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HYDRATING CHARACTERISTICS OF MODIFIED PORTLAND WITH Ba-BEARING SULPHOALUMINATE MINERALS

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The hydrating characteristics of modified Portland cement with Ba-bearing sulphoaluminate minerals were studied in this paper. Scanning Electron Microscopy-Energy Dispersive Spectrometer (SEM-EDS), mercury intrusion porosimeter(MIP) and compressive strength were determined to characterize hydrating products and microstructure. Results show that basic physical properties of modified Portland cement with Ba-bearing sulphoaluminate minerals (SMPC) are similar with PC except the shorter setting time. Ettringite and C–S–H are the main hydrating produces in SMPC, which is similar to Portland cement (PC). Because of volume expansion of ettringite, SMPC paste structure is denser than PC according to SEM-EDS analysis and the pore size and pore content of SMPC pastes was smaller especially for the harmful pores. Because sulfur aluminum barium calcium was a new early-strength mineral and parts of BaO went into the C_2S lattice and caused lattice distortion to enhance C_2S hydration activity, the compressive strengths of SMPC grew faster and higher than PC.

INTRODUCTION

The manufacture of Portland cement (PC) not only consumes a vast amount of energy and high calcite but also produces undesirable CO_2 emissions [1-3]. 0.97 tons of CO_2 to produce per ton of PC are released into atmosphere: 0.54 tons of CO_2 from decomposition of calcite in the kilns, and on average, 0.34 and 0.09 tons of CO_2 from the burning of the fuel and electricity for the milling, respectively [4-6].

However, belite-sulphoaluminate cement is a new kind of binding materials, called a sort of environment-friendly cement [7-8]. Alite, the main component of PC, is formed at the temperature of about 1450°C. Belite is formed at about 1200°C. Its sintering temperature is 100 ~ 150°C lower than PC, which can save amounts of energy consumption. Further, it is more friable than PC due to higher porosity, which reduces the energy needed for grinding [9]. In addition, the manufacture of belite-sulphoaluminate cement can make use of low-grade limestone and harmful industrial barium slag. These three facts may cause a reduction of 0.16 tons of CO_2 to produce per ton of belite-sulphoaluminate cement. It is up to 16 % CO_2 emission reduction compared to PC. Therefore, belite-sulphoaluminate cement has the obvious advantages over PC.

The most common formulation of belite-sulphoaluminate cements are C_2S, $C_4A_3\check{S}$ and C_4AF [10-13]. It contains more than 50 wt. % of C_2S, classified as belite-rich materials. In spite of the complexity of the hydration reactions, there is already a significant number of literature on the subject. Y.B. Pliego-Cuervo et al. reported that in C_2S–$C_4A_3\check{S}$–$C_{12}A_7$–CA system aluminate phases and $C_4A_3\check{S}$ were responsible for the early strength development, while the C_2S provided good secondary hardening [14]. H. Li et al. reported some non-hydraulic phases accompanied by $C_4A_3\check{S}$, such as C_2AS or $C_5S_2\check{S}$. F.P. Glasser et al. studied the hydration reactions of the cement pastes at early stages at different curing temperatures. It was inducted that at present early cementing performance of belite-sulphoaluminate was not good enough to satisfy the requirement of wide engineer, especially compared to PC [15].

In this paper, modified Portland cement with sulphoaluminate minerals (SMPC) was designed to improve early cementitious property on the basis of saving energy. It contained C_3S, C_2S, C_4AF, C_3A, $C_{2.75}B_{1.25}A_3\check{S}$ and $CaSO_4$ as the main phases. $C_{2.75}B_{1.25}A_3\check{S}$ could be synthesized at a lower temperature of 1350°C to 1400°C, rather than the 1400°C to1500°C of Portland cement clinker. And its decomposition temperature was more than 1400°C, approximately 50°C higher than $C_4A\check{S}$. In theory, a chance was provided for $C_{2.75}B_{1.25}A_3\check{S}$ to coexist with C_3S in the same system. In addition, the substitution of Ba^{2+} for Ca^{2+} could improve the performance of $C_4A_3\check{S}$ [16-19]. The Ba-bearing calcium sulphoaluminate mineral content of clinker and the Ba^{2+} ion content of the mineral contributed greatly to the cement characteristics, such as rapid hardening and early strength. In the series of Ba-bearing calcium sulphoaluminates, substitution of 1.25 mol Ba^{2+} ions for Ca^{2+} ions provided the highest strength. $C_{2.75}B_{1.25}A_3\check{S}$ was a good hydraulic binding mineral and had high early strength. However, so far, there had been few previous studies to improve cement manufacture and properties with $C_{2.75}B_{1.25}A_3\check{S}$. The aim of the present study was to investigate the possibility of coexistence of $C_{2.75}B_{1.25}A_3\check{S}$ and PC clinker as well as hydrating characteristics of the new cementitious material, including analyses of physical and mechanical properties, hydration products and microstructure of hydrating pastes.

EXPERIMENTAL

Raw material

$CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, $BaSO_4$, $BaCO_3$ and CaF_2 were pure chemical reagents. The fineness was below 6.3 % (residue on 0.08 mm sieve). PC came from Shandong cement plant in China. Gypsum came from Zibo in China. The chemical compositions of PC and gypsum performed with the X-ray fluorescence (XRF-1700) analyzer were presented in Table 1.

Preparing process of SMPC clinker

All the raw materials were dried in an oven at 100°C for 4 h and ground to pass 0.08 mm sieve before batch compositions were made. The batch compositions were mixed thoroughly. After thorough homogenization, raw meals were nodulized to the size of approximately 15 mm diameter each. Nodules were dried in an oven at 100°C for 1h before introducing into the furnace. The batch compositions were fired at 1380°C. The sintering duration was 1.5 h. Then SMPC clinker was obtained. The mineral composition of belite-barium calcium sulphoaluminate clinker designed in this paper was shown in Table 2. The fired clinker was relatively soft and friable, and easy to grind; consequently, the whole process results in considerable saving of energy.

XRD pattern of SMPC clinker was presented in Figure 1. The primary minerals were C_3S, C_2S,C_4AF, C_3A and $C_{2.75}B_{1.25}A_3\check{S}$, which was consistent with experimental program in Table 2.

$C_{2.75}B_{1.25}A_3\check{S}$ was generated at 1350°C and decomposed at 1400°C. Though sintering temperature of SMPC clinker in this paper was about 70°C lower than PC clinker, in the calcination process SO_3 and BaO played the roles of mineralizers and fluxes, which, to a certain extent, could promote the synthesis of C_3S. Therefore, as was shown in Figure 1, $C_{2.75}B_{1.25}A_3\check{S}$ could coexist with C_3S at 1380°C.

Table 2. Mineral composition of SMPC clinker designed (wt.%).

	C_3S	C_2S	C_3A	C_4AF	$C_{2.75}B_{1.25}A_3\check{S}$
SMPC clinker	37.5	39.5	4.6	11.46	7

Experimental design

The hydrationg reactions of SWPC can been described by the following set of Equation 1-6.

$$C_3S + nH \rightarrow C\text{–}S\text{–}H + (3 - x)CH \quad (1)$$

$$C_2S + nH \rightarrow C\text{–}S\text{–}H + (2 - x)CH \quad (2)$$

$$2C_3A + 27H \rightarrow CAH_{19} + C_4AH_{13} \quad (3)$$

$$C_3A + 3C\check{S}H_2 + 26H \rightarrow C_6A\check{S}_3H_{32} \quad (4)$$

$$C_4AF + 4CH + 22H \rightarrow 2C_4(A,F)H_{13} \quad (5)$$

$$C(B)_4A_3\check{S} + 2C\check{S}H_2 + 34H \rightarrow C_6A\check{S}_3H_{32} + 2AH_3 \quad (6)$$

If $C\check{S}H_2$ is not adequate, because of AH_3 and C_4AH_{13}, the paste will be flash setting; But if $C\check{S}H_2$ is too much, the paste will retard. So $C\check{S}H_2$ content must be proper.

Assuming $C\check{S}H_2$ content is enough, full hydrating reactions of C_3A and $C(B)_4A_3\check{S}$ are given as:

$$C(B)_4A_3\check{S} + 8C\check{S}H_2 + 6CH + 74H \rightarrow 3\ C_6A\check{S}_3H_{32} \quad (7)$$

$$C_3A + 3C\check{S}H_2 + 26H \rightarrow C_6A\check{S}_3H_{32} \quad (8)$$

It can be calculated that 7 g of $C(B)_4A_3\check{S}$ consumes 7 × (136.14 × 8) / 731.79 = 10.42 g $C\check{S}$ per 100 g of SWPC clinker. Similarly, using Equation 4, 4.6 g C_3A of consumes 4.6 × (136.14 × 3) / 270.2 = 6.95 g $C\check{S}$

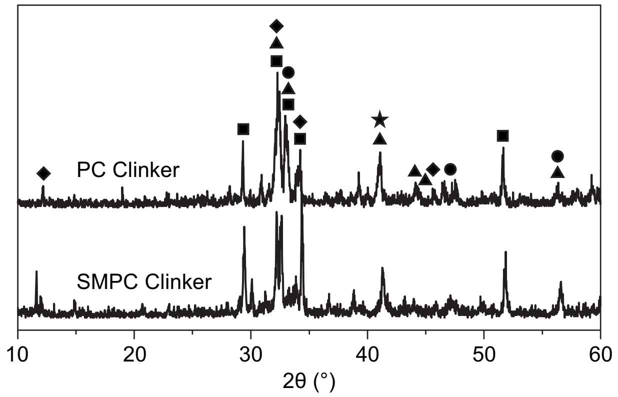


Figure 1. XRD patterns of clinkers.

Table 1. Chemical compositions of PC clinker (wt. %).

Sample	Chemical compositions							Mineral composition			
	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C_3S	C_2S	C_3A	C_4AF
PC clinker	3.21	21.37	5.68	3.59	61.03	1.3	0.8	54.3	21.9	7.04	10.0

per 100 g of SWPC clinker. So, full hydrating of C_3A and $C(B)_4A_3\check{S}$ consumes 17.37 $C\check{S}$ per 100 g of SWPC clinker.

If $C\check{S}$ run out before C_3A completely hydrated, $C_6A\check{S}_3H_{32}$ react with C_3A into Afm, shown as Equation 9.

$$2C_3A + C_6A\check{S}_3H_{32} + 4H \rightarrow 3(C_6A\check{S}_3H_{12}) \quad (9)$$

Combining with Equation 6 and Equation 9, 1 mol of $C(B)_4A_3\check{S}$ equivalently reacts with 2 mol of C_3A. So, 7 g of $C(B)_4A_3\check{S}$ reacts 7 × (270.2 × 2) / 731.79 = 5.17 g C_3A per 100 g of SWPC clinker.

Therefore, in case of excessive $C\check{S}$ affecting setting time and stability, in paper 8 % and 10 % of $C\check{S}$ were selected and the cement samples are recorded as SWPC8 and SWPC10, respectively.

EXPERIMENTAL

Scanning electron microscopy

A Hitachi S-2500-scanning electron microscopy was used to analyze the microstructure of the hardened cement paste. Specimens were fractured and the internal small pieces were selected as the samples. After termination of sample hydration with alcohol, the samples were dried in vacuum at 70°C.Then they were affixed to the scanning electron microscope specimen holder with epoxy resin. Specimens then were coated with a very thin layer of gold to promote electrical conductivity.

Compressive strength

The compressive strength of pastes was tested at 1, 3, 7, and 28 days in accordance with GB T17671-1999. Each compressive strength value was the average of three samples. Three cubic samples, with size of 40 × 40 × 160 mm^3, were used for each age. The specimens produced from fresh mortar were demoulded after 24 h with 20 ± 2°C and 95 % relative humidity, and were then cured in water with the temperature of 20 ± 2°C until the specimens were then used for compressive strength tests at 1, 3, 7, and 28 days.

Table 3. The basic physical properties of SMPC.

Sample	Specific surface Blaine ($m^2 \cdot kg^{-1}$)	f-CaO (%)	Setting time (min)		Water demand
			Initial	Final	
PC	380	0.72	120	200	0.29
SMPC8	382	0.34	60	121	0.32
SMPC10	397	0.33	65	130	0.33

RESULTS AND DISCUSSION

Physical properties of SMPC

SMPC was prepared by mixing SMPC clinker with 10 % gypsum. The basic physical properties of SMPC were shown in Table 3. The setting time of SMPC was in line with the requirement in Chinese Standard GB175-2007 for ordinary PC. But compared with PC, initial and final setting time was obviously short. It was attributed to the existence of $C_{2.75}B_{1.25}A_3\check{S}$ and the mineralization of SO_3 and BaO. Normally the water required for standard consistency of PC was in a range of 0.25 - 0.30 [20]. The water demand for standard consistency of SMPC was higher than that of PC, which could be mainly attributed to loose surface structure of sulphoaluminate mineral particles and more gel water of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) than C–S–H as the hydrating product. It can be inferred that the basic physical properties of SMPC are similar to that of PC and the former could to some extent replace the latter.

Pore structure analysis of hydrating pastes

Pore structures of hydrating pastes cured for 3 days and 28 days were shown in Table 4. The porosity values of both SMPC pastes and PC pastes reduced significantly with curing time increasing. It indicated that the hydration reactions went on and hydration products gradually filled the pores, especially with a diameter of > 100 nm. And compared with PC pastes at the same curing time, the pore size of SMPC pastes was smaller. The harmful pores content with a diameter of > 50nm in SMPC8 paste was 76.1 % which was 5.5 % less than PC cured for 3 days. The harmful pores content with a diameter of > 50 nm in SMPC10 paste was 74.7 % which was 6.9 % less than PC cured for 3 days.

Table 4. Pore structure analysis of the pastes.

Sample No.	Curing time (d)	Most possible aperture (nm)	Porosity (%)	Pore diameter distribution (%)			
				< 25 nm	25 ~ 50 nm	50 ~ 100 nm	>100 nm
PC	3	6.8	37.7	6.9	11.5	30.2	51.4
	28	5.4	18.2	16.4	26.2	33.1	24.3
SMPC8	3	6.6	36.7	8.2	15.7	32.1	44.0
	28	5.3	14.9	17.2	23.1	35.7	24.0
SMPC10	3	6.4	34.9	9.4	15.9	33.7	41.0
	28	5.2	13.7	21.8	23.9	36.7	17.6

The percentage of harmful pores in SMPC8 paste was 59.7 % which was 7.7 % less than PC cured for 28 days. The percentage of harmful pores in SMPC10 paste was 54.3 % which was 13.1 % less than PC cured for 28 days.

SEM-EDS analysis of hydrating products

The microstructures of the SMPC10 and PC pastes hydrating at 3 days were shown in Figure 2. At the age of 3 days, paste structure was relatively loose. A large amount of unhydrated particles were left. Hydration products were presented by the reticulated C–S–H gel coating on the surface of the grains and the needle-shaped ettringite crystals, resulting in a dense structure and low porosity. Crystallized $Ca(OH)_2$ could not be found in SEM observation of SMPC paste, which resulted from that $C_{2.75}B_{1.25}A_3\check{S}$ reacted with $Ca(OH)_2$ generated during C_3S hydrating to delay the precipitation of crystallized $Ca(OH)_2$.

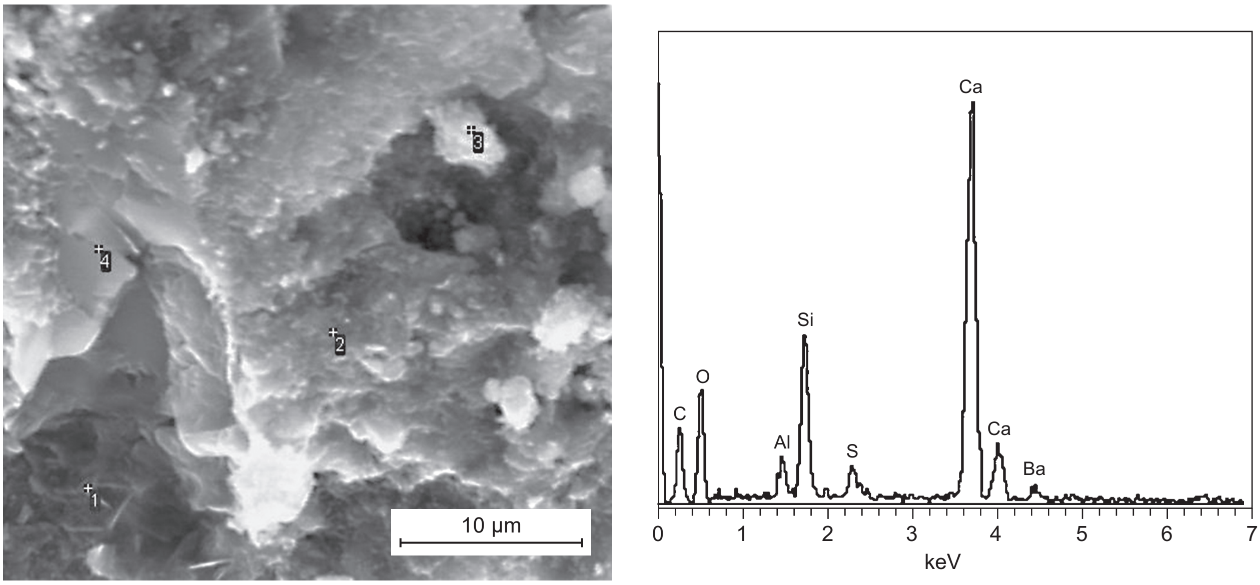
Equations 10-13 showed the common hydration reactions of $C_{2.75}B_{1.25}A_3\check{S}$ in SMPC.

$$C\check{S} + 2H \rightarrow C\check{S}H_2 \tag{10}$$

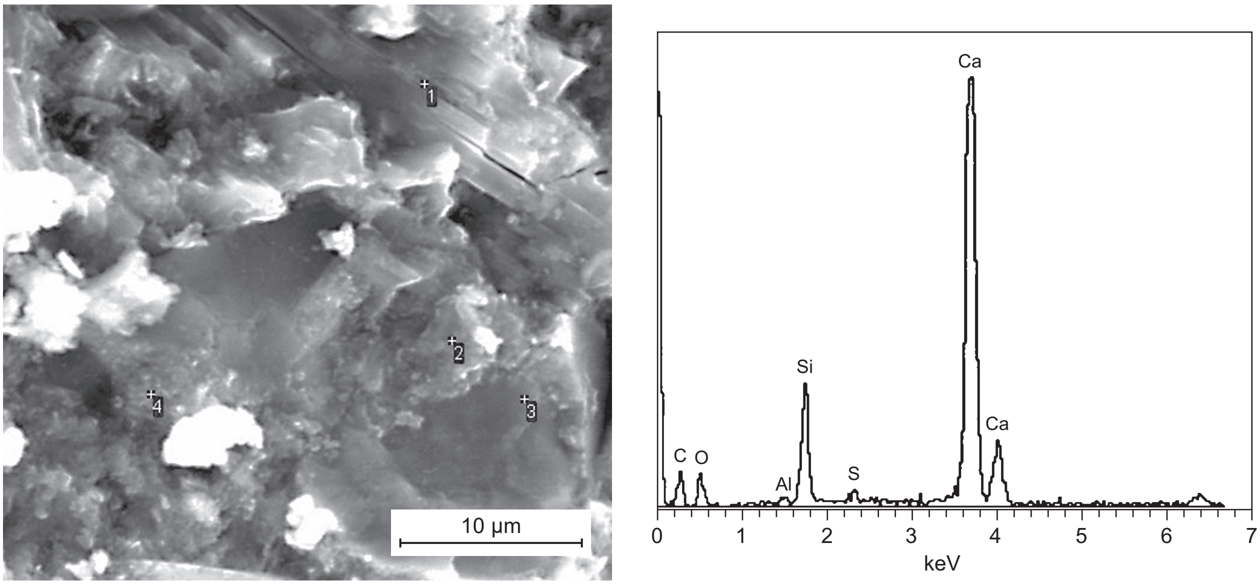
$$C(B)_4A_3\check{S} + 2C\check{S}H_2 + 34H \rightarrow (B)_6A\check{S}_3H_{32} + 2AH_3 \tag{11}$$

$$C(B)_4A_3\check{S} + 8\,C\check{S}H_2 + 6CH + 74H \rightarrow 3\,C(B)_6A\check{S}_3H_{32} \tag{12}$$

$$AH_3 + 3CH + 3C\check{S}H_2 + 20H \rightarrow C_6A\check{S}_3H_{32} \tag{13}$$

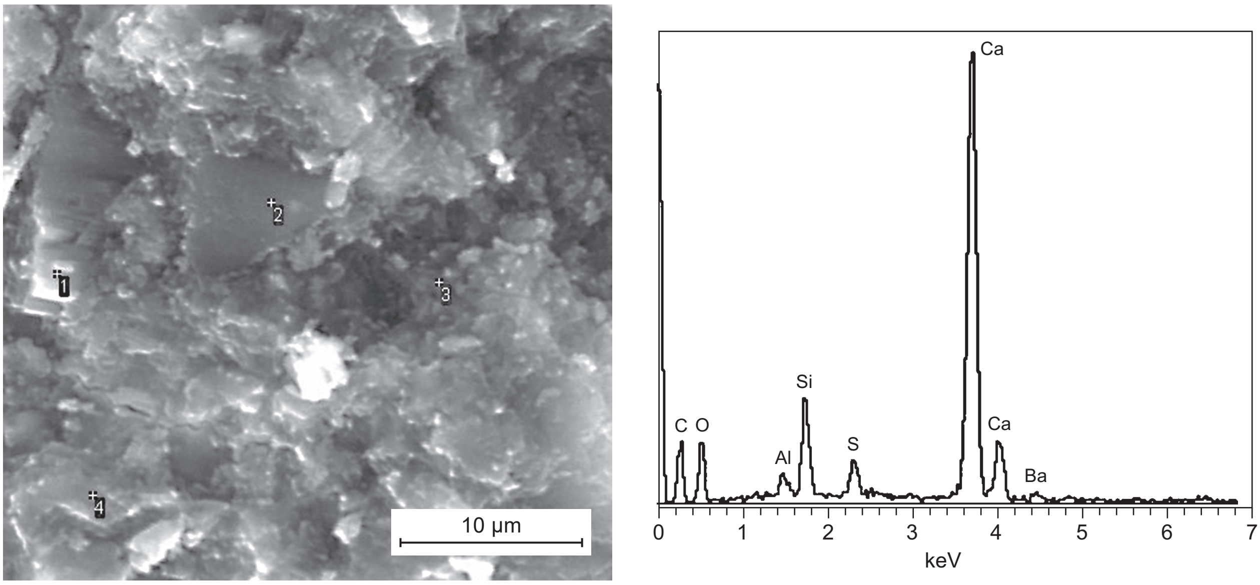


a) SMPC10 hydrating for 3 days

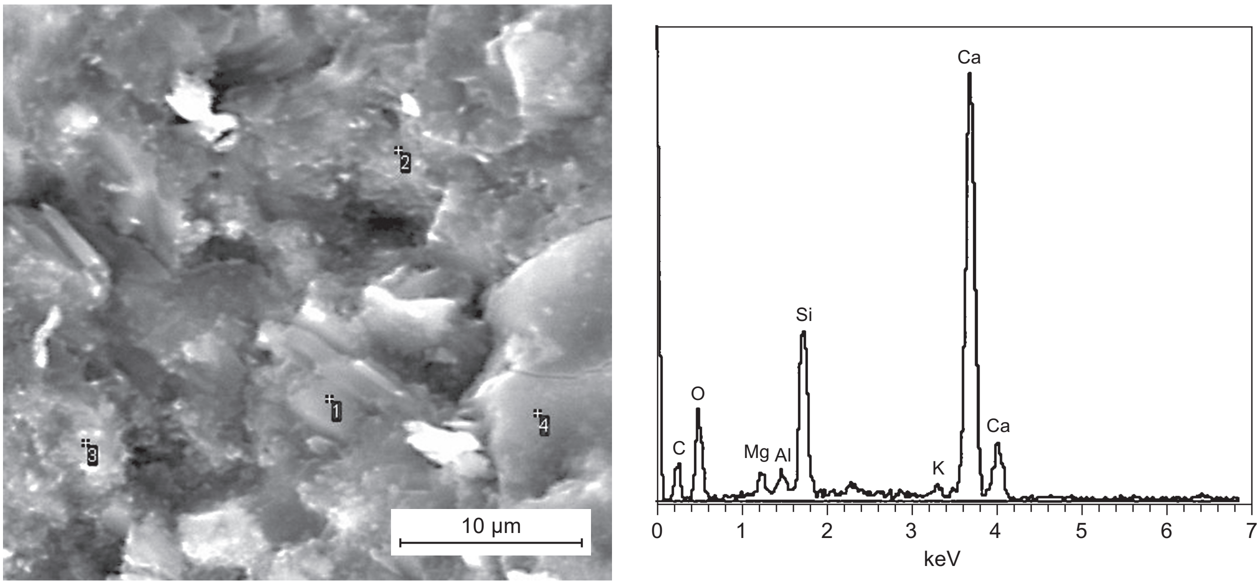


b) PC hydrating for 3 days

Figure 2. SEM-EDS photographs of cement pastes at 3 days.



a) SMPC10 hydrating for 28 days



b) PC hydrating for 28 days

Figure 3. SEM-EDS photographs of cement pastes hydrating for 28 days.

The microstructures of the SMPC and PC pastes hydrated at 28 days were shown in Figure 3. At the age of 28 days, it was noted that the hardened SMPC and PC pastes were compact and continued integrated morphological characteristics. Unhydrated particles were partially covered by thick and dense hydration products. Comparing SMPC and PC pastes, the latter structure was relatively loose, which was consistent with the results in Table 4. And CH crystal was visible. SMPC paste alkalinity was lower, which was beneficial to excellent durability and corrosion resistance.

EDS pattern of SMPC paste cured for 3 days and 28 days showed that ettringite bearing Ba was early hydration product and existed stably in the pastes. It indicated that Ba^{2+} went into the network skeleton of sulphoaluminate minerals, which was consistent with XRD analysis in Figure 1.

Expansibility analysis of hydrating pastes

The expansibility analysis of hydrating pastes of SWPC and PC were shown in Figure 4. Compared to PC, the expansion ratios of SWPC8 and SWPC10 are higher than those of PC samples, which is attributed to much more AFt during SWPC hydrating. 31 - 32 water molecules are combined in the process of AFt formation, including 6 lattice firmly bound water molecules and 26 coordination water molecules, which makes AFt solid-phase volume increasing by about 125 %. And at the same time, in the process of hydration hardening, due to crystallization and water absorption expansion deformation under the constraint condition into the cement compressive stress, tensile deformation has been better.

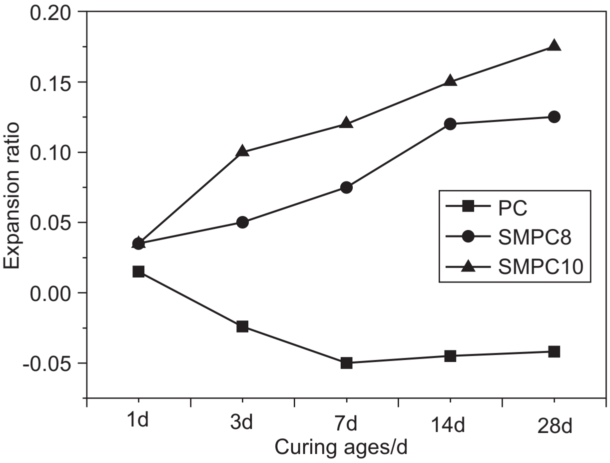


Figure 4. Expansion ratios of cements at different curing ages.

Compressive strength of SMPC

The compressive strengths of SMPC8, SMPC10 and PC were shown in Figure 5. PC was used as the reference sample in the test of strength development. The compressive strengths of SMPC8 and SMPC10 pastes cured for 1, 3, 7 and 28 days were higher than those of PC respectively. Especially the compressive strengths of SMPC8 and SMPC10 grew faster than PC at the early curing ages. The strengths of the SMPC8 and SMPC10 pastes cured for 1day were 15.4 % and 9.5 % higher than PC respectively. The strengths of the SMPC8 and SMPC10 pastes cured for 3days were 28.6 % and 31.4 % higher than PC respectively. The strengths of the SMPC8 and SMPC10 pastes cured for 7 days were 17.5 % and 20.2 % higher than PC respectively. It was indicated that sulfur aluminum barium calcium was a new early-strength mineral [21] and its hydration speed and contribution to the strength was superior to C_3S, so SMPC8 and SMPC10 had higher hydration speed and compressive strength.

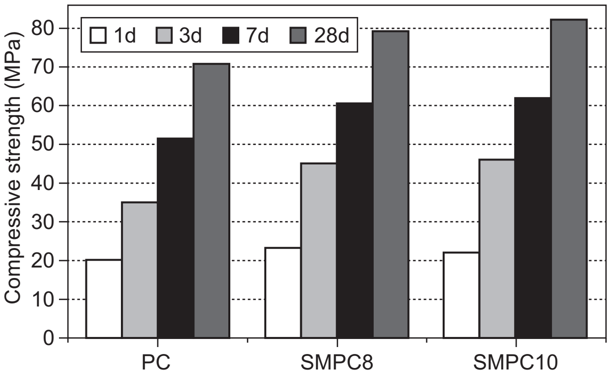


Figure 5. Compressive strength of cements at different curing temperatures.

The strengths of the SMPC8 and SMPC10 pastes cured for 28days were 11.7 % and 15.9 % higher than PC respectively. During sintering SMPC clinker parts of BaO went into the C_2S lattice and caused lattice distortion, which could enhance C_2S hydration activity [22-24]. Therefore, the compressive strength of SMPC was superior to PC even at the late curing age.

CONCLUSIONS

- Basic physical properties of modified Portland cement with Ba-bearing sulphoaluminate minerals with C_3S, C_2S, C_4AF, C_3A and $C_{2.75}B_{1.25}A_3\check{S}$ as the main phases are similar with PC, except that the setting time including initial time and final time is shorter.
- Ettringite and C–S–H are the main hydrating produces in SMPC, which is similar to PC. Because of volume expansion of ettringite, SMPC paste structure is denser than PC according to SEM-EDS analysis and the pore size of SMPC pastes was smaller. The harmful pores content with a diameter of > 50nm in SMPC8 and SMPC10 was 5.5 % and 6.9 % less than PC cured for 3days. The percentage of harmful pores in SMPC8 and SMPC10 was 7.7 % and 13.1 % less than PC cured for 28 days.
- Because sulfur aluminum barium calcium was a new early-strength mineral and its hydration speed and contribution to the strength was superior to C_3S, the compressive strengths of SMPC8 and SMPC10 grew faster than PC at the early curing ages. During sintering SMPC clinker parts of BaO went into the C_2S lattice and caused lattice distortion to enhance C_2S hydration activity, the strengths of the SMPC8 and SMPC10 pastes cured for 28days were 11.7 % and 15.9 % higher than PC respectively.

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