Pergamon

Cement and Concrete Research 31 (2001) 213–216

CEMENT AND CONCRETE RESEARCH

Influence of fluorite on the Ba-bearing sulphoaluminate cement

Chang Jun*, Cheng Xin, Liu Futian, Lu Lingchao, Teng Bing

Department of Materials Science and Engineering, Shandong Building Materials Institute, Jinan, Shandong 250022, China

Received 30 September 1999; accepted 12 October 2000

Abstract

In this paper, minorcompounds CaF_2, MnO_2, MgO, and P_2O_5 were mixed into the raw meals of $2.75CaO{\cdot}1.25BaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ (abbr. $C_{2.75}B_{1.25}A_3\bar{S}$) that were burned under different temperatures and treating times. The strength was determined. Through the orthogonal experiment, we found that the mineral is of optimal strength when containing 1.4% CaF_2 and treated 2 h at 1350°C. Based on this conclusion, the Ba-bearing sulphoaluminate cement has been burned with Ba-bearing industrial wastes and fluorite. In addition, the hydration mechanism of the cement was analyzed.

Keywords: $2.75CaO{\cdot}1.25BaO{\cdot}3Al_2O_3{\cdot}CaSO_4$; Fluorite; Compressive strength

1. Introduction

The Ba-bearing calcium sulphoaluminates were synthesized as having high strength [1–3]. These series of minerals were studied [4–6]. Through the study of Ba-bearing calcium sulphoaluminate minerals, we found that the pure mineral composition with optimal strength is $C_{2.75}B_{1.25}A_3\bar{S}$. Based on this composition, Ba-bearing sulphoaluminate cement was produced with Ba-bearing industrial wastes. We found that the strength of $C_{2.75}B_{1.25}A_3\bar{S}$ was improved by mixing it with CaF_2. Therefore, we tried to use fluorite for enhancing the strength of Ba-bearing sulphoaluminate cement. And last, the hydration mechanism of the cement was analyzed.

2. Experimental

2.1. Influence of mineral additions on $C_{2.75}B_{1.25}A_3\bar{S}$

Pure analytical reagents $CaCO_3$, $BaCO_3$, Al_2O_3, and $CaSO_4$ were used as raw materials. According to the stoichiometry molar ratio of $1.75CaO{\cdot}1.25BaO{\cdot}3Al_2O_3{\cdot}CaSO_4$, each reagent was weighed accurately in proportion, then CaF_2, MnO_2, MgO, and P_2O_5 were added. The meals were homogenized and ground to pass a 75-μm sieve. They were pressed to cylinders, ϕ 60 × 10 mm. These cylinders were dried for 1 h at 100°C, then burnt at 1350°C for 2 h. Finally, the samples were taken out to cool to room temperature and ground to 3500 cm^2/g (Blaine). Free CaO in all clinkers was determined by the ethylene glycol method. We mixed the clinkers with water to W/S ratio 0.35 and put the paste into the 2 × 2 × 2 cm^3 moulds with vibration. These pure cement paste specimens were demoulded after being cured in moist

Table 1
The compressive strength of each clinkers (w/c = 0.35)

Admixtures	Contents	Compressive strength (MPa)			
		1d	3d	7d	28d
P_2O_5	0.2	67	55	54	53
	0.4	37	41	34	42
	0.6	44	34	46	52
	0.8	47	37	36	42
MgO	0.2	27	28	34	36
	0.4	29	31	49	50
	0.6	20	26	37	39
	0.8	28	20	40	42
MnO_2	0.2	34	49	69	70
	0.4	48	66	70	75
	0.6	34	39	51	70
	0.8	25	36	49	54
CaF_2	0.9	60	49	49	56
	1.2	59	75	85	87
	1.5	30	74	82	89
	1.8	67	38	64	60

* Corresponding author. Tel.: +86-531-712-3911; fax: +86-531-797-4453.

E-mail address: mlchang@etang.com (J. Chang).

0008-8846/01/$ – see front matter
PII: S0008-8846(00)00450-6

Table 2
The result of experiments

No.	A. (temperature) 1	B. (treating time) 2	C. (contents) 3	4	3d compressive strength (MPa)	f-CaO
1	1150 [1]	90 [1]	1.3 [1]	1	51	0.24
2	1150 [1]	120 [2]	1.4 [2]	2	63	0.17
3	1150 [1]	150 [3]	1.5 [3]	3	49	0.09
4	1250 [2]	90 [1]	1.4 [2]	3	32	0
5	1250 [2]	120 [2]	1.5 [3]	1	55	0
6	1250 [2]	150 [3]	1.3 [1]	2	40	0
7	1350 [3]	90 [1]	1.5 [3]	2	51	0
8	1350 [3]	120 [2]	1.3 [1]	3	54	0
9	1350 [3]	150 [3]	1.4 [2]	1	77	0
K_1	163	134	145	183	The sum 472 MPa	
K_2	127	172	172	154		
K_3	182	166	155	135		
$\overline{K}_1$	54	45	48	61		
$\overline{K}_2$	42	57	57	51		
$\overline{K}_3$	61	55	52	45		
R_i	19	12	9	16		

air at 20°C for 1 day, then the specimens were cured in water to each age for measurement of the compressive strength. The results are listed in Table 1.

From Table 1, it is found that the specimens blending CaF_2 have optimal compressive strength. Choosing orthogonallist $L_9(3^4)$, (L — orthogonal experiment, 9 experiments, 3 factors, and 4 tiers), as experiment regulation, the results are listed in Table 2. From the 3 day-strength, we obtain the tendency curves about the relation between each factor and strength. From Fig. 1, the best burnt project is $A_3B_2C_2$, in which the conditions are mixing 1.4% CaF_2 and treating 2 h at 1350°C (F specimen). The F specimen was burnt again to validate its strength. In addition, from the temperature tendency curve we can see that the strength rises with the temperature rise. So we burnt the F specimen at 1380°C. At the same time, we compared it with the standard sample. The results are listed in Table 3.

Table 3 shows that the strength of F specimen is better than that of others at 1350°C, and goes down at 1380°C.

2.2. Influence of fluorite on the Ba-bearing sulphoaluminate cement

Based on above results, we blended fluorite in the raw meal according to 1.4% CaF_2 of Ba-bearing calcium sulphoaluminate minerals in clinker. The pure cement paste

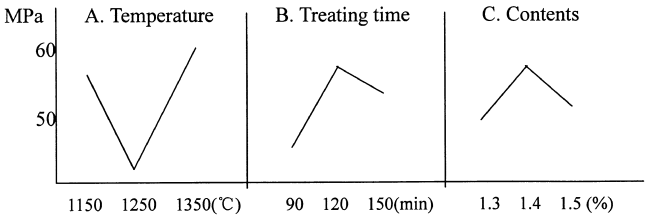


Fig. 1. The tendency curves.

Table 3
The suitable conditions and the results

Specimen	Temperature (°C)	Treating time (min)	Contents (%)	Compressive strength (MPa) 1d	3d	7d	28d
F	1350	120	1.4	50	90	95	113
F	1380	120	1.4	41	39	67	74
No fluorite	1350	120	0	35	59	72	76

Table 4
The compressive strength of cement

Sample	Compressive strength (MPa) 1d	3d	7d	28d
No fluorite	79.4	92.8	97.3	98.9
With fluorite	91.6	92.1	108.8	115.3

specimens were obtained by the same way like the last experiment. The results of compressive strength are listed in Table 4. It shows that the compressive strength of Ba-bearing sulphoaluminate cement with fluorite is better than that with no fluorite.

3. Results and discussion

3.1. The XRD analysis of clinker and hydrated samples

The XRD pattern of F clinker with fluorite shows (Fig. 2) that the major minerals are Ba-bearing calcium sulphoaluminate and β-C_2S. From the XRD patterns of hydrated samples (Fig. 3) it is found that CAH_{10}, $BaSO_4$, and unhydrated Ba-bearing calcium sulphoaluminates exist in 1d hydrated production. On 3d and 28d the XRD peaks of Ba-bearing calcium sulphoaluminates are low and the CAH_{10} peak is growing gradually. In addition, the peaks

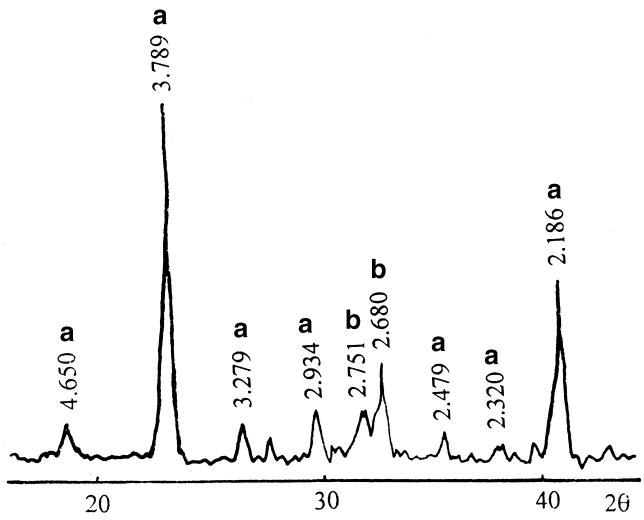


Fig. 2. XRD pattern of the clinker.

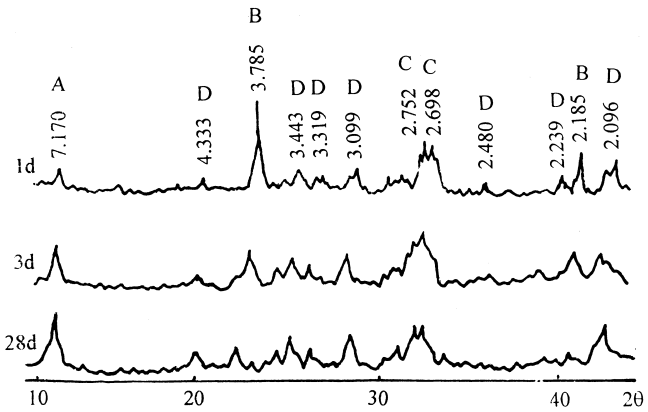


Fig. 3. XRD patterns of hydrated samples. A—CAH_{10}; B—$C_{2.75}B_{1.25}A_3\bar{S}$; C—β-$C_2S$; D—$BaSO_4$.

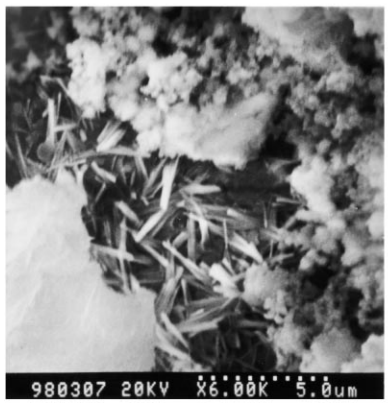
of hydrated samples are weaker than those of the hydrated sample without fluorite. It shows that abundant colloid exists in hydrated production.

3.2. The SEM analysis of hydrated samples

Fig. 4 shows more colloids than needle-shaped CAH_{10} crystals phase at 1d hydrated sample. The same as the result of XRD analysis that CAH_{10} crystals increase in 3d and 7d hydrated sample; in addition, a small quantity of cubic-shaped C_3AH_6 and unhydrated rhombus dodecahedron-shaped Ba-bearing calcium sulphoaluminates exist in 7d hydrated sample; C_3AH_6 crystals are increased in 28d hydrated sample. It shows that some CAH_{10} transforms to steady C_3AH_6. From SEM photos we can see that the structure of the hydrated sample is dense.

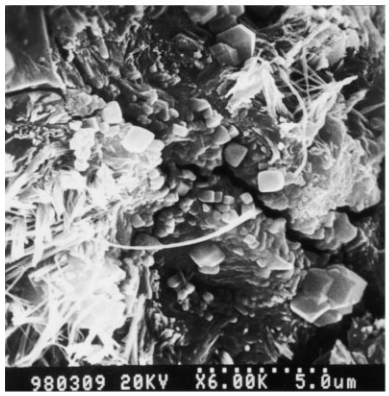
4. Conclusions

The strength of $C_{2.75}B_{1.25}A_3\bar{S}$ can be improved by CaF_2, and the optimal composition combines 1.4% CaF_2 and was treated 2 h at 1350°C.



1d hydrated sample

3d hydrated sample



7d hydrated sample

28d hydrated sample

Fig. 4. SEM photos of hydration samples.

The compressive strength of Ba-bearing sulphoaluminate cement was improved by fluorite at each age.

The hydrated products of Ba-bearing sulphoaluminate cement with fluorite are mainly CAH_{10} and $BaSO_4$.

Acknowledgments

This work was financed by National Natural Science Foundation of China and Natural Science Foundation of Shandong Province.

References

[1] I. Teoreanu, M. Muntean, I. Dragnea, Type 3($CaO \cdot Al_2O_3$) ($M_x \cdot SO_4$)$_y$ compounds and compatibility relations in $CaO - CaO \cdot Al_2O_3 - M_x(SO_4)_y$ systems, Il Cemento 83 (1) (1986) 39–45.

[2] X. Cheng, Study of Ba-bearing calcium sulphoaluminate minerals and cement, Cem. Concr. Res. 30 (2000) 77–81.

[3] J. Chang, Study on Ba-bearing calcium sulphoaluminate cement mineral, J. Chin. Soc. 27 (6) (1999) 644–650.

[4] X. Cheng, Formation and bond performance of some ettringites by quantum chemistry methods, Cem. Concr. Res. 27 (7) (1997) 1085–1092.

[5] J. Chang, Study on new type Ba-bearing cement, Master's degree thesis, Wuhan University of Technology, Wuhan, China, 1998.

[6] P. Yan, Hydration of Sr- and Ba-bearing sulphoaluminates in the presence of sulphates, Adv. Cem. Res. 18 (5) (1993) 65–69.