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Microwave promoted clinkering of sulfoaluminate cement

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Abstract

Sulfoaluminate clinkers were made by combination of electric heating and microwave processing. When raw sulfoaluminate materials were heated to 1000–1200 °C conventionally, microwaves were inputted for 1–2 min. The f-CaO of the obtained clinkers was zero. Comparatively, when the samples with the same composition were conventionally heated at 1300 °C for 1 h, the f-CaO of the obtained clinkers was as high as 1.03–4.78%, and when the samples with the same composition were heated only by microwave for 25 min, $CaCO_3$ in the raw materials was not decomposed completely. It is shown that combination of electric heating and microwave processing greatly accelerate clinkering reaction. The X-ray diffraction (XRD) of the clinkers indicates that their mineral composition and XRD patterns are the same as those of the clinkers prepared by conventional firing methods. It has also been proven that Fe_2O_3 contributed to sulfoaluminate cement clinkering.

Keywords: Microwave processing; Sulfoaluminate; CaO; X-ray diffraction

1. Introduction

When microwaves interact with materials that are fairly lossy, the materials are heated volumetrically and the microwave sintering of material is achieved. So far, the report about microwave clinkering of sulfoaluminate cement has never been seen. The first experiment attempt of microwave burning of cement clinker was reported by Quéméneur et al. [1,2] and Yi et al. [3] reported microwave clinkering of ordinary and colored Portland cements. Haoxuan et al. [4] reported formation and hydration of C_3S prepared by microwave and conventional sintering. In these reports, the heating methods are all direct microwave heating. Most compounds in cement, such as SiO_2, $CaCO_3$, Al_2O_3, etc., are transparent to microwaves at room temperature and hardly absorb microwave energy. According to our experiments, after sulfoaluminate cement was heated with microwaves only for 25 min, the $CaCO_3$ in the raw material was not decomposed completely. Obviously, this method is not suitable for cement and thus is difficult to be adopted in industries. On the other hand, when the materials are heated to a critical temperature, they have stronger microwave absorbability. According to this character, we tried a new heating method. First, raw cement materials were heated to a certain temperature by electric furnace to strengthen microwave absorbability of the materials. Then, the materials were sintered with microwaves. In this way, cement clinker can be obtained in a very short time (about 1 min) of microwave processing. This heating process has higher efficiency than conventional heating process and has a great potential for industrialization.

2. Experimental

2.1. Starting materials

Analytical pure chemical reagents, $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and $CaSO_4{\cdot}2H_2O$ were used to make raw material samples.

2.2. Materials composition

Considering the influence of Fe_2O_3, the designed minerals of sulfoaluminate cement are shown in Table 1.

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Table 1
Mineral composition of sample (%)

No.	C_4A_3S	C_2S	C_4AF
1	50	25	25
2	60	25	15
3	65	30	5
4	70	30	0

2.3. Preparation of samples

The chemical compositions (the percentage of CaO, SiO_2, Al_2O_3, SO_3, Fe_2O_3) of the samples were calculated according to the mineral compositions of Table 1. The compositions of cement materials (the percentages of $CaCO_3$, SiO_2, Al_2O_3, $CaSO_4{\cdot}2H_2O$, Fe_2O_3) were calculated, and raw material samples were prepared accordingly.

In order to compare the difference in sinterability of powder sample and the piece sample, samples 1–3 were fired in the forms of powder and piece, respectively; samples of composition #4 were fired in the form of piece. Powder samples were put in alumina crucibles directly and compressed tightly. Piece samples were compacted at 20 kN to $\Phi 30 \times 15$ mm circular pellets. The weight of each fired sample (including both powder and piece samples) was 15 g.

2.4. Sintering setup

Cement clinker was fired in a high temperature furnace and a domestic microwave cavity. The power of high temperature furnace was adjustable. The maximum power was 3 kW. The microwave cavity was 23 l, 2.45 GHz in frequency, 700 W in power and with a power density of 30 kW/m^3. Microwave cavity was modified properly to suit high temperature processing. In order to obtain better thermal insulation effect, a double-alumina-crucible configuration was used. The space of the two alumina crucibles was filled with light weight alumina powder. A circular foamed alumina piece was used as a lid on the alumina crucibles (Fig. 1).

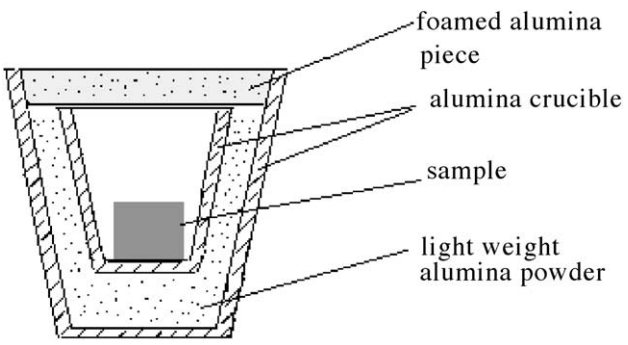

Fig. 1. Sample sintering and insulation configuration.

2.5. Firing method

The powder samples and piece samples in alumina crucibles were heated to 1000, 1100 and 1200 °C, respectively, in an electric furnace and then transferred into the microwave cavity for microwave processing.

The results showed that the microwave absorption of the preheated materials was substantially improved. When the microwave field was input, the liquid phase appeared immediately. Repeated experiments showed that the samples preheated at 1000 °C were well-clinkered after microwave clinkering for 2 min. When preheated at 1100 °C, about 1 min and 30 s were enough. When preheated at 1200 °C, only 1-min microwave clinkering was needed.

In order to compare with conventional processing, each sample was fired at 1300 °C for 1 h in an electric furnace.

In order to compare with direct microwave processing, sample #2 was heated from room temperature in the microwave cavity for 25 min.

2.6. The f-CaO content of clinkers

In order to evaluate the clinkering degree, the clinkers were ground. The f-CaO contents were determined with glycerine–alcohol method.

3. Results and discussion

3.1. Experimental observations

When samples were preheated to certain temperature in an electric furnace and then transferred to the microwave cavity, the temperature of samples decreased slightly (about 50–80 °C) in the course of transforming. So the temperature of samples put into microwave cavity was lower than the preheating temperature, i.e., lower than 1000, 1100 and 1200 °C. In the process of microwave heating, luminescence and sound of electric arc were observed frequently. The

Table 2
The f-CaO values of clinker

No.	Electric heating temperature (°C) / MW heating time (min)	1000 / 2.0	1100 / 1.5	1200 / 1.0	1300(1 h) / 0	Room temperature / 25
1	Powder sample	0	0	0	4.78	
	Piece sample	0	0	0	3.73	
2	Powder sample	0	0	0	2.46	(13.4)[a]
	Piece sample	0	0	0	1.56	
3	Powder sample	0	0	0	1.03	
	Piece sample	0.45	0	0	1.82	
4	Piece sample	33	33	1.0	2.32	

[a] Powder sample #2 was heated for 25 min with microwaves only and the loss was 13.4%, which indicates that $CaCO_3$ was not yet decomposed. So the f-CaO contents are undetermined.

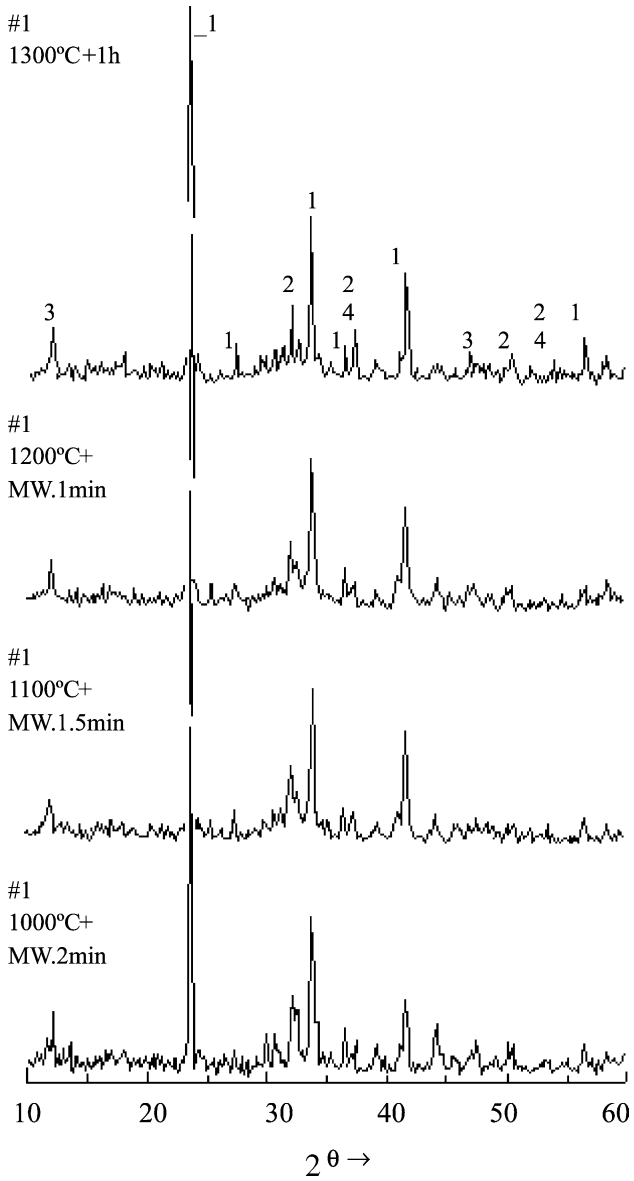

Fig. 2. XRD patterns of sample #1.

higher the temperature of electric heating was, or the more Fe_2O_3 the samples contained, the earlier the luminescence and sound of electric arc appeared. Both the powder samples and piece samples were dense and hard after being fired in the microwave cavity. Microwave heating was a process of volumetric heating, the temperature inside material was higher than that of the surface. Sometimes some insufficiently fired powder was found on the surface. The sample fired in the microwave cavity from room temperature did not turn red, and no phenomenon of electric arc was observed in 25 min either. The fired sample was loose, and $CaCO_3$ was not decomposed completely. However, because the time of microwave heating was very short and there were phenomena of luminescence and electric arc, the temperature measurement during microwave heating was difficult. The actual temperature of the sample was unknown. This is a technical problem to be solved.

3.2. Result of f-CaO

The f-CaO values of clinker are listed in Table 2.

Table 2 shows that: (a) When conventional electric heating and microwave promoted clinkering were used, the clinkering speed of cement was raised greatly (more than 60 times). For example, when the samples were heated to 1000, 1100 and 1200 °C in electric furnace, respectively, and then processed in the microwave cavity and heated for 2, 1.5 and 1 min, respectively, the f-CaO content decreased to zero. In contrast, the samples with the same composition but fired to 1300 °C and soaked for 1 h in the electric

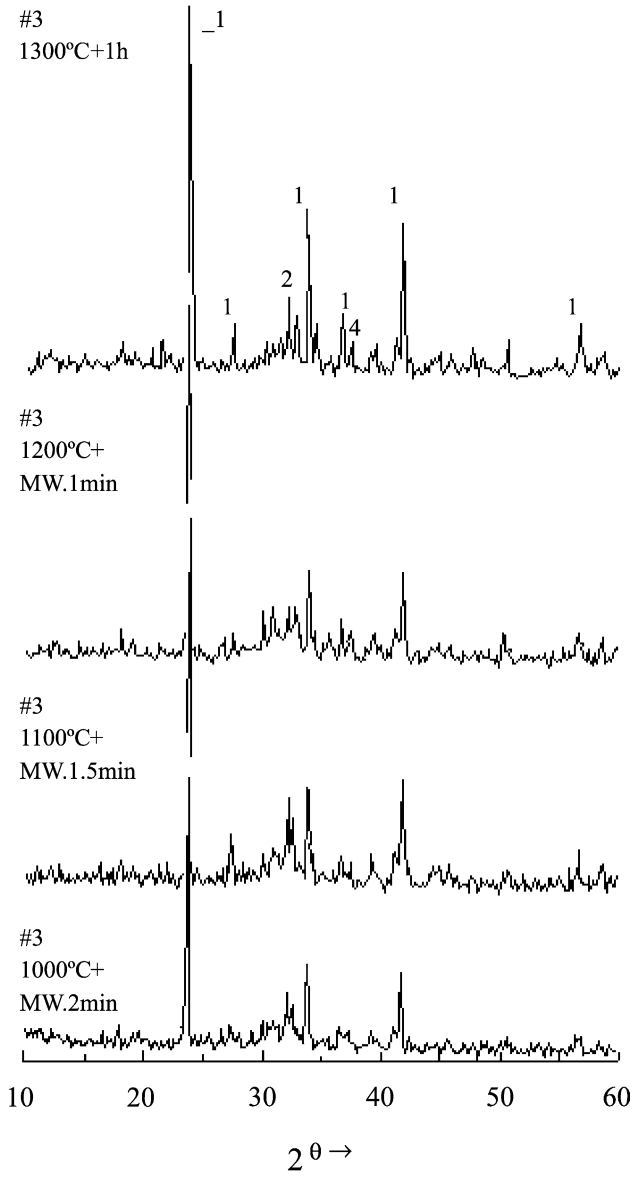

Fig. 3. XRD patterns of sample #3.

furnace had much higher f-CaO content (1.03–4.78%). (b) The higher the temperature at which a sample was transferred into the microwave cavity, the shorter the time needed for microwave heating. For example, the microwave clinkering time was 2 min when the sample was fired to 1000 °C; while at 1200 °C, only 1 min was needed. (c) It seems that the form of sample (powder or piece) had little influence on microwave absorption. The clinkering process in both cases was quick. In the case of conventional process, the clinking process of the piece samples was faster than powder samples. (d) Fe_2O_3 has strong ability of absorbing microwave and thus enhanced microwave clinkering. Sample #4 did not contain Fe_2O_3. When it was fired to 1000 and 1100 °C in the electric furnace then transferred to microwave cavity and heated for 2–1.5 min, the f-CaO content was as high as 33%. It showed that CaO basically has not taken part in reaction. The microwave absorption of the sample increased substantially only when the heating temperature reached 1200 °C. However, after microwave heating for 1 min, the f-CaO content of the sample was still up to 1.05%. In short, Fe_2O_3 must be mixed when microwave is used to promote clinkering of sulfoaluminate cement. The quantity of Fe_2O_3 mixed could be varied. The current experiments indicated that the range of Fe_2O_3 mixed might be 1.23–6.06%. This supplies a wide processing window for industrial practice.

3.3. X-ray diffraction (XRD) analysis

The XRD patterns of sample #1 (piece sample) obtained under different conditions are shown in Fig. 2. The XRD patterns of sample #3 (powder sample) obtained under different conditions are shown in Fig. 3. The diffraction peaks of $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ [d=3.76, 2.65, 2.166], β-C_2S [d=2.795, 2.744, 2.780] are found. Their diffraction peaks are the same as that heated at 1300 °C by conventional process, and the mineral composition of these clinkers agreed with the mineral composition expected. In the three main diffraction peaks of the ferrite solid solution (d=2.64,2.77,1.93), the first and second diffraction peaks overlap that of $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ and C_2S, but its characteristical diffraction peak (7.30) is very clear in the patterns of sample #1.

4. Conclusions

(1) When raw meals of sulfoaluminate cement are preheated by conventional process and then heated by microwave to promote clinkering, the speed of clinkering increases by above 100 times than conventional process and by tens of times than simple microwave process.

(2) To sulfoalminate cement, the suitable way is that the raw material is preheated to 1000–1200 °C first by conventional process and then processed by microwaves for 1–2 min. The form of materials (powder or piece) has little influence on clinkering.

(3) Fe_2O_3 contributes to sulfoaluminate cement clinkering. It can both reduce the calcination temperature of conventional process and enhance the microwave absorption of materials. The range of Fe_2O_3 addition was 1–6%.

(4) XRD shows that the sulfoaluminate cements obtained by microwave promoted process are the same as that obtained by conventional process. The mineral compositions of these clinkers are the same.

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