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Study on a cementing system taking alite-calcium barium sulphoaluminate as main minerals

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A mineral system of alite-calcium barium sulphoaluminate with high cementing characteristic was synthesized with chemical reagents. The influences of the mineral constituent, sintering temperature and some microelements on the performance of the clinker system were studied. Alite and calcium barium sulphoaluminate minerals can be synthesized at 1360°C synchronously and can coexist in a clinker system. The suitable content of calcium barium sulphoaluminate in the clinker is less than 10 wt%. The compressive strength of some clinkers is nearly 90 MPa at 28 days age. The constituent, structure and morphology of the clinker minerals were analysized by means of XRD, SEM-EDS and light microscope.

1. Introduction

Portland cement, which contains alite (C_3S) as the primary mineral, is used extensively all over the world. However, the early strength of Portland cement is low and its sintering temperature is high (about 1450°C). How to increase the early strength and to reduce the sintering temperature are primary problems. In 1986, & Teoreanu [1] synthesized a single constituent mineral, calcium barium sulphoaluminate ($3CaO{\cdot}3Al_2O_3{\cdot}BaSO_4$), and found that it had high early strength. Since 1988, Cheng [2–4] and Feng [5, 6] have synthesized a series of the minerals of calcium barium sulphoaluminate $(3-x)CaO{\cdot}xBaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ (abbreviated as $C_{(4-x)}B_xA_3\bar{S}$ or $C(B)_4A_3\bar{S}$) and found that the compressive strength of $C_{2.75}B_{1.25}A_3\bar{S}$ was the highest among them, up to 35.1, 59.3 and 72.1 MPa at 1, 3 and 7 days age, respectively. The sintering temperature of the mineral is lower (about 1350°C) and the rate of hydration-hardening is faster than that of Portland cement. They also studied the relationships between its compositions, structures and performances. This experiment is to synthesize a new mineral system in which the primary minerals are alite and calcium barium sulphoaluminate in order to obtain high early strength cement.

2. Experiment methods

2.1. Raw materials

Pure analytical reagents $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, $BaSO_4$, $BaCO_3$ and CaF_2 were used as raw materials.

2.2. Experiment methods

Each reagent was weighed accurately in proportion. The meals were homogenized and ground to pass a sieve with a size of 80 μm. They were pressed into cylinders 5 mm high by 50 mm in diameter. These cylinders were burnt at 1360°C for 60 min then cooled to room temperature. After adding 5 wt% gypsum, the clinker was ground to fine powders whose fineness is indicated by the residue of the 80 μm sieve. Free CaO in clinkers was determined by the ethylene glycol method.

The clinkers were mixed with water to a cement paste with a W/C ratio of 0.3. The paste was put into a $2 \times 2 \times 2$ cm^3 mould by vibration. These paste specimens were demoulded after being cured in moist air at 20°C for 24 h, then were cured in water at 20°C to each age for measuring the compressive strength.

The clinker minerals were analyzed by a D/max-ra X-ray diffractometer (XRD), the mineral feature and structure were recorded on a Hitach S-2500 scanning

electron microscope (SEM), equipped with an Oxford energy dispersive spectrometer (EDS) and the structure of the clinkers was observed by a 4XZ light microscope.

3. Results and discussion

3.1. Components and performances of the mineral system

A suitable mineral component is the foundation to obtain high performance cementing materials. Sintering temperature of C_3S and $(CB)_4A_3\bar{S}$ are about 1450°C and 1350°C, respectively. How to obtain a clinker system containing both C_3S and $(CB)_4A_3\bar{S}$ at a low temperature is the key of this research. The designed mineral components are listed in Table I. CaF_2 was added into every sample and its content in all clinkers was 1.5 wt%. The experiments were divided into groups A, B, C and D (see Table I).

Table II gives the content of free-CaO in the clinkers burnt at 1360°C for 60 min. It is found that the average content of free-CaO in every group of clinker is very low, indicating that the solid-phase reaction in the clinkers is complete at the burning temperature.

The compressive strengths of the clinkers of groups C and D are listed in Table III. That of groups A and B is not given because the pastes occur to quick setting. It leads to some macro-defect on the samples of hardened cement pastes and the compressive strengths of the samples cannot be measured accurately. The result shows the designed content of the $(CB)_4A_3\bar{S}$ in the clinkers is not suitable to exceed 10 wt% under the condition of the experiment. From Table III, it can be also seen that the early compressive strengths of the clinker of groups C and D are high and the strength of group D is much higher than that of group C. This shows further that mineral $C_{2.75}B_{1.25}A_3\bar{S}$ benefits the increase of the early strength of the clinkers.

TABLE I The mineral components of clinkers (wt%)

Group	no.	$C_{2.75}B_{1.25}A_3\bar{S}$	C_3S	C_2S	C_3A	C_4AF
C	1	10	50	20	20	0
	2				15	5
	3				10	10
	4				5	15
	5				0	20
D	1	6	54	20	20	0
	2				15	5
	3				10	10
	4				5	15
	5				0	20

TABLE II The free-CaO content of clinkers (wt%)

	Group			
No.	A	B	C	D
1	0.48	0.33	0.74	0.15
2	0.26	0.61	0.49	0.05
3	0.25	0.53	0.16	0.13
4	0.53	0.16	0.25	0.10
5	0.37	0.16	0.70	0.13

TABLE III The compressive strength of clinkers

			Compressive strength (MPa)		
Group	No.	Fineness (%)	3 d	7 d	28 d
C	1	2.0	32.1	44.3	58.8
	2	1.0	37.3	48.2	50.2
	3	6.0	37.3	56.6	80.4
	4	4.0	34.4	50.6	68.1
	5	2.0	31.8	52.4	77.8
D	1	3.1	37.3	46.8	65.2
	2	2.2	48.9	55.9	74.3
	3	4.3	60.3	75.5	86.2
	4	2.8	51.6	70.0	85.5
	5	3.0	41.5	58.0	79.8

3.2. XRD analysis of clinkers

The XRD patterns of the clinkers in groups C and D are depicted in Figs. 1 and 2. From Fig. 1, it can be seen that the clinkers in group C contain the minerals of $(CB)_4A_3\bar{S}$, C_3S, C_2S, C_3S and C_4AF. The result shows

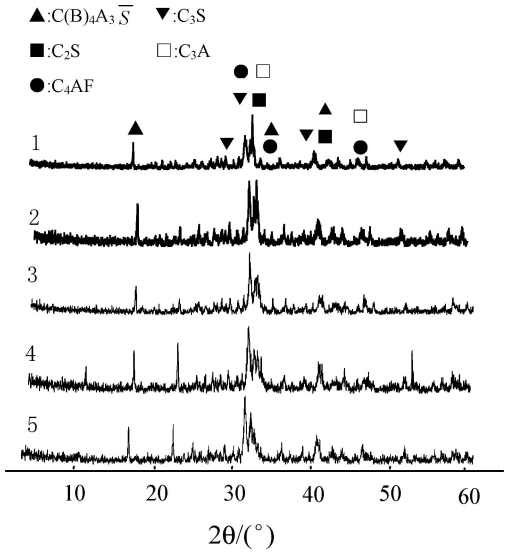

Figure 1 XRD patterns of clinkers of group C.

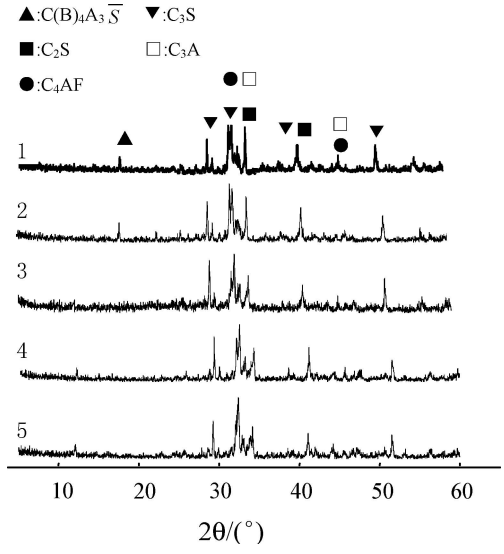

Figure 2 XRD patterns of clinkers of group D.

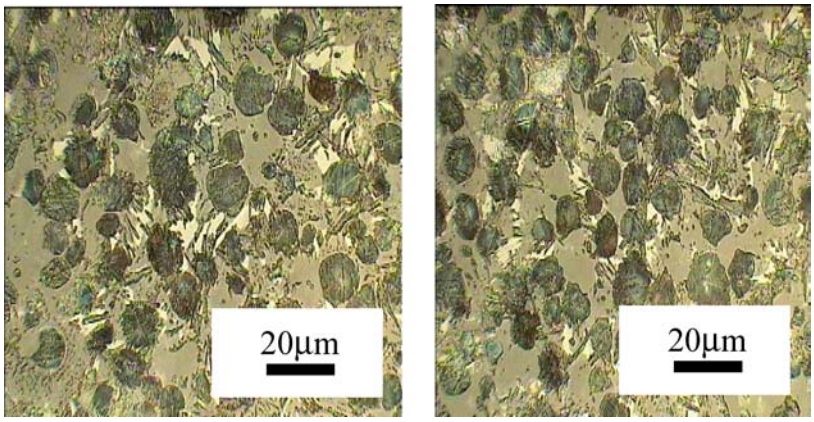

Figure 3 Light microscopy of clinker C3.

that C_3S and $(CB)_4A_3\bar{S}$ can be formed and coexist in a clinker at 1360°C, which is the basis establishing the mineral system of C_3S - $(CB)_4A_3\bar{S}$ with high cementing characteristics.

From Fig. 1, it can also be seen that the intensity of the C_3S diffraction peak at 51.84° ($d = 1.76$) is weak and the peak is not overlapped, which suggests that the real content of C_3S is lower than its designed content (50 wt%) in clinker C3. The result shows also that the minerals of the clinker are not formed according to the designed proportion and indicates that all kinds of minerals in the clinkers may influence each other. Similarly, according to Fig. 2, the XRD patterns of the clinkers in group D shows that the intensity of the $(CB)_4A_3\bar{S}$ peak is weak and the designed content of the mineral is also much less. However, the relative amount of C_3S in the clinkers of group D is much more than in group C and thereby its diffraction peaks had a high intensity. It might be one of the reasons that the clinker strength of the group D is much higher both at the early and late ages.

From the above analysis, the primary results are obtained: The compressive strength, especially the early strength for clinker C3, which contains a higher amount of $(CB)_4A_3\bar{S}$ (10 wt%), is not high. However, the clinker D3, which contains a lesser amount of $(CB)_4A_3\bar{S}$ (6 wt%) has higher early and late strength as compared with clinker C3. This is disobedient with the characteristic of the mineral $(CB)_4A_3\bar{S}$ which has proved to have an excellent performance of high-early strength [2]. The phenomena suggests that the minerals in the clinker system, such as $(CB)_4A_3\bar{S}$, C_3S , C_2S, C_3A and C_4AF, can influence each other.

3.3. Light microscopy of clinkers

Light microscopy provides much information on clinker microstructure. Figs. 3 and 4 are the micrographs of clinker C3 and D3. The small and rounded regular particles are belite (C_2S) and the angular particles are alite (C_3S). From Fig. 3, it can be seen that the content of belite is far more than the designed content (20 wt%). On the contrary, alite is less than the designed content and the shape is irregular. Fig. 4 shows that the content of alite in clinker D3 is greater than that of clinker C3 and angularity is improved. This suggests that alite content and angularity improves compressive strength because, as indicated previously, the compressive strength of the clinker D3 is higher than that of C3. However, the content of C_3S in clinker C3 and D3 is still lower than the designed values in Table I and thereby restricts the further improvement of the clinker performance.

3.4. SEM-EDS analysis of clinkers

Fig. 5 gives SEM-EDS graph of clinker C3. The rounded C_2S and similar hexagonal C_3S can be

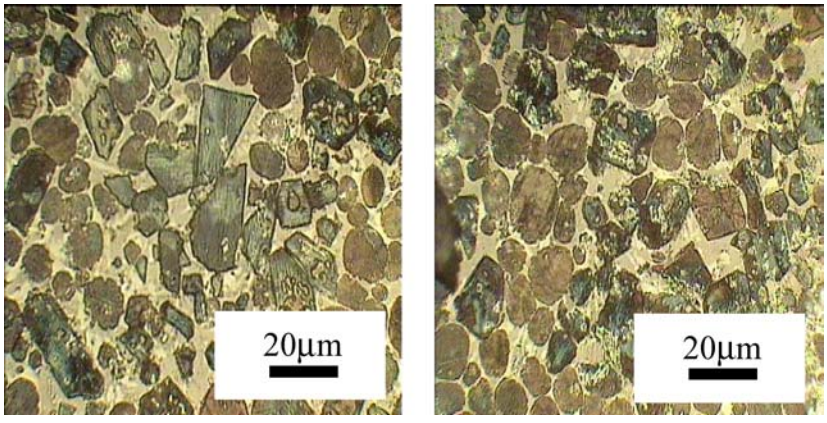

Figure 4 Light microscopy of clinker D3.

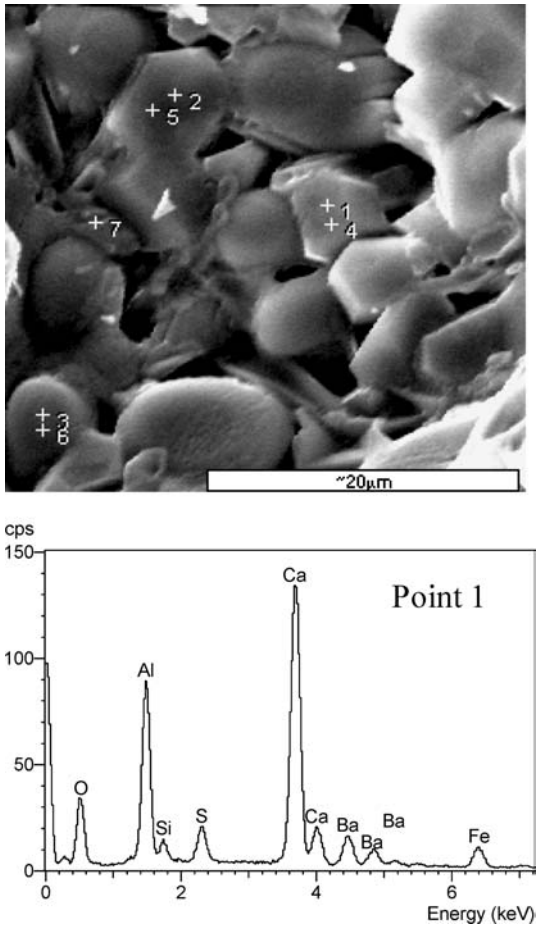

Figure 5 SEM-EDS pattern of clinker of C3.

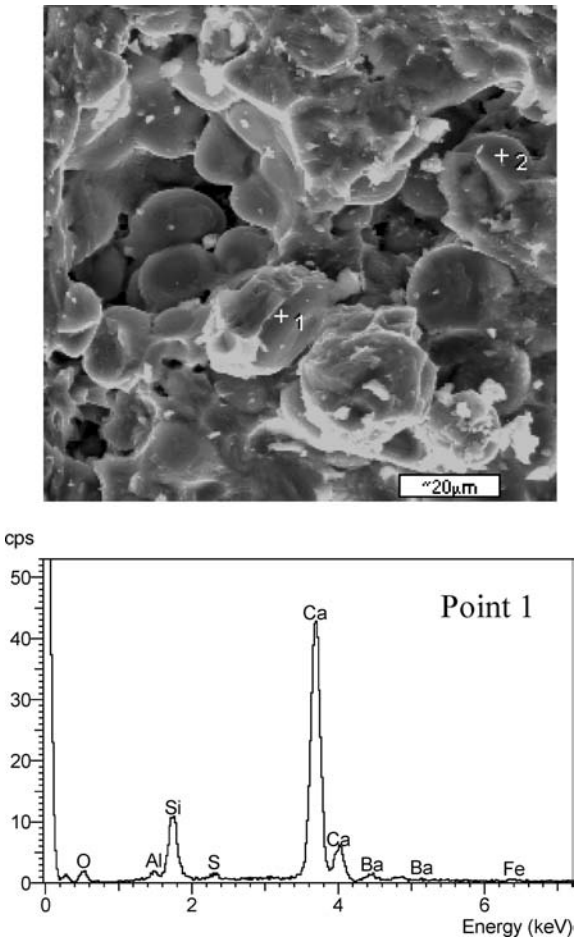

Figure 6 SEM-EDS pattern of clinker of D3.

seen. The shape of $(CB)_4A_3\bar{S}$ is a rhombic dodecahedron and has a regular morphology. EDS analysis for point 1 in Fig. 5 indicates that it is calcium barium sulphoaluminate and its composition is $C_{3.59}B_{0.92}\ A_{2.72}\bar{S}$.

Many $(CB)_4A_3\bar{S}$ are formed in the gaps between other minerals and their sizes are less 10 μm, such as point 1 in Fig. 5. It can also be seen that the clinker system has many rounded minerals about 10–20 μm. Fig. 6 is the SEM-EDS analysis result of clinker D3. It only reveals the existence of alite and belite. The mineral $C(B)_4A_3\bar{S}$ is not observed. The mineral shape of alite is not as clear as that in the traditional Portland cement. However, belite in the holes is quite clear and its content is much higher.

SEM-EDS analyses of the clinkers further confirm that there is a great difference between the designed component of the clinker minerals and the real component, which is an important reason restricting the increase in the performance for the clinker system.

4. Conclusions

(1) The minerals of $(CB)_4A_3\bar{S}$ and C_3S can coexist in a clinker, which is an important foundation making the mineral phase system of alite-calcium barium sulphoaluminates with high cementing characteristics.

(2) The suitable content of $(CB)_4A_3\bar{S}$ in the mineral system is less than 10% by weight.

(3) The compressive strength of some of the clinker samples was nearly 90 MPa at 28 days age, which shows a good prospect.

(4) There was a difference between the real and designed mineral component in this system, which needs to be researched further.

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