Optimization of mineralogy and microstructure of solidified BOF slag through SiO₂ addition or atmosphere control during hot-stage slag treatment

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Abstract

Valorization of basic oxygen furnace (BOF) slag is of significant importance for mitigation of the steel production's environmental impact. The present work aims to investigate the influence of SiO₂ addition and oxygen partial pressure on the mineralogical modification of a typical industrial BOF slag. The slag basicity (mass ratio of CaO/SiO₂) was varied from 1.8 to 4.4 by mixing specific amounts of SiO₂ with the master BOF slag. The original and modified slags were re-melted and solidified under argon and/or air atmosphere followed by slow cooling. The experimental observations were then compared with the results of thermodynamic modelling to achieve a thorough understanding. With decreasing the basicity, free lime is eliminated as it forms dicalcium silicate (Ca₂SiO₄). With increasing the oxygen partial pressure, wustite is oxidized to hematite, which combined with free lime to form calcium aluminoferrite (C₂AF). The effects of SiO₂ addition and oxygen partial pressure were finally evaluated with respect to the energy consumption for the BOF slag valorization. The modified slag is suitable as a precursor for value-added applications.

Key words: BOF slag; Microstructure; Valorization; Basicity; Oxygen partial pressure;

Contribution of Chunwei Liu: The experiments were performed by Shuigen Huang and Chunwei Liu. Chunwei Liu analysed the samples, interpreted the results and wrote the paper. The co- authors assisted in discussion of the results and writing process.

5.1 Introduction

Steel slag, generated during the steelmaking process, is a main by-product in steel industry. Depending on the steel grade, 100 - 150 kg slag is discharged for producing 1 tonne of steel [1]. About 20 million tonnes of steel slag are produced annually in Europe [2], of which BOF slag accounts for almost half of the volume [3]. Storage of the huge amount of slag burdens the environment and is an economic liability to steel industry. Recycling and reutilization of slags towards added-value applications are therefore of significant importance for the sustainability of steel industry.

In the past decades, metallurgical slag valorization has been intensively explored to apply the slag in various fields, such as landfill liner [4,5], hydraulic binder [6–8], and fertilizer [9]. Among these, hydraulic binder that can be used for constructional application appears to be more interesting as they create higher value. However, application of BOF slag for constructional materials is limited by its volume expansion during natural aging [10–12]. This dimensional instability is induced by the hydration of free lime and free magnesia in the slag [11]. During the hydration, free lime and magnesia exhibit around 10 pct swelling [13], leading to the disintegration of bulk slags. Typically, the lime content in the BOF slag is markedly higher than that of magnesia, thus the lime is the main concern for the volume instability [10]. Recent research addressed that 4 wt pct free lime in BOF slag is the limit for applying the slag as a construction material [10]. Different methods have been investigated to stabilize free lime in BOF slag, amongst which, SiO_2 and Al_2O_3 were reported as effective additions to eliminate the free lime [14–16]. The addition of SiO_2 results in more silicate after solidification, which accommodates the extra CaO and therefore eliminates the free lime, while the addition of Al_2O_3 produces more C_2AF as it combines with free lime [15]. Also, Gautier *et al.* studied the effect of the cooling method on slag microstructure and mineralogy in air, and found that the free lime content was decreased in the solidified slag [17]. The elimination of free lime was tentatively attributed to the suppression of the decomposition of tricalcium silicate by a rapid cooling. Additionally, hot-stage carbonation of the free lime has been investigated in recent years [3,11,18]. The mechanism is to stabilize the free lime by forming geochemically stable calcium carbonate. But size reduction of BOF slag is needed to perform an effective carbonation, which inhibits the application of this method [11,18]. By summarizing

previous studies, it can be concluded that: (1) recycling BOF slag has shown significant importance but high value-added application is limited due to the presence of free lime; (2) SiO₂ addition is effective to stabilize the slag, yet quantitative knowledge on the mineralogical evolution associated with SiO₂ addition is needed; (3) although previous study provided evidence that an oxidizing atmosphere may facilitate slag stabilization, the underlying mechanisms remain unclear.

The present study aims to provide a fundamental understanding of the effects of SiO₂ addition and oxygen partial pressure on BOF slag microstructure and mineralogy after solidification, targeting a quantitative and effective control of the slag product that is microstructurally and mineralogically tailored to achieve better hydraulic properties. Experiments were carried out to assess the influence of basicity by mixing specific amounts of SiO₂ with the master BOF slag. Also, the original and modified BOF slags were re-melted and solidified under argon and/or air atmosphere followed by slow cooling. Experimental results were compared with the thermodynamic calculation using FactSage to reveal the underlying mechanism. Thereafter, the promising methods were evaluated from the perspective of energy consumption. The findings of this work suggest a novel approach to optimize the microstructure/mineralogy of the solidified slag through hot-stage slag engineering, providing a precursor for high value-added applications.

5.2 Experiments and thermodynamic modelling

5.2.1 Materials preparation and experimental procedure

A typical BOF slag was used as the starting material, which was sampled from a slag yard at different locations and depth from the surface. The slag was then mixed, ground and milled to powder below 200 μm . The typical chemical composition and mineral constitution of the BOF slag are listed in Tables 5.1 and 5.2 respectively. The basicity (mass ratio of CaO to SiO₂) of the master slag is 4.4.

Table 5.1. Chemical composition of the master slag, wt pct

CaO	*T.Fe	SiO ₂	MnO	MgO	Al ₂ O ₃	P ₂ O ₅	TiO ₂	Basicity
42-55	14-20	9-15	0-8	0-5	0-3	0-2	0.89	3.5-5.0

* Fe is given as the total iron. Measured by X-ray fluorescence (XRF, Panalytical PW 2400).

Table 5.2. Mineral composition of the master slag

Mineral phase	Free lime	Wustite	Calcium aluminoferrite	Beta dicalcium silicate
Chemical formula	CaO	RO (FeO-MgO-MnO)	Ca ₂ (Al, Fe) ₂ O ₅	β-Ca ₂ SiO ₄
(wt pct)	15-22	15-25	25-35	25-35

To investigate the effect of basicity on the solidification microstructure and mineralogy, 100 g of master slag was individually mixed with 5.0, 10.0, and 15.0 grams of SiO₂ in ethanol for 24 hours by using a multidirectional mixer (Turbula type). The mixtures were dried in a rotating evaporator at 65°C. 10 grams of the mixture with different basicity was loaded in a MgO crucible (inner diameter 15mm, height 40mm) and melted in a graphite heating furnace (W100/150-2200-50 LAX, FCT Systeme, Rauenstein, Germany) under vacuum atmosphere at 1600 °C for 1 hour to homogenize the slag composition, afterwards the slag was cooled down to room temperature inside the furnace at a cooling rate of 5 °C·min⁻¹.

To study the effect of oxygen partial pressure, 20 grams of master slag were loaded in MgO crucibles (inner diameter: 32 mm, height 70 mm). For the tests under Ar, the sample was placed in a vertical tube furnace (HTRV 100-250/18, GERO, Germany) under Mg-purified Ar atmosphere with a flow rate of 0.4 l·min⁻¹. After maintaining at 1400 °C for 1 hour, the slag was cooled down to room temperature in the furnace at 5 °C·min⁻¹. The oxygen partial pressure was measured by an oxygen sensor (Rapidox 2100, Cambridge Sensotec, United Kingdom) and was maintained below 10⁻¹⁸ atm. For the tests in air, the slag was melted at 1400 °C for 1 hour in a bottom loading furnace (AGNI - ELT 160-02. Spring type), then cooled down to room temperature in the furnace at 5 °C·min⁻¹.

5.2.2 Characterization of the slag samples

The slag specimens were mounted in a low viscosity resin (Epofix), ground by silicon carbide papers and polished with diamond paste. The polished specimens were coated with carbon for compositional and microstructural analyses, which was achieved by electron probe micro-analysis (FE-EPMA, JXA-8530F, JEOL Ltd, Japan), equipped with a wavelength dispersive spectroscopy (WDS) that allows fully quantitative chemical composition analysis. The beam current and accelerating voltage were set as 15 nA and 15 kV, respectively. After crushing the slags to powder with size below 100 µm, X-Ray

Fluorescence (XRF, Panalytical PW 2400) was used to measure the composition while X-Ray Diffraction (XRD, 3003-TT, Seifert, Ahrensburg, Germany) was used to identify the minerals. Quantitative analysis of the XRD pattern was achieved with the aid of the Rietveld refinement method.

5.2.3 Thermodynamic modelling

Thermodynamic modelling of the phase evolution during solidification were performed by using FactSage 7.0 associated with FactPS and FToxid databases. The FactSage software has been successfully used in modelling the slag system in recent years [19–22]. Experimental observation was integrated with the simulation to understand the effect of oxygen partial pressure on the BOF slag mineralogy.

5.3 Results and discussion

5.3.1 Influence of SiO₂ addition

Figure 5.1 presents the quantitative XRD analysis of the slags with different SiO₂ additions treated at 1600 °C under Ar atmosphere by means of Rietveld refinement. Major phases presented in these slags are calcium aluminoferrite, beta dicalcium silicate (β -C₂S), wustite (RO) and free lime (formula CaO). The formula of calcium aluminoferrite is Ca₂(Al_xFe_{1-x})₂O₅ (in short C₂AF), with x in the range of 0-0.7 [23]. There is 20 wt pct free lime detected in the master slag with a basicity of 4.4. With SiO₂ addition of 5, 10 and 15 wt pct, the basicity was accordingly decreased to 2.8, 2.4, and 1.8, respectively. The content of free lime is significantly lowered with the decrease of basicity, as indicated by the solid line in Figure 5.1. In the slags with basicity of 2.8, the content of free lime is decreased to 1.9 wt pct, which is less than the critical limit (4 wt pct) for the slag application as construction materials [10]. While in the slags with basicity of 2.4 and 1.8, free lime is eliminated completely. In contrast, the content of C₂AF phase is decreased with the addition of SiO₂ due to the strong affinity of SiO₂ with CaO at high temperature. In the slag with a basicity of 1.8, bredigite (formula Ca_{1.75}Mg_{0.25}SiO₄, in short CMS) indicated by the dashed line becomes a major phase, and accordingly β -C₂S phase is decreased drastically compared to other minerals. Chemical reactions of the free lime stabilization and bredigite formation are respectively given in reactions (5.1) and (5.2). According to the mass balance

calculation with reaction (5.1), 0.54 wt pct SiO₂ is consumed to stabilize 1 wt pct free lime. Thus, stabilization of 20 wt pct free lime in the present study consumes 10.7 wt pct SiO₂. In practice, however, the actual consumption of SiO₂ should be less than 10.7 wt pct due to the fact that CaO can also react with FeO, MnO and MgO and form RO as seen in reaction (5.3). For this reason, free lime was completely eliminated even in the test with 10 wt pct SiO₂ addition (basicity of 2.4).

Figure 5.1. Quantitative XRD analysis of minerals content in the slag treated at 1600 °C for 1 hour and cooled at 5 °C·min⁻¹ in Ar

To have a quantitative understanding of the chemical composition of each phase, the microstructure of the solidified slag was analyzed using EPMA-WDS. Figure 5.2 shows the typical microstructures of the slags with different SiO₂ additions. The microstructure of the original slag is shown in Figure 5.2 (a). WDS analysis confirms that free lime is a CaO-based solid solution which also incorporates FeO, MgO and MnO. The typical CaO

content in the lime phase is above 68 wt pct. β -C₂S crystal can be observed and constitutes one of the major phases in the slags, except for the one with a basicity of 1.8 (Figure 5.2 (d)). WDS analysis suggests that the β -C₂S phase is typically associated with P₂O₅ (>2 wt pct), forming a solid solution of Ca₂SiO₄-Ca₃PO₄, in short C₂S-C₃P [24–26]. It has been reported that [PO₄]³⁻ acts as a substitution of [SiO₄]⁴⁻ anion groups in the C₂S-C₃P solid solution [24]. According to previous studies, incorporation of 0.5 wt pct P₂O₅ can stabilize β -C₂S, and this phase is crucial to prepare Portland cement [27,28]. RO (a bright phase in Figure 5.2) is another main phase in all the cases. The RO phase is a FeO-based solid solution with a typical FeO content over 60 wt pct, and other oxides found in RO are MgO, MnO and CaO. It is noteworthy that two typical morphologies of RO can be found: small (<10 μ m) grains dispersed in C₂S-C₃P and free lime (indicated by circles in Figure 2); larger (>20 μ m) RO grains that were separated from other phases. In the slag with basicity of 1.8, a large amount of bredigite (CMS) was formed (see Figure 5.2 (d)). The chemical formula of CMS (Ca_{1.75}Mg_{0.25}SiO₄) is close to the C₂S (Ca₂SiO₄), with a few CaO substituted by MgO. But CMS has a distinct structure compared to the C₂S, and the impurities in the slag such as Mn can partially replace Mg [29,30]. It has been reported that the bredigite reacts slowly with water, and the compressive strength of lime-activated bredigite cubes is too low to be of use for a cementitious material [30]. Therefore, it should be avoided to generate CMS for utilizing the slag as a binder in constructional application. Furthermore, both the mineralogical and microstructural analysis show that no free MgO exists in the slag. WDS analysis confirms that Mg incorporates with RO and C₂S phases in the slags with $R=2.4$, 2.8 and 4.4. In the case of $R=1.8$, however, Mg concentrates in RO, C₂S and bredigite. Free MgO can cause slag instability by its hydration, thus, it is preferred to avoid free MgO for preparing binder materials.

Based on the above findings, it is confirmed that free lime is effectively eliminated by forming C₂S or CMS through SiO₂ additions. In the current study, by decreasing the basicity to 2.8, the free lime has been lowered to a level (1.9 wt pct) that satisfies the requirement of the volume stability for constructional application. Decreasing the basicity to 1.8, however, leads to a precipitation of CMS phase with poor cementitious property. Therefore, to stabilize free lime and obtain a better cementitious property of the BOF slag, the slag should be modified at hot-stage towards a basicity ranging from 1.8 to 2.8.

Figure 5.2. Microstructures of slags treated at 1600 °C for 1 hour and cooled at 5 °C·min⁻¹ in Ar. (a) R=4.4 (matrix slag); (b) R=2.8; (c) R=2.4; (d) R=1.8. 1: β -C₂S; 2: C₂AF; 3: RO; 4: CaO; 5 CMS.

5.3.2 Influence of oxygen partial pressure

The original BOF slag was treated at 1400 °C for 1 hour under a controlled atmosphere, followed by furnace cooling at 5 °C·min⁻¹. Figure 5.3 (a) shows the XRD patterns of the air and Ar-treated slags. The characteristic 2 theta values of free lime are 37.34° and 53.86° using Cu K α radiation. In this work, the 2 theta positions of free lime shifted to the diffraction angles of 37.51° and 54.16° (dashed lines in Figure 5.3 (a)). This is probably due to the incorporation of MgO and FeO in the lime phase, which is commonly observed in BOF slag [31]. In the present study, 1.60 and 18.98 wt pct MgO and FeO were identified in the lime phase. The interplanar distance of MgO and FeO are relatively smaller than that of CaO, so that the peaks shift to larger 2 theta positions [32]. Free lime was detected in the Ar-treated slag, but was eliminated completely in the air-treated slag. The other major phases, *i.e.* C₂AF, β -C₂S and RO are observed in both the Ar and Air treated slags.

Quantitative analysis of the mineralogical composition was achieved by using Rietveld refinement method, and the result is shown in Figure 5.3 (b). The predominant phase in the Ar-treated slag is β -C₂S (>40 wt pct). But C₂AF becomes the predominant phase (>65 wt pct) in the air-treated slag. Consequently, the amount of RO and β -C₂S phases in the air-treated slag is considerably lower than in the Ar-treated slag. Additionally, 3.8 wt pct MgO was found in the air-treated slag.

Figure 5.3. (a) XRD spectra of the slags treated under Ar (top) and air atmosphere (bottom) (dashed lines represent the characteristic position of free lime); (b) Comparison of the minerals in the air-treated and Ar-treated slags, as quantified by Rietveld refinement of XRD spectra

The microstructure of the air and Ar-treated slag is shown in Figure 5.4. The size of C₂AF crystal is much larger in the air treatment condition. The WDS analysis confirms that the free lime, RO, and periclase are solid solutions. In the air-treated slag, only small RO grains are observed and those grains are dispersed in the periclase, as shown in Figure 5.4 (a). The RO phase in the Ar-treated slag, as shown in Figure 5.4 (b), appears in two different morphologies, *e.g.* big RO grains as a separated crystal, and tiny grains dispersed inside the lime solid solution (indicated by the circles in Figure 5.4 (b)). Figure 5.5 shows the phase diagram of CaO-FeO_x system in contact with iron. The system is under a low oxygen partial pressure that is comparable to the present study. The maximum solubility of FeO_x in the lime solid solution is 12 wt pct when the system is equilibrated at 1130 °C [33]. WDS analysis indicates that 19.0 wt pct FeO_x was incorporated in the overall lime phase, resulting in the precipitation of FeO_x (RO). According to Figure 5.5, FeO_x should

precipitate from the lime rich CaO-FeO_x solid solution in the temperature range of 1130 to 1045 °C. The periclase is a MgO-based solid solution with a typical MgO content over 70 wt pct. WDS results indicate that the overall MgO content in the slag treated in air is higher than that in Ar (5.61 wt pct to 3.79 wt pct), implying a slight dissolution of the MgO crucible into the air-treated slag. This is probably due to the increase of Fe₂O₃ (oxidation of FeO under air treatment condition), which behaves as an acidic substance and facilitates the dissolution of MgO. In the industrial practice, there will be less MgO pickup because of the lower surface to volume ratio and relatively short duration of the treatment.

Figure 5.4. Microstructures of the master slag treated under (a) air and (b) Ar atmosphere. Green circles represent the dispersed RO in lime matrix. The yellow rectangles represent local magnification. (1) C₂AF; (2) β-C₂S; (3) RO (the shining points), (4) CaO (the grey matrix); (5) MgO (the black matrix). Scale bar is 10 μm. 1: C₂AF; 2: β-C₂S; 3: RO; 4: CaO; 5: MgO.

Figure 5.5. Phase diagram of CaO-FeO_x system in contact with iron, adapted from Ref [33]. L-liquid; ss-solid solution

Figure 5.6 (a) and (b) present the phase evolution respectively for air and Ar-treated slags, as predicted by FactSage equilibrium calculations. The C₂S transforms from β -type to γ -type in the FactSage calculation, since the stabilization of β -C₂S by phosphorus is not considered. To avoid such a discrepancy, all the C₂S is given in the form of β -C₂S in Figure 5.6. Figure 5.6 (c) indicates that the calculated quantities of major phases agree well with the experimental results. According to the calculation, the change of the oxygen partial pressure affects the crystal precipitation sequence. C₂S is the first crystal precipitated in the air-treated slag (at 1605 °C), followed by C₃S (at 1435 °C) and C₂AF (at 1365 °C). In the Ar-treated slag, however, CaO will firstly precipitate at 1690 °C, followed by C₃S (at 1500 °C), MgO (1440 °C) and C₂S (1352 °C), respectively. Durinck *et al* have reported on the influence of the oxygen partial pressure on the crystallization sequence in the EAF slag [34], and found that the C₂S precipitation temperature in air-cooled slag was higher than that in Ar-cooled slag. In the present work, above 1500 °C, 23.1 wt pct C₂S is

generated in air-treated slag, but no C₂S precipitated from the slag melted in Ar until 1352 °C. According to the calculation, a large amount of free lime is formed by the decomposition of C₃S between 1400 and 1300 °C, as expressed by reaction (5.4).

The amount of C₃S generated in the air-treated slag is decreased markedly due to the decrease in basicity after the formation and precipitation of C₂S, therefore the CaO formed by C₃S decomposition is also decreased. Additionally, as indicated by the circles in Figure 5.6 (a) and (b), C₂AF starts precipitating at a much higher temperature in air (1370 °C) than in Ar (1180°C). This means in the case of slag treatment under air, C₂AF has more time to grow after its precipitation during cooling, which explains the larger C₂AF crystals observed in Figure 5.4 (b) than that in Ar-treated slag. Also, the calculated amount of C₂AF is much higher in air than in Ar condition, which agrees with the experimental data. The large amount of C₂AF generated under air condition consumes more Ca²⁺ and contributes to the removal of free lime in the slag.

The elimination of CaO, the decrease of the RO content, and the concurrent increase in C₂AF content for the air-treated slag can be better understood from reactions (5.5) and (5.6). When the slag is heated up in air, Fe²⁺ in the slag (FeO) is oxidized to Fe³⁺ (Fe₂O₃), as expressed by reaction (5.5).

Fe₂O₃ then reacts with CaO at around 1370°C to produce C₂AF through the reaction (5.6) during solidification process,

Assuming that the contribution of Al₂O₃ in reaction (5.6) was negligible and FeO can be oxidized completely during the treatment, stabilization of 1 mole CaO consumes 1 mole FeO, *i.e.* stabilizing 1 wt pct CaO needs 1.28 wt pct FeO. Therefore, 25.6 wt pct FeO is needed to completely remove 20 wt pct of the free lime in the original BOF slag. In the BOF slag, however, due to the presence of Al₂O₃ and Mn₂O₃ (respectively 5.49 and 3.76 wt pct in our study), and the presence of FeO in the lime phase, stabilization of 1 wt pct free lime may require less than 1.28 wt pct FeO.

Figure 5.6. Phase evolution during solidification as calculated by FactSage under (a) Ar and (b) air atmosphere; (c) comparison between the experimental and calculated results

5.3.3 Evaluation for lime stabilization of BOF slag with respect to energy consumption

The current BOF slag stabilization treatment lies in the introduction of additives and/or increasing oxygen partial pressure to remove the free CaO by reactions towards a stable matrix of calcium silicates and/or ferrites. Based on the results we obtained in aforementioned sections, the effective stabilization methods are evaluated with respect to energy consumption. The energy consumption during the hot-stage engineering is estimated under assumptions: (1) during treatment, the melt temperature was fixed at 1600 °C, *i.e.* the energy needed to maintain such a temperature during the treatment is calculated; (2) 20 tonne slag is charged to a slag pot at 1600 °C, which can be simplified to a circular truncated cone with upper diameter 3.5 m, lower diameter 2.5 m and height 3.5 m; (3) the treatment time is 10 min.

(a) Energy consumed during the stabilization by lowering the slag basicity (through SiO₂ addition)

Stabilization of BOF slag by adding SiO₂ can effectively decrease the basicity and eliminate free lime by forming C₂S. As suggested in the present study, 5 wt pct SiO₂ addition is sufficient to stabilize the free lime. To stabilize 20 tonne slag, 1 tonne SiO₂ is injected for the treatment in 10 min. The energy required for heating up the SiO₂ from 20 to 1600 °C can be calculated by Eq. (5.7)

$$Q_1 = C_p^{Si} \cdot m_{Si} \cdot \Delta T \quad (5.7)$$

where C_p^{Si} is the heat capacity of SiO₂ (0.719 J·g⁻¹·K⁻¹) [36]; m_{Si} is the mass of SiO₂ (kg).

The enthalpy changed ($\Delta H_{1600^\circ\text{C}}$) by the formation of C₂S through the reaction of CaO with SiO₂ (reaction (1)) is -1.76×10^4 J·mol⁻¹, as calculated by FactSage. The negative sign “-” represents the reaction is exothermic.

Thus, energy released during the reaction is

$$Q_2 = \Delta H_{1600^\circ\text{C}} \cdot n_{SiO_2} \quad (5.8)$$

where n_{SiO_2} is the molar number of SiO₂ (mol).

The energy loss due to the radiation can be calculated by Eq. (5.9)

$$Q_3 = E \cdot A \cdot t \quad (5.9)$$

where A is the surface area of the slag pot (top and inclined surface, m²), t is the processing time (s). $E = \sigma \cdot T^4$ is the radiation of the slag (W·m⁻²), where $\sigma = 5.67 \times 10^{-8}$ W·m⁻²·K⁻⁴ is the Stefan-Boltzmann constant [37], T is the absolute temperature (K).

The convective contribution to the heat loss is

$$Q_4 = \alpha \cdot A \cdot t \quad (5.10)$$

where $\alpha = 50$ W·m⁻²·K⁻¹ is the convective coefficient of the air [38].

By substituting values of parameters into the Eqs. (5.7) to (5.10), the total energy exchange Q during the slag treatment is obtained:

$$Q = Q_1 + Q_2 + Q_3 + Q_4 = 1.79 \times 10^{10} J \quad (5.11)$$

(b) Energy consumed during the stabilization by oxidizing the slag (through oxygen partial pressure control)

By increasing the oxygen partial pressure, the wustite is oxidized to hematite, and then stabilizes the free lime by forming C₂AF. Similarly, 20 tonne slag (with 15 wt pct FeO) is assumed to be charged in a slag pot at 1600 °C. The energy required for heating up the oxygen is negligible compared to other energy consumptions. The enthalpy change during the oxidation from FeO to Fe₂O₃ can be calculated by FactSage,

$$\Delta H'_{1600^\circ\text{C}} = -1.46 \times 10^5 J \cdot \text{mol}^{-1} \quad (5.13)$$

So that the energy released during the oxidation can be calculated as

$$Q'_1 = \Delta H'_{1600^\circ\text{C}} \cdot \frac{n_{FeO}}{2} \quad (5.14)$$

where n_{FeO} is the molar number of FeO. Due to the Al₂O₃ content in the slag is much lower than that of FeO and Fe₂O₃, $\chi = 0.1$ is assumed in the Ca₂(Al _{χ} , Fe_{1- χ})₂O₅. Thus, the enthalpy change of reaction (6) can be calculated by FactSage,

$$\Delta H''_{1600^\circ\text{C}} = 1.23 \times 10^5 J \cdot \text{mol}^{-1} \quad (5.15)$$

Thereby the energy change of stabilizing all the free lime becomes

$$Q'_2 = \Delta H''_{1600^\circ\text{C}} \cdot \frac{n_{CaO}}{2} \quad (5.16)$$

where n_{CaO} is the molar number of the free lime. Considering heat loss due to the radiation and convection, which can be estimated by Eq. (5.9) and (5.10) respectively,

the total energy change Q' in the slag stabilization treatment can be calculated in Eq. (5.17)

$$Q' = Q_1 + Q_2 + Q_3 + Q_4 = 1.34 \times 10^{10} J \quad (5.17)$$

Compared with SiO₂ addition, energy consumption during the stabilization treatment by oxidizing slag under high oxygen partial pressure is lower (1.34×10^{10} to 1.79×10^{10} J). To have a thorough evaluation, following aspects should also be considered.

- (1) From the materials consumption point of view, reducing the basicity of the BOF slag consumes SiO₂ (5 wt pct in the present study) while changing oxygen partial pressure consumes only air. So that stabilization of the BOF slag by oxidation could be more material-effective.
- (2) In view of the practical operation, injection of SiO₂ or air during hot-stage treatment may increase the viscosity due to the temperature drop, as a subsequent it interferes the reaction kinetics and deteriorates the operation. The dependence of reaction kinetics on the slag viscosity and temperature should be further investigate, *i.e.* dissolution of SiO₂ and reaction between SiO₂ and free lime vs oxidation of FeO_x and reaction between Fe₂O₃ and free lime.
- (3) SiO₂ addition results in more C₂S while air atmosphere generates more C₂AF. Both C₂S and C₂AF phases facilitate the quality improvement of the slag products. The product quality with respect to volume stability and cementitious property of the stabilized slag should be further studied.

5.4 Conclusions

Effects of SiO₂ addition and oxygen partial pressure on the microstructure and mineralogy of the solidified BOF slag has been studied. The mineralogical change over SiO₂ additions was discussed in a quantitative way. FactSage calculation was performed to explore the mechanisms of oxygen partial pressure on stabilizing the slag. Finally, the methods of SiO₂ and/or oxidizing treatments were evaluated by comparing the energy consumption during hot-stage engineering. The main conclusions are summarized as follows:

(1) Free lime can be transformed to C₂S or CMS by lowering basicity through SiO₂ addition. At the basicity of 2.8, free lime can be controlled in a satisfied level to reutilize the slag in constructional application. With too low basicity ($R < 1.8$ for current case), however, large amount of CMS with poor cementitious property is formed. Based on the results of this work, an optimized basicity is suggested in the range from 1.8 to 2.8.

(2) Laboratory experiment and FactSage calculation demonstrate that free lime can be removed during hot-stage treatment under a high oxygen partial pressure condition. The reason is attributed to that under high oxygen partial pressure (“air” in current study), FeO can be oxidized to Fe₂O₃ and further consumes free lime to form C₂AF. To eliminate free lime completely, the theoretical mass ratio of free lime to FeO should be less than 1.28, which is satisfied in the as-delivered BOF slag.

(3) Energy efficiency for hot-stage slag stabilization by SiO₂ addition and slag oxidation has been evaluated. The calculation of energy consumption of the slag treatment indicates that stabilization of the free lime through the slag oxidation is more energy-effective. A comprehensive understanding is still needed to further evaluate the stabilization approaches, *e.g.* the effect of slag viscosity and temperature on the reaction kinetics of the two methods; comparison of volume stability and cementitious property of the slags stabilized by the two methods.

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