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Iron recovery and active residue production from basic oxygen furnace (BOF) slag for supplementary cementitious materials

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ABSTRACT

In this study, a new method for recycling basic oxygen furnace (BOF) slag was proposed. An additive mixture containing kaolin and carbon powder was designed and mixed with BOF slag to induce the reduction of ferric oxides. Iron metal was then recovered from the BOF slag. The additives acted as a component regulator to improve the reactivity of the residue after recovering iron. The results showed that as the basicity of the mixture of BOF slag and additives decreased, the melting temperature of the mixture decreased, whereas the iron recovery efficiency was significantly improved. In fact, when the basicity ranged from 0.97 to 1.31, the iron recovery efficiency reached more than 95%. Additionally, decreasing the basicity of the mixture increased the viscosity of the melt and the extent of the glassy phase formed in the residue during water quenching The maximum percentage of the glassy phase in the residue could reach more than 95%. Accordingly, the reactivity index was high, indicating that the residue from the mixture of BOF slag and the additives after recovering iron can be used as an active supplementary cementitious material.

1. Introduction

Basic oxygen furnace (BOF) slag is a by-product of steel production and is formed by oxidizing a slagging agent and impurities in pig iron during the steelmaking process in a BOF. BOF slag accounts for 15%-20% of the total final volume of crude steel.

Regarding recycling, BOF slag can be used for soil remediation (Chai et al., 2009), wastewater treatment (Bowden et al., 2009), CO_2 capture (Huijgen et al., 2005), etc. However, BOF slag has not been extensively recycled for these purposes. Comparatively, BOF slag is heavily recycled in the construction industry. For example, BOF slag is used for road construction (Anastasiou et al., 2015; Herrmann et al., 2010; Andreas and Diener, 2014; Poulikakos et al., 2017), cement manufacturing (Monshi and Asgarani, 1999; Tsakiridis et al., 2008; Xue et al., 2016), and slag glass ceramic preparation (He et al., 2012), as well as in blended materials for concrete mixing (Das et al., 2007; Huang et al., 2012; Mengxiao et al., 2015; Zhang et al., 2011). However, because different steel types require different raw additives and because the molten iron used for producing steel has different compositions, the chemical composition of BOF slag is subject to large fluctuations. As a result of oxygen stirring of a molten pool, uneven temperature fields and other complex physical conditions, lime, which is used as a slagging agent for steel manufacturing, is inadequate for participating in solid-phase reactions and being fully integrated into the slag. Thus, BOF slag contains free lime and has poor volumetric stability. In the steelmaking process, heating the slag to temperatures above 1650 °C increases the size of mineral crystals such as tricalcium silicate (C_3S) and dicalcium silicate (C_2S). In addition, BOF slag contains 10%-35% iron oxides (Shi, 2004), which considerably lowers its reactivity (Monshi and Asgarani, 1999; Wang and Yan, 2010). Therefore, BOF slag has received limited attention for use in cement manufacturing and concrete admixtures (Calmon et al., 2013; Mahoutian and Shao, 2016). Consequently, a large amount of BOF slag (Guo and Min Huang, 2009) is sent to landfills, which wastes land resources. Furthermore, the high iron oxide content of BOF slag makes dumping the material a huge waste of iron resources.

BOF slag discharged during the steelmaking process at temperatures above 1650 °C holds considerable waste heat. If this heat can be utilized to reduce the iron oxides in the slag, then the iron can be recovered, and the reactivity of the residue can be significantly improved. Consequently, the BOF slag can be recycled, and high economic value-added uses of the recovered iron and the residue slag can be achieved. Although the idea of recycling BOF slag has considerable economic and social potential value, few relevant studies have been reported. Li et al. (Li et al., 2011) modified BOF slag by adding electric arc furnace steel slag after slagging to increase the content of C_3S. However, the authors

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did not consider recovering iron from the BOF slag. Guo et al. (2011) recovered iron from BOF slag after fusion but failed to improve the reactivity of the residue. Chunwei Liu et al. (Liu et al., 2017) used carbothermic reduction to reduce Fe oxides and P-containing compound in BOF slag. They obtained micron-sized iron particles distributed between silicate minerals and other minerals and were able to control the formation of C_2S, C_3S and glassy crystals through the combined effects of Al_2O_3 and SiO_2 additions. Guozhu Ye et al. (Lindvall and Ye, 2012; Ye et al., 2003) recycled BOF slag using a direct current electric furnace to obtain metals that were rich in Fe, Mn, V and Cr and tentatively explored the feasibility of using the residue as a supplementary cementitious material. However, the authors did not systematically study the effect of additives on the efficiency of iron recovery and the residue properties.

In this paper, an additive mixture was combined with BOF slag to recover iron from the BOF slag at a high temperature and to improve the reactivity of the residue, which can be used as a supplementary cementitious material. For the additive mixture, carbon powder was used as a reducing agent to induce the reduction of the iron oxides in BOF slag, and kaolin was used as a constituent regulator to modify the melting temperature and viscosity of the residue melt. According to the distributions of BOF slag, kaolin, and blast furnace (BF) slag in the CaO-SiO_2-Al_2O_3 ternary phase diagram, kaolin was added to the mixture to bring its chemical composition closer to that of BF slag based on the lever rule of phase diagrams. The reactivity of the residue was assumed to be improved in this manner. In addition, the effect of the additive mixture on the melting temperature and viscosity of the residue melt was measured and calculated using FactSage 7.0. The impact of the additive-modified slag melting temperature and melt viscosity on the efficiency of iron recovery from BOF slag was also discussed. The chemical and mineral compositions of the residues, which were influenced by the additive mixture, were characterized using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The reactivities of the residues were studied by performing compressive and flexural tests on cement paste specimens with the residues substituting for part of the cement.

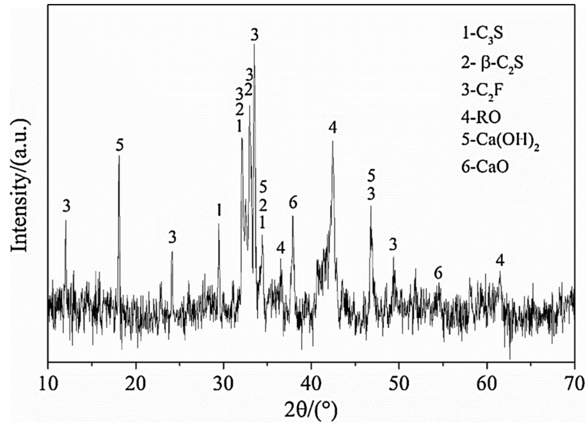

Fig. 1. XRD pattern of BOF slag.

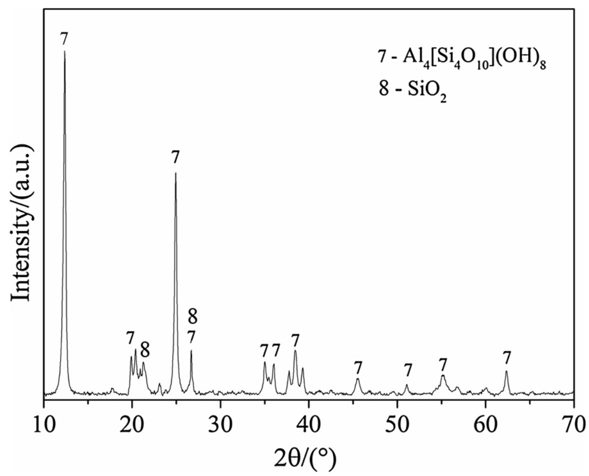

Fig. 2. XRD pattern of kaolin.

2. Materials and experiments

2.1. Materials

The BOF slag used in this study was produced by Baosteel Company, Shanghai, China and was ground until its Blaine specific surface area was 400 m^2/kg (GB/T-208, 2014; GB/T-8074, 2008). The chemical composition of the BOF slag is shown in Table 1 (BS-EN-196-2, 2005), and an XRD pattern of the BOF slag is shown in Fig. 1. According to the XRD pattern, the main minerals in the BOF slag are C_3S, C_2S, dicalcium ferrite (C_2F), an RO phase, which is a solid solution of MgO (periclase) and FeO (wustite), and $Ca(OH)_2$.

To recover iron from BOF slag and then improve the reactivity of the resulting residue, in this study, various mixtures of functional additives were investigated to determine the optimal one. Kaolin was produced by Huading Mining Company, Guangdong, China, and was received as a powder with a particle size of less than 80 μm. Its chemical composition is shown in Table 1, and its XRD pattern is shown in Fig. 2. The main crystal is $Al_4[Si_4O_{10}](OH)_8$, along with a small amount of quartz.

P · O 42.5 cement (Ordinary Portland cement, where 42.5 refers to the strength grade), which was used to study the reactivity of the residue from BOF slag after iron recovery, was produced by Guangzhou Development Group Co., Ltd., China. Its chemical composition is shown in Table 2.

2.2. Experiments

2.2.1. Design and procedure

2.2.1.1. Mixture design. Because of the mass ratio of CaO to SiO_2, BOF slag is a high basicity slag (Shi, 2004). As shown in the CaO-SiO_2-Al_2O_3 ternary phase diagram (see Fig. 3), the CaO content of BOF slag is higher than that of BF slag, whereas the SiO_2 and Al_2O_3 contents are lower. The location of kaolin in the ternary phase diagram indicates that the mineral is an ideal additive for increasing the SiO_2 and Al_2O_3 content of the mixture. According to the lever rule of phase diagrams, increasing the kaolin content of mixtures of BOF slag with kaolin can

Table 1
Chemical composition of BOF slag and kaolin/mass fraction%.

NO	Sample	Chemical composition												
		CaO	SiO_2	Al_2O_3	T-Fe*	MgO	SO_3	K_2O	Na_2O	MnO	P_2O_5	f-CaO	LOI	others
B0	BOF slag	39.86	11.08	2.35	29.43	9.95	0.01	0.02	0.11	0.42	1.15	5.87	2.04	3.58
K	Kaolin	0.51	46.52	35.25	1.56	0.49	0.32	–	–			–	13.47	1.88

T-Fe refers to total iron, LOI refers loss on ignition.