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Study of Ba-bearing calcium sulphoaluminate minerals and cement

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Abstract

In this paper, we synthesized a series of new cement minerals, Ba-bearing calcium sulphoaluminates, by the substitution of Ba^{2+} for Ca^{2+} ions of $C_4A_3\overline{S}$ ($3CaO \cdot 3Al_2O_3 \cdot CaSO_4$). The strength development was studied. The results show that the strength of Ba-bearing calcium sulphoaluminates is higher than that of $C_4A_3\overline{S}$, and the optimal composition has been found. Based on this conclusion, Ba-bearing calcium sulphoaluminte cement has been burned with Ba-bearing industrial wastes. In addition, the hydration mechanism of the cement was analyzed by X-ray diffraction, scanning electron microscopy, and infrared spectrophotometry.

Keywords: $(3\text{-}x)CaO \cdot xBaO \cdot 3Al_2O_3 \cdot CaSO_4$; Hydration; Compressive strength

1. Introduction

$C_4A_3\overline{S}$ is one of the main minerals in calcium sulphoaluminate cement. The substitution of Ba^{2+} for Ca^{2+} to improve the performance of $C_4A_3\overline{S}$ has been reported [1–4], but systematic characterization has not been done. In this study we found that substituting Ba^{2+} ions increases the strength of minerals, but the strength decreases when the content of Ba^{2+} ions exceeds a fixed value under the same burning condition. Thus the optimal composition was found. According to this principle, the Ba-bearing calcium sulphoaluminate cement was burned using Ba-bearing industrial wastes, in which the gypsum is substituted by the Ba-bearing industrial wastes. The use of Ba-bearing industrial wastes also results in environmental protection and resource savings.

2. Methods

2.1. Study on the series of Ba-bearing calcium sulphoaluminate minerals

All raw materials used in the experiment, such as $CaCO_3$, $BaCO_3$, Al_2O_3, and $CaSO_4 \cdot 2H_2O$, were pure analytical reagents. According to the stoichiometry molar ratios of $(3\text{-}x)CaO \cdot xBaO \cdot 3Al_2O_3 \cdot CaSO_4$, each agent was weighed accurately in proportion as $x = 0.00$, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, 2.75, 3.00; then the agents were homogenized and ground to pass a 75-μm sieve, and pressed to round pieces as $\phi 60 \times 10$ mm. These round pieces were dried for 1 h at 100°C, then burned at 1,350°C for 2 h. Finally, the pieces were taken out to cool at room temperature and were ground to 3,500 cm^2/g (Blaine). FCaO in all clinkers was determined to be zero by ethylene glycol method. According to the ratio of water/cement = 0.35, we mixed the clinkers with water and put the paste into the $2 \times 2 \times 2$ cm^3 moulder; then we shaped them by vibration. These pure cement paste specimens were demoulded after being cured in moist 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 Fig. 1.

From the figure we can see when $x < 1.25$, the compressive strength at each age grows along with increasing x value. On the contrary, when $x > 1.25$, compressive strength at each age reduces as x value increases. When $x = 2.5$, specimens at 28 days suffer serious cracking; when $x = 2.75$, specimens at 28 days burst; and when $x = 3.00$, specimens at 7 days burst. Therefore we found that the best composition is $x = 1.25$.

2.2. Study on Ba-bearing calcium sulphoaluminate cement

Based on the result of above experiment, Ba-bearing calcium sulphoaluminate cement was prepared using Ba-bear-

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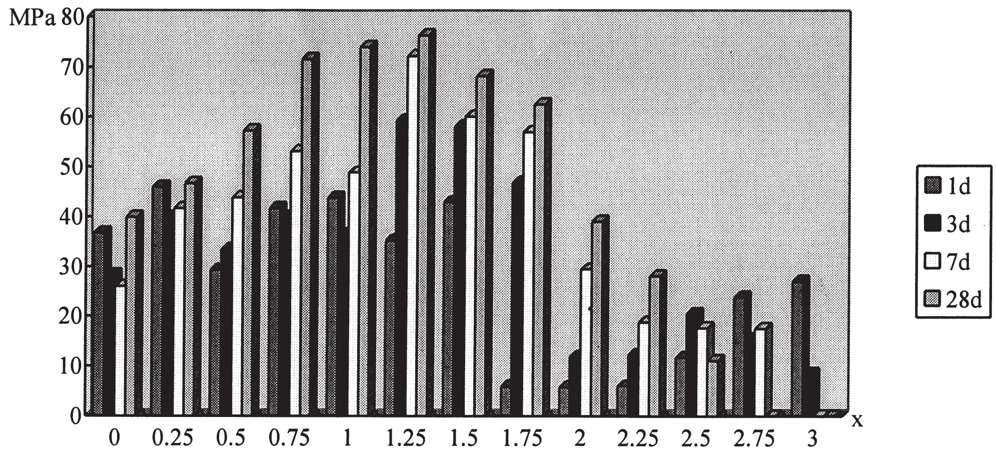

Fig. 1. Compressive strength of (3-x)CaO · xBaO · $3Al_2O_3$ · $CaSO_4$ samples (water/cement = 0.35).

ing industrial wastes. The chemical compositions of raw materials used for the experiment are shown in Table 1.

In the experiment, we assumed that the mineral composition of clinker was $C_{4-x}B_xA_3\overline{S}$, β-$C_2\overline{S}$, C_4AF. x was the mole number of CaO substituted by BaO, and designed as 1.25, 1.00, 0.75, 0.50, 0.25, 0.00. They were identified with the symbols K, L, M, N, P, and O, respectively. We obtained the compressive strength of each clinker in the same way as used in the above experiment and the mineral compositions of them are listed in Table 2.

Table 1
Chemical compositions of raw materials

Raw materials	Chemical composition (%) CaO	SiO_2	Al_2O_3	BaO	Fe_2O_3	SO_3	MgO	Loss
Limestone	50.01	4.18	1.13	0.00	0.48	0.00	2.23	41.28
Bauxite	1.45	10.42	60.39	0.00	4.58	0.00	1.88	
Ba waste	3.12	14.54	5.52	44.18	1.75	17.6	0.50	12.64
Gypsum	33.33	4.10	1.11	0.00	0.31	41.31	0.44	19.50

3. Results and discussion

3.1. Results

From Table 2, the results of K_1, K_2, and K_3 show that the compressive strength of the cement containing the same x value increases with the increasing of Ba-bearing calcium sulphoaluminate content at each age. From K_1, L, M, N, P, and O, we can see that the compressive strength increases with increasing Ba^{2+} ions content. Therefore, the Ba-bearing calcium sulphoaluminate mineral content of clinker and the Ba^{2+} ion content of the mineral contribute greatly to the cement characteristics, such as rapid hardening and early strength.

The results also show that the burning temperature influ-

Table 2
Mineral compositions and compressive strengths of clinkers

Number	x value	Temperature (°C)	$C_{4-x}B_xA_3\overline{S}$	β-C_2S	C_4AF	Compressive strength (MPa) 1 day	3 days	7 days	28 days
K_1	1.25	1,300	60	35	5	79.4	92.8	97.3	98.9
K_2		1,300	55	40	5	88.7	90.9	88.4	96.3
K_3		1,300	50	45	5	63.0	49.5	84.6	68.8
K_1		1,280	60	35	5	34.9	46.4	57.6	48.6
K_1		1,250	60	35	5	20.6	22.1	25.2	27.3
L	1.00	1,300	60	35	5	93.1	68.7	94.5	88.9
M	0.75	1,300	60	35	5	40.9	58.3	75.2	79.9
N	0.50	1,300	60	35	5	52.5	62.8	64.2	78.6
P	0.25	1,300	60	35	5	42.1	52.0	44.6	55.4
O	0.00	1,300	60	35	5	44.0	45.8	49.8	47.6

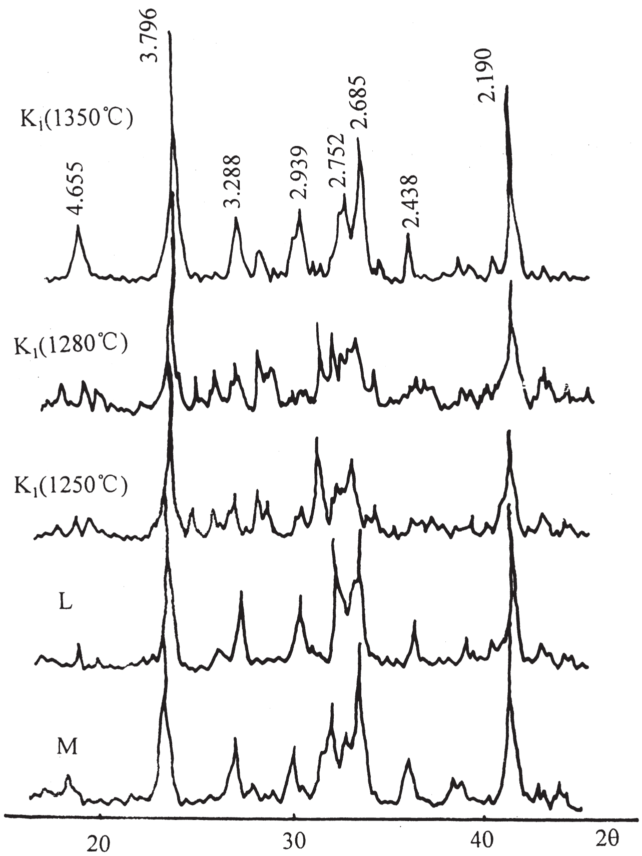

Fig. 2. XRD patterns of some clinkers.

ences the properties of cement. Ba-bearing calcium sulphoaluminate cement burned at 1,300°C provides high strength. When the temperature is too low (i.e., at 1,250 or 1,280°C), 1 to 3% f-CaO is found and the strength decreases.

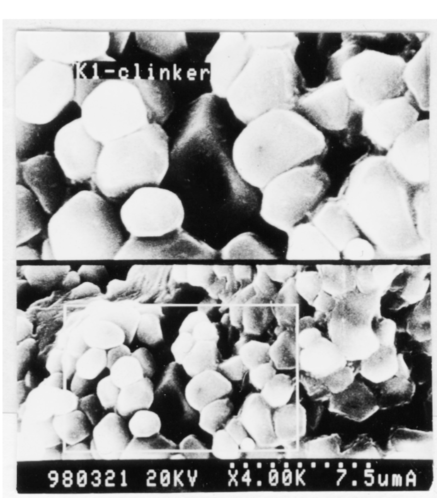

Fig. 3. SEM photo of K_1 clinkes.

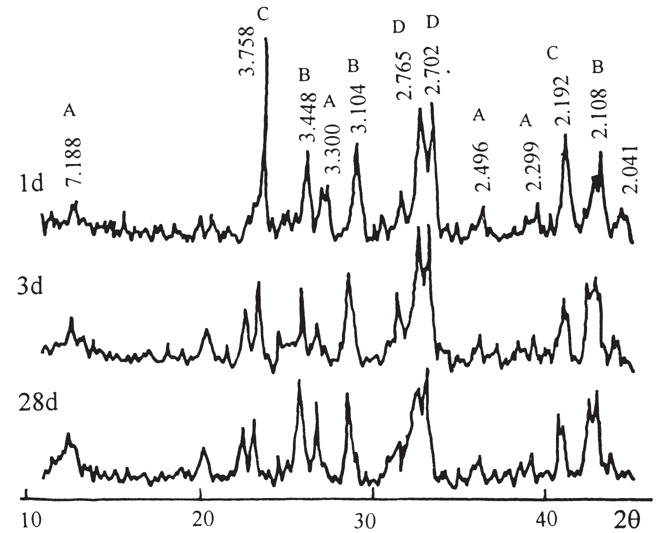

Fig. 4. XRD patterns of hydrated samples A-CAH_{10} B-$BaSO_4$ C-$C_{2.75}B_{1.25}A_3\overline{S}$ D-β-C_2S.

3.2. X-ray diffraction and scanning electron microscopy analysis of clinkers

Fig. 2 shows that the main minerals are Ba-bearing calcium sulphoaluminates(3.796, 2.685, 2.190Å) and β-C_2S (2.778, 2.752, 2.685Å) in each clinker. From X-ray diffraction (XRD) patterns, the K_1 clinkers burned at three different temperatures produce Ba-bearing calcium sulphoalminate and other minerals, but the quantities are different.

From the scanning electron microscopy (SEM) photos of K_1 clinker (Fig. 3), we can see that the large quantities of rhombohedral granules are Ba-bearing calcium sulphoaluminate and rubble granules are β-C_2S.

3.3. SEM and XRD analysis of K_1 hydration samples

XRD patterns (Fig. 4) of each hydration sample show that the CAH_{10}, $BaSO_4$, a small amount of C_3AH_6, and unhydrated Ba-bearing calcium sulphoalminate exist in hydration samples. From their SEM photos (Fig. 5),mixtures of microcrystalline $Al(OH)_3$ and $BaSO_4$ are found on 1-day K_1 hydrated samples. A great deal of hydrated calcium aluminate is present in 3- and 28-day hydrated samples.

3.4. Infrared spectral analysis of K_1 clinker and hydrated samples

Each clinker mineral has its own unique infrared band. The 1,098 cm^{-1} and 641 cm^{-1} bands are those of $C_4A_3\overline{S}$, and 520 cm^{-1} is that of β-C_2S [5]. The K_1 clinker and hydrated sample were analyzed by infrared spectrophotometry (Fig. 6). The main absorption band of Ba-bearing calcium sulphoaluminate is 1,099.96, 634.25 cm^{-1}, and that of β-C_2S is 515.42 cm^{-1}. The absorption band at 1,099.96 cm^{-1} is the result of un-

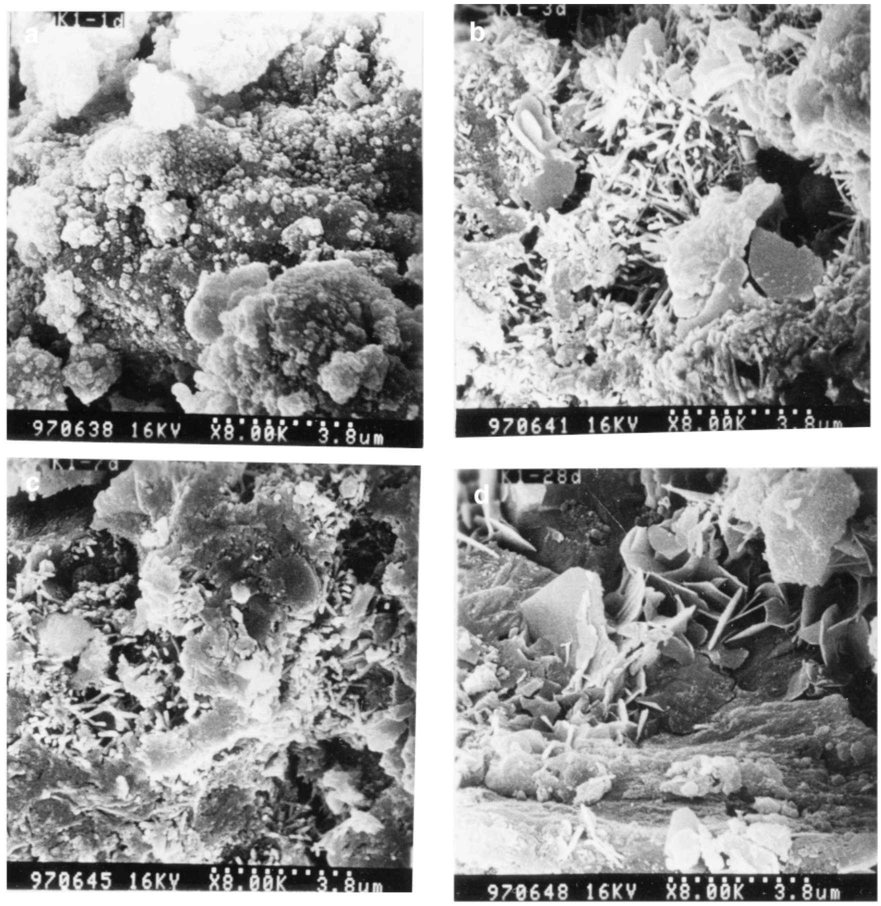

Fig. 5. SEM photos of K_1 hydration samples.

symmetrical stretching-shrinking vibration of $[SO_4]$ tetrahedrons, which moves to 1,069.94 cm^{-1} on 1-day hydration. It shows the hydration speed of Ba-bearing calcium sulphoaluminate is fast. A small amount of unhydrated Ba-bearing calcium sulphoaluminate survives in the hydrated samples from 7 to 28 days. The band at 3,500 cm^{-1} is the stretching-shrinking absorption vibration peak of bound water in AH_3 and C-S-H. The presence of AH_3 is indicated by the 1,020 cm^{-1} band; C-S-H is indicated by the 970 cm^{-1} band, which is unsymmetrical stretching-shrinking vibration of $[SiO_4]$ tetrahedron [5].

The combination of XRD and SEM analysis indicates Ba-bearing calcium sulphoaluminte hydrates produce $BaSO_4$, CAH_{10}, and AH_3; C_2S hydrates to produce C-S-H gel that fills porosity of crystals, and results in a dense structure. Thus, the cement obtains high strength.

4. Conclusions

In the series of Ba-bearing calcium sulphoaluminates, substitution of 1.25 mol Ba^{2+} ions for Ca^{2+} ions provides the highest strength.

Ba-bearing calcium sulphoaluminate is a good hydraulic binding mineral and the Ba-bearing sulphoaluminate cement has high strength, especially high early strength.

Burning temperatures lower than 1,300°C produce fCaO and the strength decreases.

The strength of the cement increases with the Ba content in Ba-bearing calcium sulphoaluminate and the Ba-bearing calcium sulphoaluminate content in cement.

Acknowledgments

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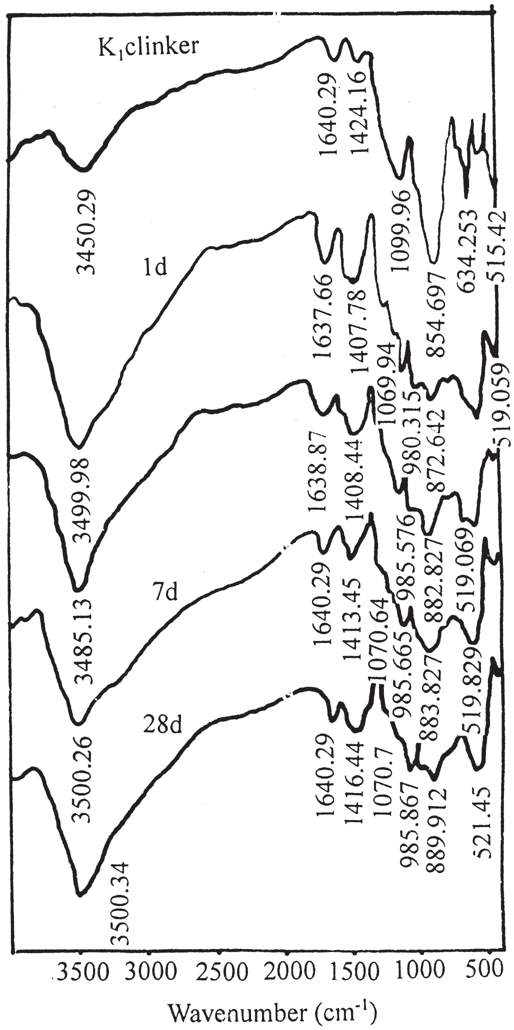

Fig. 6. IR of K_1clinker and hydration samples.