of D hydration products.

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