

Research on the sintering process and characteristics of belite sulphoaluminate cement produced by BOF slag



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HIGHLIGHTS

- BOF slag can improve the sintering degree of CSA clinkers.
- 14% BOF slag can be reused to produce CSA.
- The rational ratios of C₂S, C₄A₃S, C₄AF in CSA clinkers stand at 50%, 30%, 20%.

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ABSTRACT

The sintering process of belite sulphoaluminate cement (CSA¹) clinker is still not clear to date. Besides, there are few reports concerning producing CSA by recycled BOF slag. Therefore, the sintering process of CSA was investigated from this perspective and the results can be a reference for BOF slag disposal. Four kinds of CSA clinkers with different additions of BOF slag were sintered at 1300 °C for 30 min. The sintering process was traced by heating microscope and the characteristics were analyzed by XRD, SEM-EDS and TAM Air. The results showed that the sintering degree of CSA clinker could be predicted by analyzing its sintering process. Furthermore, BOF slag could improve the melting state of CSA clinkers due to its composition containing iron oxide, manganese oxide and magnesium oxide. However, expansion was detected when the temperature reached 420 °C, which was arose by combined factors, namely volatilization of CO₂ decomposed from MgCO₃ and the thermal expansion of raw materials itself. The rational ratios of C₂S, C₄A₃S, C₄AF in CSA clinker with 14% BOF slag as raw material stood at 50%, 30%, 20% and its early hydration behavior was better than that of ordinary Portland cement (OPC) at the initial 16 h.

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1. Introduction

Belite sulphoaluminate cement clinker is produced by limestone, clay, bauxite and gypsum with sintering temperature ranging from 1250 °C to 1350 °C [1]. It is 100 °C to 200 °C lower than that of OPC, which can save large amount of energy consumption. Besides, the emission of CO₂ can also be reduced during the sintering process as the early high strength phase C₄A₃S in CSA replaces C₃S in OPC. The amount of CO₂ emission is 0.216 g when 1 g C₄A₃S is produced, while the amount is 0.578 g per gram of C₃S [2], which indicates that the CO₂ emission decreases by 63%. Therefore, it is

supposed to save more fuels and reduce more emission of greenhouse gas CO₂ by producing CSA.

CSA is widely applied to architecture engineering, emergency repairs, permeability resistance engineering, cement manufactures, etc. due to its superior performance such as high early strength, short setting time and lower alkalinity [3,4]. Many researchers have investigated the formation and performance of CSA [5–13], including sintering method, early hydration performance, mechanical property, volume stability and heavy metal leaching. Besides, a lot of attention has been paid to reusing industrial solid wastes, such as fly ash [14,15], gypsum [16], slag [17,18] and other wastes [19] when producing CSA. This kind of cement has been developed and produced for about 40 years in China. It is, however, not widespread in other countries at present [20].

BOF slag is a kind of by-product that is obtained from steel making process. It is mainly used for construction field including, for instance, road engineering [21,22], cement [23–25] especially

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¹ The abbreviations used in this essay are listed as below: belite sulphoaluminate cement = CSA, ordinary Portland cement = OPC, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, S̄ = SO₃, H = H₂O.

OPC, concrete [26,27] due to the hydration activity of BOF slag. Moreover, when BOF slag is applied to CSA, the main chemical composition such as CaO, SiO₂, Al₂O₃ and Fe₂O₃ can be supplied by BOF slag. Therefore, a number of natural resources can be conserved as well.

However, only few researchers focused on CSA produced by BOF slag. Shan et al. [28] reported that the hydration performance of BOF slag was activated and the mechanical properties of CSA with 10% BOF slag achieved the same level compared with standard CSA. Yan et al. [29] studied the mechanical strength and volume stability of CSA with various proportions of BOF slag, BF slag, limestone and CSA clinker. It was indicated that the CSA that met the national standard of 32.5 composite Portland cement could be obtained with the addition of 35% BOF slag. Besides, Adolfsson [30] sintered CSA clinker with BOF slag (14%) and other steelmaking slags. The results demonstrated that it was potential to recycle BOF slag as raw material for producing CSA.

The disposal of BOF slag takes up a vast priceless land at present. The aim of this study is to investigate the sintering process of CSA clinker mixed with BOF slag. Besides, the reasonable design of CSA clinker and the appropriate addition of BOF slag are also determined. These results are beneficial for both steel and cement industries to achieve sustainable as well as environment-friendly development.

2. Experiments

2.1. Materials

The BOF slag which was used for synthesizing CSA clinkers was from a steel plant. While other materials were gypsum and chemical pure such as CaO, SiO₂, Al₂O₃, CaSO₄ and H₃BO₃. All these materials were grinded to powders with particle sizes under 150 μm. Meanwhile, OPC was chosen as a comparison in order to evaluate the early hydration behavior of CSA. The chemical composition of BOF slag and OPC is presented in Table 1 and the mineral phases of BOF slag are shown in Fig. 1. It is observed that BOF slag contained more CaO and iron oxide together with some SiO₂ and MgO. These oxides were beneficial to prepare CSA clinkers except MgO. Besides, the mineral phases of BOF slag were calcium iron oxide, RO phase, larnite, lime, magnesite and akermanite.

2.2. Preparations for CSA clinkers

Four kinds of CSA clinkers with different additions of BOF slag were designed according to modified Bouge equations [30,31]. Table 2 lists the contents of mineral phases and chemical composition of designed CSA clinkers. The range of C₂S, C₄A₃S̄ and C₄AF were 40% ~ 60%, 10% ~ 30% and 10% ~ 40% respectively. Based on Table 2, YA1, YB1, YC1 and YF1 were separately mixed with 7%, 14%, 21%, 28% of BOF slag, as shown in Table 3. Pure Fe₂O₃ powder was not added as iron oxide in BOF slag can be a replacement.

Table 1
Chemical composition of BOF slag and OPC.

Chemical composition/wt%	CaO	SiO ₂	Total Fe	Al ₂ O ₃	MgO	MnO	P ₂ O ₅
BOF slag	40.70	8.58	21.20	1.12	8.37	3.59	0.81
OPC	63.23	18.68	2.24	5.25	1.10	0.59	0.11
Chemical composition/wt %	Na ₂ O	K ₂ O	V ₂ O ₅	TiO ₂	Cr ₂ O ₃	S	
BOF slag	0.01	0.02	6.51	1.78	0.53	0.06	
OPC	0.00	1.33	0.01	0.29	0.00	1.44	

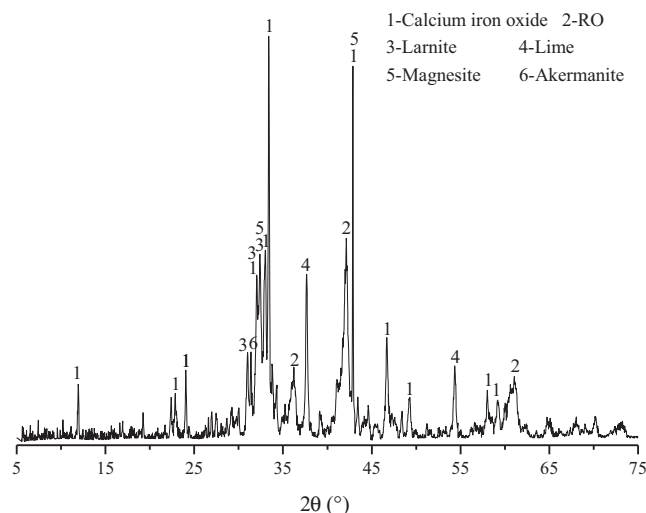


Fig. 1. Mineral phases of BOF slag.

Table 2
Mineral phases and chemical composition of designed CSA clinkers.

Components of designed CSA clinkers/wt%	Mineral phases			Chemical composition				
	C ₂ S	C ₄ A ₃ S̄	C ₄ AF	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃
YA1	60	30	10	54.70	20.93	17.15	3.30	3.93
YB1	50	30	20	52.81	17.44	19.24	6.60	3.93
YC1	60	10	30	56.59	20.93	11.31	9.90	1.31
YF1	40	20	40	51.86	13.95	18.42	13.20	2.62

Table 3
Addition of materials for each CSA clinker.

Addition of materials/wt%	BOF slag	CaO	SiO ₂	Al ₂ O ₃	CaSO ₄	H ₃ BO ₃
YA1	7.14	49.16	20.22	16.88	6.59	0.25
YB1	14.12	44.58	16.12	18.68	6.50	0.25
YC1	20.93	47.35	18.85	10.74	2.11	0.25
YF1	27.60	39.31	11.54	17.35	4.20	0.25

Meanwhile, 0.25% H₃BO₃ was blended in all of clinkers in case of expansion.

For each clinker, 30 g CSA raw material was molded to briquette which was a cylinder with a diameter of 40 mm and a height of 11 mm. Afterwards, these briquettes were sintered in a muffle furnace at 1300 °C for 30 min. They were finally taken out and quenched immediately by compressed air.

2.3. Methods

Heating microscope equipment, presented in Fig. 2, was operated to determine the morphology change of BOF slag and CSA clinkers during the whole sintering process at the temperature from 200 °C to 1550 °C. A small cylindrical sample (φ2 mm × 3 mm) was prepared and heated in a small tube furnace. The heating rates were 15 °C/min from 200 °C to 600 °C and 10 °C/min from 600 °C to 1550 °C. With the lighting and imaging devices, the photos of longitudinal section of samples were taken when the temperature elevated per 50 °C. Meanwhile, the area of the longitudinal section was measured per second. The characteristic temperatures such as sphere, hemisphere and flow temperature and the photos corresponding to them were detected as well.

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