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Influence of CaF_2 on the formation kinetics of belite-calcium barium sulphoaluminate cement clinker

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Abstract. This paper studies the formation dynamics of belite-calcium barium sulphoaluminate cement clinker with and without CaF_2. The results suggest that, under the condition of the experimental preparation process, the formation process of belite-calcium barium sulphoaluminate cement clinker is controlled by diffusion mechanism in the temperature range of 1250-1380℃ and the formation dynamics fits nicely with $D_4=1-2\alpha/3-(1-\alpha)^{2/3}=kt$. Apparent activation energy was calculated to be 250 $kJ\cdot mol^{-1}$and 195 $kJ\cdot mol^{-1}$ for sample clinker without and with 0.6% CaF_2 content. It is concluded that CaF_2 contributes a lot to the reduction in energy consumption during the process of sintering belite-calcium barium sulphoaluminate cement clinker.

Introduction

The Portland cement (PC) clinker manufacture requires a large amount of heat energy, which is about 3100 MJ/ton clinker [1–4]. This energy is necessary to get the cement raw mixture to temperature exceeding 1450°C that allows the alite phase to form, which determines the required cement quality [1]. One approach to the reduction in energy consumption of the cement production is to reduce the lime saturation factor (LSF) of the raw mixture [3]. Previous papers have found that belite-calcium barium sulphoaluminate cement clinker can form at temperature of approximately 1350℃, which is about 100℃ lower than the temperature used for PC production.

During the manufacture process of belite-calcium barium sulphoaluminate cement clinker, 0.6% CaF2 is added into the raw meal, promoting the formation of the clinker. Therefore, this paper investigate the influence of CaF_2 on the formation kinetics of belite-calcium barium sulphoaluminate cement clinker.

Experimental

The clinker was synthesized with chemical reagents such as $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, $BaCO_3$, $BaSO_4$ and $CaSO_4$ which were weighed accurately according to the mineral composition of the clinker (C_3S 37.5%, C_2S 37.5%, C_3A 4.6%, C_4AF 11.4%, $C_{2.75}B_{1.25}A_3\overline{S}$ 9.0%). Excessive sulfur (50%) and barium (80%) were added due to evaporation and solid solution at high temperature. In order to investigate the influence of CaF_2 on the formation kinetics of belite-calcium barium sulphoaluminate cement clinker, 0.6% CaF_2 was added into the raw meal.The reagents were mixed with water by planetary ball mill and dried by an oven to obtain the raw meal. Afterwards, mixed the raw meal with 8% water and compressed into discs of 60 mm×8mm. And then, the discs were dried in an oven at 105℃ for 2h and sintered in a resistance furnace with a heating-up velocity of 5℃/min at different temperatures (1250℃, 1300℃, 1350℃, and 1380℃) for different heat preservation times (30min, 60min, 90min and 120min). Eventually, the discs were removed from the resistance furnace and cooled rapidly by fan. The content of *f*-CaO in the samples was determined chemically after dissolving the sample with ethanol-glycerin.

Results and discussions

Burn-ability of the clinker. Fig. 1 shows the variation of f-CaO content in the samples with and without CaF_2 at different burning temperature, which is generally considered as an index of burn-ability. With the rise of sintering temperature, the f-CaO content decreases sharply in the samples with and without CaF_2. Similarly, CaF_2 content influences the f-CaO content greatly. At the same sintering temperature. The f-CaO content of samples with 0.6% CaF_2 is much lower than that of the blank samples. This effectiveness is due primarily to the presence of fluoride anions, characterized by high electronegativity, which interact with the anions (Ca^{2+} and Si^{4+}) on the solid surface. The surface maintained in a high-energy state, leading to polarization and rearrangement of atoms, which increases the solid activity to form new phase [1]. Therefore, the absorption of f-CaO is promoted.

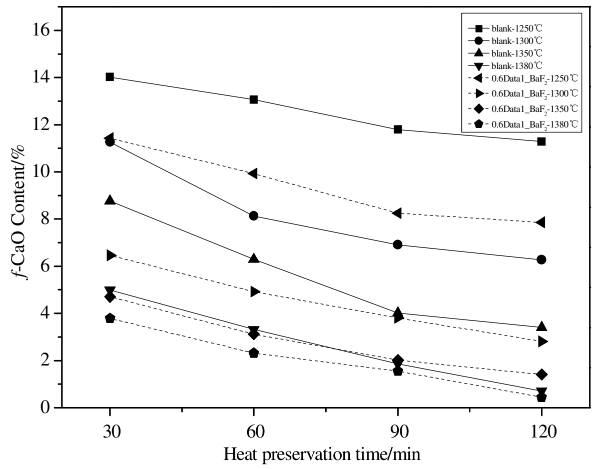

Fig.1 *f*-CaO content of the clinker samples

Extent of formation of clinker. After obtaining the f-CaO content and loss on the ignition of the clinker samples, The extent of formation of clinker can be figured out by the following equation:

$$\alpha=\frac{\omega-(f\text{ - CaO}+\frac{56}{44}\text{L})\frac{100}{100-\text{L}}}{\omega}. \tag{1}$$

Where α is the extent of formation of belite-calcium barium sulphoaluminate cement clinker; L is the loss on the ignition of the clinker samples; *f*-CaO is free lime content of the clinker samples; ω is the CaO content of clinker samples.

The extent of formation of belite-calcium barium sulphoaluminate cement clinker at different sintering temperatures are listed in Table 1.

Kinetics model. The formation of belite-calcium barium sulphoaluminate cement clinker is typical solid phase reaction. During the formation process of C_3S and C_2S, the solid phase reaction between CaO and SiO_2 is controlled by the diffusion of Ca^{2+}. Also, the formation of $C_{2.75}B_{1.25}A_3\overline{S}$ belongs to solid state reaction. Therefore, the solid phase reaction is controlled by three dimensional diffusion mechanism. Both Ginstling equation and Jander equation are representative equations which can be applied to describe the three dimensional diffusion mechanism solid state reaction controlled by three dimensional diffusion mechanism. Oweing to more accuracy and wider use range, the formation kinetics of belite-calcium barium sulphoaluminate cement clinker was invested by Ginstling equation [5]:

$$g(\alpha)=1-2\alpha/3-(1-\alpha)^{2/3}. \tag{2}$$

Table 1 Extent of formation of belite-calcium barium sulphoaluminate cement clinker

Sintering temperature/℃	Heat preservation time/min	Extent of formation/%	
		blank	0.6% CaF_2
1250	30	67.00	67.80
	60	66.47	69.10
	90	68.66	74.30
	120	72.39	75.56
1300	30	73.94	76.33
	60	79.59	79.47
	90	81.97	82.58
	120	83.24	86.83
1350	30	81.41	84.70
	60	85.88	89.46
	90	89.87	91.77
	120	91.27	94.81
1380	30	88.96	88.05
	60	92.48	92.41
	90	95.06	95.08
	120	97.21	98.15

Reaction constant and apparent activation energy. All these solid phase reaction kinetics equations could be described as function:

$$g(\alpha)=kt. \tag{3}$$

where k and t are the reaction rate constant and the heat preservation time (s).

Substituting the extent of formation of belite-calcium barium sulphoaluminate cement clinker into Eq. 2, the value of $g(\alpha)$ was obtained. An analysis using simple linear regression is done, where $g(\alpha)$ and t (heat preservation time) are ordinate and abscissa separately. The result is shown in Fig. 2. Reaction rate constant k (the slope of the linear regression line) reflected the degree of difficulty of the reaction. From Fig. 2, it is observed that the slope of the linear regression lines turned bigger with 1% CaF_2 added into the raw meal, proving that the solid phase reaction becomes easier. The value of reaction rate constant, which will latter be applied to calculating the apparent activation energy, was shown in Table 2.

The linear regression coefficient (R^2) indicates the degree of linear correlation. Therefore, it is reasonable to believe that the formation kinetics complies with the model if correlation coefficient is close to 1. The linear coefficient between D_4 and heat preservation time was shown in Table 2. From Table 2, it is observed that the coefficient is close to 1, indicating that Ginstling equation can adequately describe the solid state reaction.

The reaction rate constant k follows the Arrhenius dependence:

$$k=\mathrm{A}\exp(-E_a/\mathrm{R}T). \tag{4}$$

where k, A, E_a, R and T are the reaction rate constant, pre-exponential factor, apparent activation energy(kJ mol^{-1}), ideal gas constant and sintering temperature(K), respectively.

To make the calculation easy, Eq. 4 should be transformed into the following logarithmic form:

$$\ln k=\ln\mathrm{A}-E_a/\mathrm{R}T. \tag{5}$$

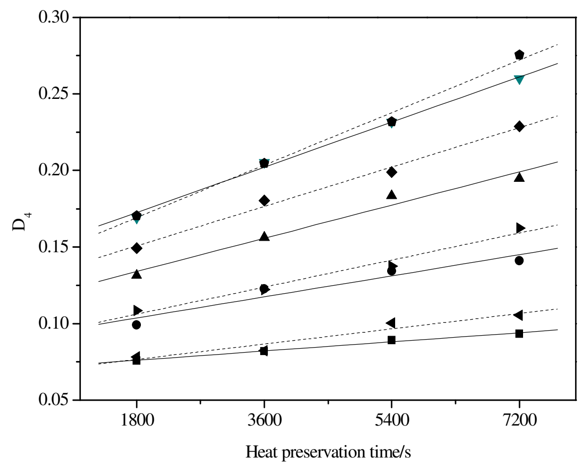

Fig.2 Linear regression lines between D_4 and heat preservation time

Table 2 Linear coefficient and reaction rate constant

	Sintering temperature/ ℃	R^2	k/s^{-1}
Blank	1250	0.99	3.33E-06
	1300	0.93	8.05E-06
	1350	0.97	1.20E-05
	1380	0.99	1.64E-05
0.6%CaF_2	1250	0.93	5.54E-06
	1300	0.98	9.82E-06
	1350	0.99	1.43E-05
	1380	0.99	1.90E-05

The relationship curve between –ln*k* and 1/*T* can be drawn. The apparent activation energy (E_a) is determined from the slope (E_a/R) of the line. Fig. 3 is the regression line between –ln*k* and $10^4/T$. In the temperature range of 1250-1380℃, the apparent activation energy of belite-calcium barium sulphoaluminate cement clinker without CaF_2 formation is calculated to be 250 kJ·mol^{-1}, while the one with 0.6% CaF_2 is calculated to be 195 kJ·mol^{-1}.

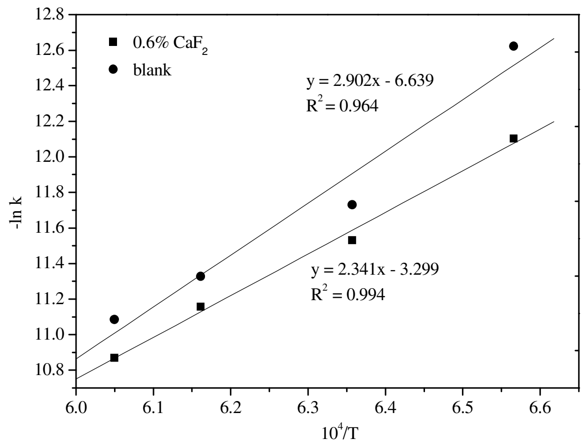

Fig. 3 The regression line between –ln*K* and $10^4/T$

Conclusions

Under the condition of the experimental preparation process, the formation process of belite-calcium barium sulphoaluminate cement clinker is controlled by diffusion mechanism in the temperature range of 1250-1380℃ and the formation dynamics fits nicely with $D_4=1-2\alpha/3-(1-\alpha)^{2/3}=kt$. The apparent activation energy was calculated to be 250 $kJ\cdot mol^{-1}$ and 195 $kJ\cdot mol^{-1}$ for sample clinker without and with 0.6% CaF_2 content. It is concluded that CaF_2 contributes a lot to the reduction in energy consumption during the process of sintering belite-calcium barium sulphoaluminate cement clinker.

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