



# Metal Recovery from BOF Steel Slag by Carbo-thermic Reduction

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**Abstract:** BOF steel slag is a main by-product in steelmaking. The valorization of BOF slag is good for the industry and the environment. In the present study, the carbo-thermic reduction of BOF slag has been investigated, the reduction of Fe and P containing phases (i. e. oxide and compounds) is discussed, and the effects of  $\text{Al}_2\text{O}_3$  additions on the reduction process are described. XRD and EPMA have been applied for characterizing the slag. We conclude that, by controlling the test conditions, it is possible to purify the recovered Fe.

**Keywords:** BOF slag, Metal recovery, Carbo-thermic reduction

## Metallrückgewinnung von Stahlschlacken durch carbo-thermische Reduktion

**Zusammenfassung:** BOF Stahlschlacke ist ein wichtiges Nebenprodukt in der Stahlerzeugung. Die Verwertung von BOF-Schlacken ist gut für die Industrie und die Umwelt. In der vorliegenden Studie werden die carbo-thermische Reduktion von BOF-Schlacke, die Reduktion von Fe- und P-haltigen Phasen (d.h. Oxide und Verbindungen) und die Wirkungen von  $\text{Al}_2\text{O}_3$ -Zusätzen auf den Reduktionsprozess beschrieben. XRD und EPMA wurden zur Charakterisierung der Schlacke angewendet. Wir schließen daraus, dass es durch die Kontrolle der Testbedingungen möglich ist, das gewonnene Fe zu reinigen.

**Schlüsselwörter:** BOF-Schlacke, Metallrückgewinnung, Carbo-thermische Reduktion

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## 1. Introduction

Steel slag is classified as BOF (*Basic Oxygen Furnace*) slag, EAF (*Electric Arc Furnace*) slag, and LM (*Ladle Metallurgy*) slag. In recent years, the EU has produced around 20 million tons annually, of which 46 wt% is BOF slag [1]. Recycling and reutilization of such large amounts of steel slag is of great importance, both for the sustainability of the metallurgical industry as well as for the environment. After modification of its chemistry and its solidification mineralogy by means of hot stage engineering, steel slag can be recycled for internal use in the steelmaking process, for road construction, for cementitious substitutes, and as an agricultural fertilizer [2–8].

Using the slag for constructional or agricultural purposes, however, does not consider the large amount of Fe present in the slag. Typically, BOF slags contain 14–29 wt% of Fe, present in iron oxides and iron-containing minerals [9]. “Zero waste” of BOF slag can be achieved by both metal recovery and slag valorization. However, the difficulty of controlling the P distribution between slag and the recovered metal prevents a full reutilization of the slag. Because of P, the recovered Fe has a limited application. Also, P stabilizes  $\beta$  dicalcium silicate ( $\beta\text{-C}_2\text{S}$ ). The complete removal of P from BOF slag leads to the disintegration of the slag due to the transformation of  $\beta$  dicalcium silicate to  $\gamma$  dicalcium silicate ( $\gamma\text{-C}_2\text{S}$ ) during cooling [10, 11]. In previous studies, the carbothermic reduction of slag was described as recovering Cr and/or Fe from stainless steel slag, hot metal dephosphorization slag, and other steel making slag [12–16], without focus on improving the purity and controlling the morphology of the metal.

In this work, the carbothermic reduction of Fe oxides and P oxides of BOF slags with different amounts of  $\text{Al}_2\text{O}_3$  additions has been investigated, and the effect of  $\text{Al}_2\text{O}_3$  on the size of the reduced Fe has been discussed. Based on experimental observations and thermodynamic calculations, a potential method to recover low P containing Fe is proposed.

TABLE 1  
Chemical composition of the master slag (wt%)

CaO	<sup>a</sup> Fe	SiO <sub>2</sub>	MnO	MgO	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>
42–55	14–20	12–18	0–8	0–5	0–3	0–2	0–1	0–0.5

<sup>a</sup>Fe is the total amount of iron in the oxides

TABLE 2  
Different additions for preparing the experimental slags

Parameters of interest	Addition (wt%)	
	C	Al <sub>2</sub> O <sub>3</sub>
Effect of C	5, 6, 7, 8	0
Effect of Al <sub>2</sub> O <sub>3</sub>	7	5, 10

## 2. Experimentals

### 2.1 Slag Preparation

A typical industrial BOF slag was collected at different positions in a slag yard. The samples were ground, followed by milling below 200 μm. After that, the powders were thoroughly mixed for homogenization and then applied in this study as the master material. Table 1 shows the chemical composition of this BOF slag, as determined by X-Ray Fluorescence spectroscopy (XRF, Panalytical PW2400).

Due to the presence of FeO, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub> in the BOF slag, a preliminary experiment was performed. The appropriate range of C for reducing the oxides was determined to be 5–8 wt%. Thus, in the present study, respectively 5, 6, 7, and 8 wt% C (Superior Graphite, Sweden, 6.5 μm) were added to the master slag. To reveal the effect of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> additions on the phase modification of the slag and metal formation in the reduction experiments, different amounts of Al<sub>2</sub>O<sub>3</sub> (Sasol, Germany, 25 μm) were mixed with the master slag, keeping the C addition fixed at 7 wt% (Table 2). Each mixture was wet-mixed using ethanol in a multidirectional mixer (Turbula type) for 24 h. The mixture was then dried by a rotating evaporator at 338 K (65 °C) and further dried at 353 K (80 °C) for 24 h.

### 2.2 Experimental Procedure and Characterization

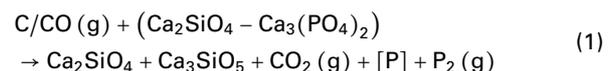
Each slag mixture (10 g) was loaded in a high purity magnesia crucible (21 mm ID, 50 mm H), which was suspended by Mo hooks in a vertical tube furnace (100–250/18, HTRV, GERO, Germany) under an Ar flow rate of 0.4 L/min. The samples were introduced at room temperature and held in the furnace at 1873 K for 1 h, followed by water quenching. The microstructure of the slag samples was quantitatively analyzed using Electron Probe Micro Analysis (FE-EPMA, JXA-8530F, JEOL Ltd, Japan) at fixed accelerating voltage (15 kV) and beam current (15 nA), focusing on the reduced Fe particles with its chemical composition, particle size, and size distribution.

## 3. Results and Discussion

Fig. 1 shows the Fe and P elemental distribution after reduction by different C additions. With the addition of 5 and 6 wt% C, most of the Fe is concentrated in the spherical metallic phase. Some Fe is found in other phases, mainly in magnesia wustite (RO). This phase is composed of monoxides, such as FeO, MnO, and MgO. With increasing C addition, Fe eventually concentrates entirely in the metallic phase as the higher C additions create stronger reduction conditions. Yet, increasing C additions also favor the transfer of P from slag to metal. As indicated by the color level, with 5 and 6 wt% C additions, very low concentrations of P can be seen in the metallic phase. At 8 wt% C addition, the concentration of P in the metallic phase is much higher.

In order to acquire accurate data on the reduction behavior of BOF slags, more than 10 metallic grains were analyzed using Wavelength-Dispersive Spectroscopy (WDS). The dissolved P content in the metallic Fe is given in Fig. 2 (black points). With 5 and 6 wt% C addition, the P content is below 0.01 wt%. With 8 wt% C addition, the P content increases to above 2 wt%. Clearly the reduction of P-containing compounds and the dissolution of P in Fe are closely related to the amount of C addition. At 5 wt% and 6 wt% C additions, the low P contents suggest that P-containing compounds cannot be reduced or volatilized after reduction. Kazuki *et al.* [12] have carried out carbothermic reduction experiments of steelmaking slag at over 1873 K using microwave processing and proved that Fe<sub>x</sub>O is more easily reduced than P oxides. Maruoka *et al.* [17] studied the distribution ratio  $L_p$  of P between metallic Fe and slag during the reduction of iron ore by CO and observed that P is reduced and dissolved in the metallic phase when the Fe<sub>x</sub>O content is below 10 wt%.

Most P in BOF slag is incorporated with Ca<sub>2</sub>SiO<sub>4</sub> (C<sub>2</sub>S) to form a C<sub>2</sub>S-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (C<sub>2</sub>S-C<sub>3</sub>P) solid solution [7]. The structure of C<sub>2</sub>S-C<sub>3</sub>P is similar to that of pure C<sub>2</sub>S, with part of the tetrahedral [SiO<sub>4</sub><sup>4-</sup>] groups substituted by tetrahedral [PO<sub>4</sub><sup>3-</sup>] groups. To maintain the charge balance, the substitution combines less Ca<sup>2+</sup> than the pure C<sub>2</sub>S [18]. During the reduction of the C<sub>2</sub>S-C<sub>3</sub>P solid solution, the P-containing compounds react with C and/or CO to break the P-O chemical bonds. After that, the released free Ca ions can combine with silicate and form Ca<sub>3</sub>SiO<sub>4</sub> (C<sub>3</sub>S). Therefore, with the reduction of P from the BOF slag, the C<sub>3</sub>S content is expected to increase. The reduction of P-rich compounds and the formation of C<sub>3</sub>S can be written as



The P distribution ratio  $L_p$  is defined as

$$L_p = \frac{(\% \text{ P})}{[\% \text{ P}]} \quad (2)$$

where (P) and [P] represent the wt% of P, respectively in

Fig. 1: Fe and P distribution at various C additions

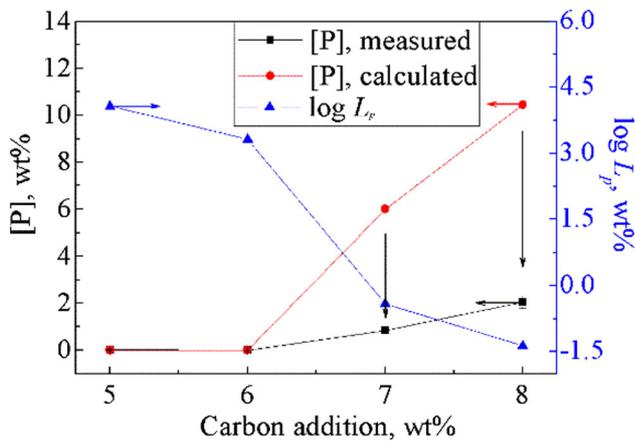
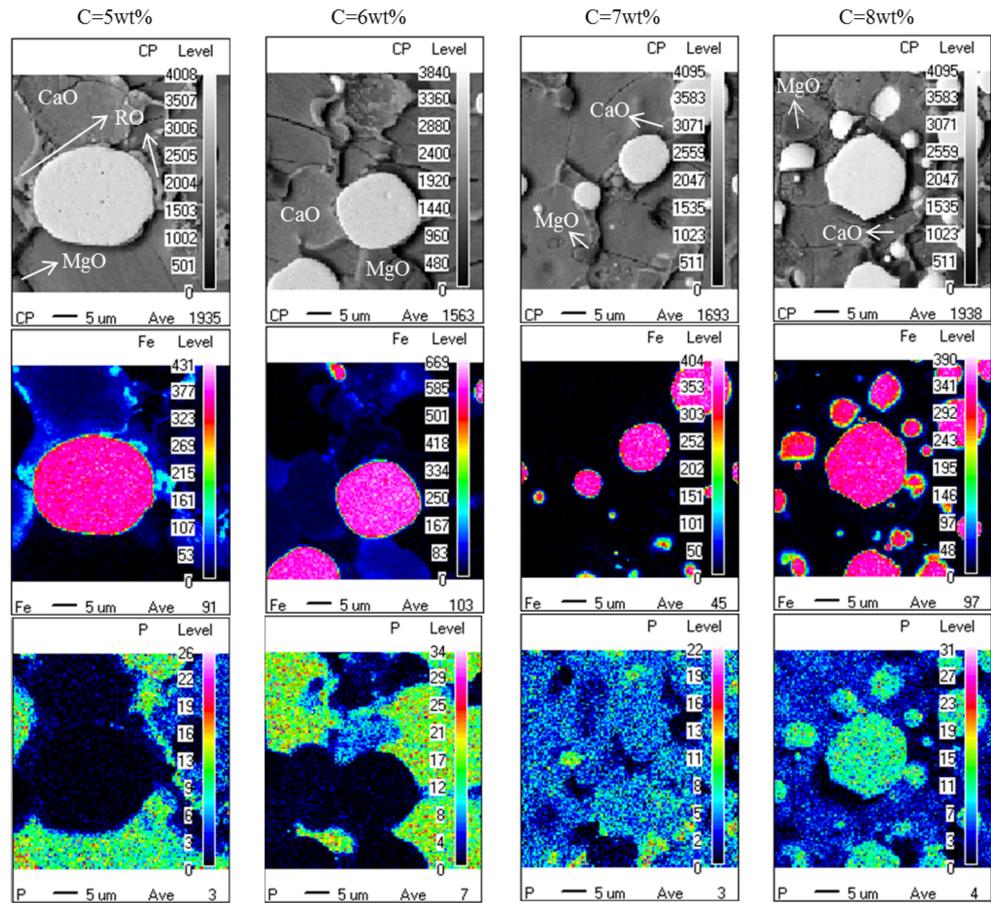


Fig. 2: P content in the metallic Fe and P distribution ratio  $L_p$

slag and metal. Lee and Fruehan [19] suggested that  $L_p$  can be estimated as

$$\log L_p = -12.24 + \frac{2000}{T} + 2.5 \log (\% \text{ FeO}) + 6.65 \log B^* + 0.13 [\% \text{ C}] \quad (3)$$

where  $T$  is the absolute temperature (K), ( $\% \text{ FeO}$ ) and  $[\% \text{ C}]$  are wt% of FeO in the liquid slag and C in the metallic Fe,  $B^*$  is the "weighted basicity" defined as  $B^* = [(\% \text{ CaO}) + 0.8(\% \text{ MgO})] / [(\% \text{ SiO}_2 + (\% \text{ Al}_2\text{O}_3) + 0.8(\% \text{ P}_2\text{O}_5))]$ .  $[\% \text{ C}]$  was

measured by WDS,  $B^*$  was calculated according to the slag composition, and ( $\% \text{ FeO}$ ) was calculated using FactSage 7.0. Then the P distribution ratio can be obtained.  $T$ ,  $[\% \text{ C}]$ , ( $\% \text{ FeO}$ ),  $B^*$  and the values of  $L_p$  are listed in Table 3.  $\log L_p$  calculated with Eq. 3 is given in Fig. 2 with the blue triangles.

By considering the mass balance of P and assuming that no P is evaporated during the reduction, the P content in the metal can be calculated as shown in the Fig. 2 (red points). The P content in the metallic Fe matches well with the experimental observation that the P-rich phase changes from the slag (mainly  $\text{C}_2\text{S}-\text{C}_3\text{P}$ ) to metallic Fe with increasing C addition (Fig. 1). With increasing C addition, the measured and calculated P contents in the metallic Fe increase significantly, but the measured increase is less than the calculated one. The reason is probably that some P evaporates after the reduction.

The consumption of C by the reduction of iron oxides can be estimated via the reaction (4):



To simplify the calculation, all iron oxides are assumed to be hematite ( $\text{Fe}_2\text{O}_3$ ). The total Fe content in the master slag is 20.58 wt% and the corresponding  $\text{Fe}_2\text{O}_3$  content is 29.4 wt%. To completely reduce the  $\text{Fe}_2\text{O}_3$ , the molar ratio of C to  $\text{Fe}_2\text{O}_3$  is 3, hence 6.48 wt% C could reduce all the iron oxides in the current slag. In the experiments, 5, 6, 7, and 8 wt% C

Carbon addition (wt%)	T (K)	[% C]	$B^*$	(% FeO)	$L_p$
5	1873	0.12	2.68	12.1	4.07
6		0.39		6.0	3.32
7		0.48		0.21	-0.41
8		1.09		0.08	-1.37

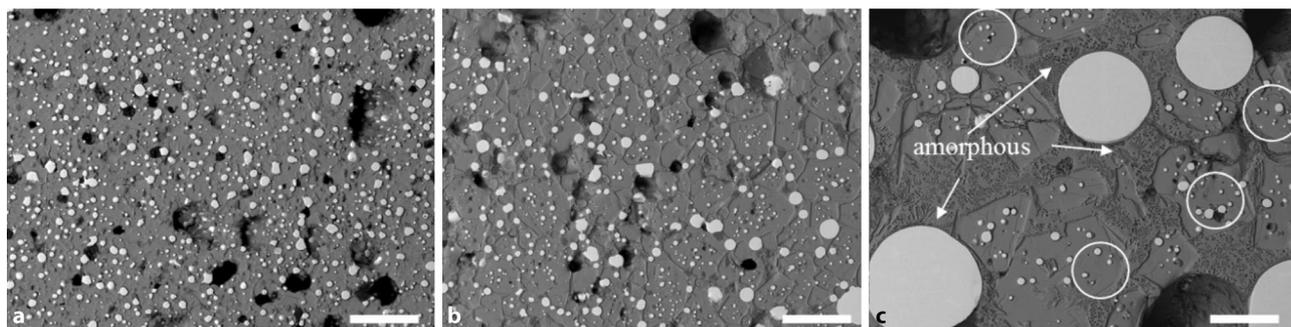


Fig. 3: Morphology of metallic Fe recovered with 7 wt% C and **a** no  $\text{Al}_2\text{O}_3$ ; **b** 5 wt%  $\text{Al}_2\text{O}_3$ ; **c** 10 wt%  $\text{Al}_2\text{O}_3$  additions. The circles show the smaller Fe particles. The scale bar is 100  $\mu\text{m}$

were used. In addition to the reduction of iron oxides, the C can also reduce other oxides, such as Mn-containing oxides and P-containing oxides. For the current slag, under the condition of 6 wt% C addition, the P content in the metallic Fe is below 0.01 wt%, and the purity of the extracted Fe is above 98 wt%, implying a promising metallic product. Therefore, to minimize the P content in the metallic Fe while maximizing the reduction of the iron oxides, it is suggested to keep the mole ratio of carbon to oxygen in the iron oxides at 1:1.

Fig. 3 shows the morphological evolution of Fe particles reduced by 7 wt% C, respectively with 0, 5, and 10 wt%  $\text{Al}_2\text{O}_3$  addition. With increasing  $\text{Al}_2\text{O}_3$  addition, the size of the particles changes significantly. Even under the same amount of  $\text{Al}_2\text{O}_3$  addition, the Fe particle size varies greatly. The particles which attach to the amorphous phase are bigger (typical diameter above 10  $\mu\text{m}$ ) than the ones which are located in the solid solutions (typical diameter below 10  $\mu\text{m}$ ).

#### 4. Conclusions

Metal recovery from a typical BOF slag with high basicity has been studied by carbothermic reduction. The reduction of Fe oxides and P oxides has been discussed, and optimized process conditions to recover high-grade metallic iron (>98 wt%) have been proposed. The formation and growth of the extracted metallic Fe has been observed, and the effects of  $\text{Al}_2\text{O}_3$  on the reduction have been investigated. With increasing C addition, the P-rich phase changes from slag to metal. By controlling C addition, it is possible to avoid contamination of metallic Fe by P during carbothermic reduction. It is suggested to keep the mole ratio of C to O in the iron oxides at 1:1, in order to minimize the P content in the metallic Fe.

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