



Technical Note

Cementitious property modification of basic oxygen furnace steel slag



Zaibo Li, Sanyin Zhao*, Xuguang Zhao, Tusheng He

School of Chemistry and Environment Engineering, Shaoguan University, Shaoguan 512005, PR China

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ABSTRACT

In this paper, we propose a new method for modifying the chemical and mineralogical compositions of steel slag by adding industrial wastes to molten basic oxygen furnace steel slag (BOFS). The effects of the composition of the modifying component and the modification parameters on the structure and the cementitious properties of modified steel slag (MSS) are investigated in a laboratory, and a pilot-scale modification research is conducted. Results indicate that the appropriate ratio of BOFS, electric arc furnace steel slag (EAFS) and coal bottom ash in MSS is 85:12.75:2.25. The modification can reduce the free-CaO content of pilot-scale MSS and remarkably improve its cementitious property. The mineralogical composition and the structure of BOFS can be modified by reacting it with EAFS and coal bottom ash at a high temperature generated by the waste heat of the molten steel slag.

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1. Introduction

It is well known that both the cement and the steelmaking industries are high energy consumption and pollution discharge industries. Steel slag from either the conversion process of iron to steel in a basic oxygen furnace (BOF) [1,2] or the melting of scrap to make steel in an electric arc furnace (EAF) [3,4] is a mass industrial by-product and waste, the amount of which is approximately 10–15% of the steel yield. The global amount of steel slag has increased continuously, and more than 100 million tons of steel slag was discharged last year in China. A large quantity of steel slag has occupied a vast amount of infield and contaminated groundwater, water resources and soil due to dust and the emission of various poisonous elements [5]. Therefore, it is necessary to explore a new technique that is helpful to improve the utilization of steel slag.

Steel slag contains a certain amount of cementitious minerals, such as C_3S , C_2S , C_4AF and C_2F . Many studies indicate that steel slag could be used as a partial substitute of cement (called mineral admixture) in cement and concrete applications, but its cementitious activity is lower than that of Portland cement [6–8]. In addition, steel slag often displays significant variation in chemical and mineralogical compositions [9], and an undesirable volume change because of high f-CaO and f-MgO content [10,11], both of which result in its limited application in the cement and concrete industry. In the past few decades, many approaches, such as fine grinding or ultra-fine grinding [12,13] and chemical and thermal activation [14,15], have been applied to improve the properties of steel slag. However, these approaches are referred to as ‘back-end modifica-

tion techniques’, in which additional energy and chemical activators are usually needed, and the modification effect varies with the chemical and mineralogical composition of steel slag.

A novel method is developed and tested in this study, which involves modification of the chemical and mineralogical compositions of steel slag by adding modifying materials to molten basic oxygen furnace steel slag (BOFS) when it is discharged during the steelmaking process. We use industrial wastes as the modifying materials. The effects of the composition of the modifying component and the modification parameters on the structure and the cementitious properties of modified steel slag (MSS) in a laboratory are investigated, and a pilot-scale modification of BOFS with electric arc furnace steel slag (EAFS) and coal bottom ash is conducted. In addition, the mechanism of the modification process at a high temperature is illustrated.

2. Raw materials and experimental methods

2.1. Materials

EAFS and the coal bottom ash, used as the modifying components and having a Blaine specific surface area of 415 and 350 $m^2 kg^{-1}$, respectively, and BOFS having a Blaine specific surface area of 400 $m^2 kg^{-1}$ were obtained from Shaogang Iron and Steel Group Co., Ltd., in China. The reference Portland cement (42.5 grade) used in this study was produced by Xingfa Cement Co., Ltd., in Beijing. The chemical compositions of the steel slag powders and the reference cement are listed in Table 1.

2.2. Experimental methods

2.2.1. Laboratory modification

The mixtures of BOFS, EAFS and coal bottom ash powders in appropriate proportions were burned in a Si-Mo oven at designed temperatures for 30 min. The burned specimens were quickly cooled to room temperature after being taken out from the oven. The MSS powder was obtained after crushing and grinding the burned specimens to a Blaine specific surface area of 400 $m^2 kg^{-1}$.

* Corresponding author. Tel.: +86 7518120118.

E-mail address: zsy_sgu@163.com (S. Zhao).

Table 1
Chemical compositions of materials (wt%).

Sample	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Fe	MgO	MnO	SO ₃	P ₂ O ₅
BOFS	40.01	18.94	2.91	8.85	13.5	1.22	5.36	2.79	0.88	1.34
EAFS	53.98	24.94	4.89	1.23	–	–	7.26	–	0.15	0.05
Coal bottom ash	0.82	61.78	21.08	4.44	–	–	0.83	–	0.06	0.11
Cement	63.11	23.52	4.48	3.04	–	–	1.28	–	2.87	–

2.2.2. Pilot-scale modification

In the pilot-scale modification process, EAFS and coal bottom ash were added to the slag ladle beforehand through the outside entrance of the basic oxygen furnace operation platform, and then, molten BOFS was discharged into the slag ladle from the converter furnace. Thus, molten BOFS was mixed with the modifying materials at high temperature, and the reconstruction reaction was conducted. The MSS was cooled by the conventional treatment process of No. 1 Steelmaking Plant of Shao-gang Iron and Steel Group Co., Ltd.; that is, water was sprayed on the MSS for 40 min and then it was naturally cooled. After the modification process, the MSS was transported to the laboratory for further treatment and performance test. The original BOFS was also collected for the investigation of the modification effect.

2.2.3. Mineral composition and microstructures

The mineralogical compositions of BOFS and MSS were determined by XRD. XRD analysis was conducted using a D/Max-III-type automatic X-ray diffractometer (Rigaku Electric Machinery Corporation, Japan), and the testing conditions were as follows: Cu target, graphite filter, tube voltage of 30 kV, current of 30 mA, scanning speed of 12°/min, scanning range of 10–80°. Both BOFS and MSS specimens for the optical microscopy observation were etched with a 1% NH₄Cl aqueous solution after sulphur casting and polishing, and then their microstructure was examined using an optical microscope (Leica DM2500P).

2.2.4. Physical and mechanical properties

Cement mortar prisms measuring 40 × 40 × 160 mm were prepared for strength measurements according to Chinese National Standard GB/T 17671-1999 Method of Testing Cements: Determination of Strength and GB/T 20491-2006 Steel Slag Powder Used for Cement and Concrete. The ratios of binder to sand, water to binder, and cement to steel slag were 1:3, 1:2 and 70:30, respectively. After demoulding, the specimens were cured in water at 20 ± 2 °C. Strength measurements were conducted after 7 days and 28 days of curing. The standard consistency, the setting times and the soundness of the cement pastes were determined according to ISO 9597.

3. Results and discussion

3.1. Effect of modification conditions on cementitious property of MSS

Table 1 indicates that the content of CaO and SiO₂ in BOFS is lower than that of the cement clinker. According to the steelmaking production practices, whose molten BOFS contains considerable heat and has good fluidity, a feasible method to improve the cementitious property of BOFS is to adjust the chemical and mineralogical compositions to approach those of the Portland cement clinker [16–18]. By adding some modifying materials to the molten BOFS during the discharge process, we could increase the content of the cementitious minerals in the product, resulting in an improved cementitious property. In this study, modifying materials were prepared using a mixture of EAFS and coal bottom ash in appropriate proportions.

Table 3
Results of the orthogonal experiments.

Sample	Factor A	Factor B	Factor C	Compressive strength (MPa)	
				7 days	28 days
Cement	–	–	–	36.3	47.3
BOFS	–	–	–	26.8	39.6
MSS-1	Level 1	Level 1	Level 1	29.7	44.5
MSS-2	Level 2	Level 1	Level 2	29.2	42.2
MSS-3	Level 3	Level 1	Level 3	28.0	40.7
MSS-4	Level 4	Level 1	Level 4	29.1	38.7
MSS-5	Level 2	Level 2	Level 1	27.8	43.6
MSS-6	Level 1	Level 2	Level 2	28.5	41.0
MSS-7	Level 4	Level 2	Level 3	29.4	43.5
MSS-8	Level 3	Level 2	Level 4	28.5	40.0
MSS-9	Level 3	Level 3	Level 1	31.0	47.4
MSS-10	Level 4	Level 3	Level 2	31.4	46.5
MSS-11	Level 1	Level 3	Level 3	30.4	42.2
MSS-12	Level 2	Level 3	Level 4	31.0	43.7
MSS-13	Level 4	Level 4	Level 1	30.3	46.7
MSS-14	Level 3	Level 4	Level 2	29.6	44.9
MSS-15	Level 2	Level 4	Level 3	27.7	40.9
MSS-16	Level 1	Level 4	Level 4	29.2	41.2
\bar{K}_1	42.23	41.53	45.55		
\bar{K}_2	42.60	42.03	43.65		
\bar{K}_3	43.75	44.78	41.83		
\bar{K}_4	43.85	43.43	40.90		
R	1.63	3.25	4.65		

The effect of the modification conditions on the cementitious property of MSS, including the ratio of BOFS to modifying materials (factor A), the ratio of EAFS to coal bottom ash (factor B) and modification temperature (factor C), was investigated through an L₁₆ (4⁵) orthogonal experiment. The factorial design and the results of the orthogonal experiments are provided in Tables 2 and 3, respectively. The 28 days compressive strengths of mortars were chosen as the assessment index of the cementitious property in the variance analysis.

From Table 3, it can be seen that the modification can significantly increase the 7 days and 28 days compressive strengths of MSS by 17.2% and 19.7%, respectively. Although early compressive strengths are low, the 28 days compressive strengths of MSS mortars are close to the compressive strength of the reference cement, for example MSS-9. The variance analysis results indicate that the modification temperature (factor C) has the most influential effect on the cementitious property of MSS and the ratio of BOFS to modifying materials (factor A) has the least. The 28 days compressive

Table 2
Factorial design and the level of orthogonal experiments.

Level	Factor		
	Factor A The ratio of BOFS to modifying materials (wt%)	Factor B The ratio of EAFS to coal bottom ash (wt%)	Factor C Modification temperature (°C)
Level 1	60:40	75:25	1000
Level 2	70:30	80:20	1100
Level 3	80:20	85:15	1200
Level 4	90:10	90:10	1300

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