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Industrial research on the high-temperature modification of Basic Oxygen Furnace slag with solid waste compound

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ABSTRACT

Basic Oxygen Furnace slag, the main by-product of steelmaking process, presents still low utilization rate due to its limitations as a partial replacement for cement. The previous fundamental research demonstrated that the slag exhibits the modulated composition and improved property via reacting with the modifier at high temperature. Herein, an industrial modification technique has been studied at the scene of the 120t steelmaking converter to improve the technical feasibility, security and compatibility with the existing steelmaking process. The slag characterization indicates that the sufficient reaction between the huge amounts of slag and modifiers occurs during the slag tapping process, which is contributed to the optimal operations and specific modifiers treatment. The modified slag tailings show the dramatically improved grindability with high availability. Moreover, the 3d and 28d active index of the cement paste consisting of modified slag tailings and cement in 3:7 wt ratio are about 20% and 12% higher than that of the system with the pristine tailings, respectively. Therefore, the modification of Basic Oxygen Furnace slag taking advantage of waste heat and solid waste as modifier is a feasible industrial technique to accelerate the cleaner production in steelmaking industry.

1. Introduction

Steel slag, the main by-product of iron and steel industry, accounts for about 10–15% of the crude steel output (Gan et al., 2015). As seen in Table 1, the yield reached about 104 Mt in 2015 in China as a country with the largest crude steel output in the world. Therefore, the recycle of steel slag especially the dominant species Basic Oxygen Furnace (BOF) slag makes a great contribute to the cleaner production and sustainable development of iron and steel industry.

In some countries, BOF slag is mainly applied in road construction in view of its high strength and wear resistance (Ferreira et al., 2016) and also as Fe based sintered materials due to its high Fe/FeO content (Yi et al., 2012). In China, BOF slag is usually used as irony correction material in cement production, which is mixed by 6–10% proportion of cement raw meal (Tsakiridis et al., 2008). Moreover, BOF slag is exploited as hydraulic binder to partially replace cement or concrete admixtures in building materials, which is an important approach to its application as secondary resources in developing more sustainable building materials (Reddy et al., 2006). However, the comprehensive utilization ratio of the slag is unfortunately 10–30% as shown in Table 1 (Li, 2010). The vast majority of BOF slag tailings is abandoned or backfilled, which leads to enormous value losses and potential environmental problems. The reasons causing the low recycling ratio could be concluded as follows: First, the slag and its tailings with amount of tough phases like iron oxide and calcium ferrite show poor grindability (Hou et al., 2009), so fine grinding for the mechanical activation, a usual way to improve their hydration property (Wang et al., 2013), suffers from a great energy consumption and is consequently not feasible for a large-scale application of slag as hydraulic binder in building materials. Second, it shows a feebly hydraulic activity and low hydration rate because of the low content of hydraulic phases like C_3S (Belhadj et al., 2012). Even via varying the cool type (including water-cooling and air-cooling) in slag cooling process (Mostafa et al., 2001), the slag still cannot fulfill the requirements for the comparable hydraulic activity to the clinker. Third, the free lime and periclase contained in slag would produce volume expansion which leads to poor durability of concrete product (Zhang et al., 2012a; Chen et al., 2016). Steel slag is generally performed hot steaming after deslagging to accelerate the hydrolysis

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Table 1
The production and utilization of steel slag in China from 2001 to 2015.

Y	Crude steel output① /Mt	Steel slag output② /Mt	Utilized steel slag② /Mt	Utilization ratio /%
2001	152	22.83	5.94	26
2002	182	27.23	7.35	27
2003	222	33.35	3.34	10
2004	283	40.85	4.08	10
2005	353	51.09	4.85	9.5
2006	419	61.34	5.58	9.1
2007	489	65.00	6.50	10
2008	503	65.10	6.51	10
2009	572	79.50	17.49	22
2010	637	81.47	17.11	21
2011	685	93.60	19.89	21
2012	724	93.00	20.46	22
2013	813	101.00	30.30	30
2014[a]	823	115.18	25.22	22
2015[a]	804	104.49	22.05	21

Data source: ①National Bureau of Statistics; ②China Association of Metalscrap Utilization.
[a] Note: The data in 2014 and 2015 need further vertification.

reaction of free lime and periclase, but the operation faces great challenges of high consumption of water resources, explosion risk of vapor and combustible gas. The above congenital deficiencies are responsible for the application issues of BOF slag as secondary resources.

High temperature modification technique of BOF slag has been proposed to deal with above problems. In the fundamental research, steel slag and modifier powders were mixed homogeneously and then transferred to the muffle furnace for the heat-treatment. The results indicated that additional reaction occurs in the mixture of slag and a certain modifiers at high temperature (i.e. ≥1250 °C) to realize the modulation of the chemical and mineral composition of the slag, which contributes to high availability of the slag (Zhang et al., 2012b). Li et al. (2011) reported that C_3S content is increased from 8.2 to 20.9% after BOF slag reacts with electric arc furnace (EAF) slag at 1350 °C. Li et al. (2013) made the thermodynamic analysis on high temperature reaction between slag and modifier in CaO-Al_2O_3-SiO_2 ternary phase diagram. Zhao et al. (2010) suggested that the modification effect depends on the modifier species and the reaction temperature on the premise of homogeneous mixing and direct contact between slag and modifiers.

Our previous research in the lab indicated that the BOF slag modified by iron tailings at 1300 °C exhibits the significantly reduced f-CaO content from 4.84 to 1.82% (Lian et al., 2013). Moreover, mixed with modifier consisting of iron tailings and quick lime in ratio of 1:2, the BOF slag showed the migration of chemical composition from C_2S-C_3A-$C_{12}A_7$(point a) to C_3S-C_2S-C_3A(point b) deputy triangle in CaO-Al_2O_3-SiO_2 ternary phase diagram as seen in Fig. 1, which makes possible more silicates and aluminates formed after calcined at 1350 °C. The experimental results confirmed that C_3S content was increased from 19.32 to 34.48% and C_3A content from 2.66 to 9.22% after the modification of the slag. Furthermore, the cement mortar sample with 30% modified slag exhibits the 28d compressive strength of 95.5% vs. the clinker system, which is 17% higher than the one with pristine slag (Zhang et al., 2015). The reports on the high temperature modification of BOF slag demonstrate the feasibility of the composition modulation from the point of view of thermodynamics.

The heat containing in the slag is released to the environment and wasted in the normal BOF steelmaking operation. In this work, an industrial modification approach has been developed taking advantage of waste heat in the slag. As well as know, to ensure the thermodynamic conditions of the reaction between slag and modifier is of first importance at the scene of the 120t steelmaking converter. In detail, the calculation using the sensible heat of the slag (1.25 kJ/(kg·°C)) suggests that the slag should be at the temperature above 1405 °C as mixed with the modifier (by 15 wt %) in ambient temperature to guarantee the mixture higher than 1250 °C. Furthermore, about 10t slag is discharged from the 120t steelmaking converter for a single heat, and it is impossible to add new equipments in the confined space near BOF, so the homogeneous mixing between large amount of slag and modifier is another challenge at the scene. Finally, the modification operation should be compatible with existing steelmaking process, in which negative effects on the service life of converter and dust pollution or any potential hazards are avoided compulsively. In this case, the process of the industrial modification has been optimized. Although some approaches had to be abandoned considering no significant modified effects and the potential risk on site, the typical optimization and major effects of the modification process are included in the paper in view of the technical volubility, especially the optimal approach was elucidated in detail herein to demonstrate the

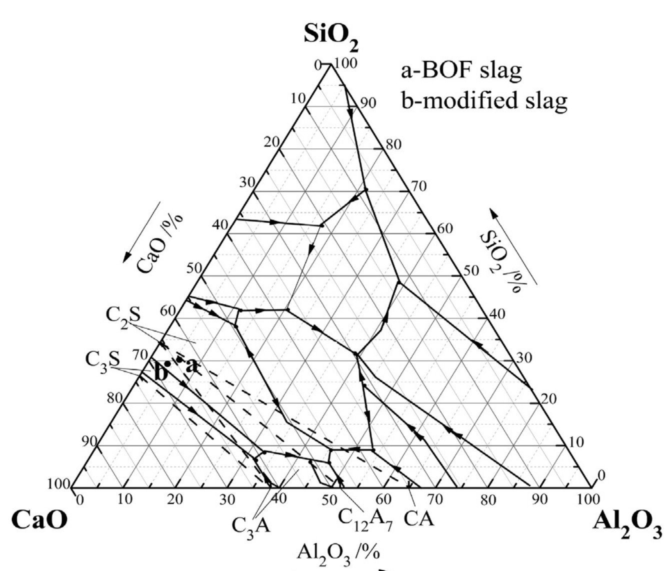

Fig. 1. The chemical composition of BOF slag and modified slag located in CaO-SiO_2-Al_2O_3 ternary phase diagram.