

## RECOVERY OF IRON FROM COPPER SLAG BY CARBOTHERMIC REDUCTION AND MAGNETIC SEPARATION IN THE PRESENCE OF CaO

The carbothermic reduction of copper slag at the different binary basicity (CaO/SiO<sub>2</sub>) was carried out for recovering iron by wet magnetic separation. Calcium carbonate is found to be capable of improving the iron recovery, as well as increasing the particle size of metallic iron significantly. Experimental evidence showed that CaO reacted with SiO<sub>2</sub> to form calcium silicate and FeO was liberated from the 2FeO·SiO<sub>2</sub>, decreased the content of Fe in the slags, which improved the iron recovery during the magnetic separation. The final product, assaying 90.23%Fe<sub>total</sub> (representing a metallization degree of 93.94%) and 0.58% Cu at the iron recovery of 85.70% was achieved at the basicity of 0.60, which can be briquetted as a burden material for weathering resistant steel making by electric arc furnace to replace part of scrap.

*Keywords:* copper slag, recovery of iron, carbothermic reduction, magnetic separation

### 1. Introduction

Copper slag is a solid waste during pyrometallurgical production of copper from copper sulfide concentrates, about 2.2 tonnes of which being generated per tonne of metal copper production. In China, it is estimated that about 10 million tonnes of copper slag are generated every year and about 100 million tonnes of copper slag are stacked [1,2]. Dumping or disposal of such huge quantities of slag causes not only secondary environmental pollution due to the high content of Cu, Pb, Zn and S in copper slag, but also wastes resources because of about 40% iron occurring in copper slag [3-5]. Therefore, the research of recovering valuable metals from copper slag has notable economic benefits and significant social benefits.

In order to utilize the copper slag, various methods were investigated to recover the valuable metals in the previous research, such as pyrometallurgical, hydrometallurgical, and mixed pyro-hydrometallurgical processes [3,6-8]. Since the iron of copper slag mainly exists in the form of fayalite and magnetite with the fine particle size, it is difficult to separate iron from copper slag. Carbothermic reduction is an effective technology to treat the secondary resources containing ferrous and refractory iron ores [9-12]. Li et al., reported the recovery of iron from copper slag by deep reduction and magnetic separa-

tion and the metallic iron was obtained [13]. But the reduction temperature was higher at 1300°C and reduction duration was longer for 180 min. Long et al., reported that calcium fluoride (CaF<sub>2</sub>), can effectively improve the iron grade and recovery in treating copper slag using carbothermic reduction and magnetic separation [14], but fluorine is harmful to the metallic iron. Many works and evidences proved that most iron exists in the form of fayalite, and CaO is more easily react with SiO<sub>2</sub> than FeO [15-16], and calcium silicate is more stable than fayalite in the high temperature. Therefore, the calcium carbonate (CaCO<sub>3</sub>) was employed as a additive in this paper.

### 2. Experimental

#### 2.1. Raw materials

The copper slag used in this study was collected from Tongling nonferrous company, China. Table 1 shows the chemical composition of the copper slag. The contents of Fe<sub>total</sub>, FeO and SiO<sub>2</sub> are 38.95%, 43.36% and 32.76%, respectively. As shown in Fig. 1, iron mainly exists as the fayalite (2FeO·SiO<sub>2</sub>) and magnetite. The size distribution of the copper slag is 95% passing 0.074 mm.

TABLE 1

Chemical composition of copper slag /wt%

Element	TFe	FeO	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Cu	Pb	Zn	S
Content	38.95	43.36	32.76	4.25	1.33	2.91	0.42	0.20	2.64	0.15

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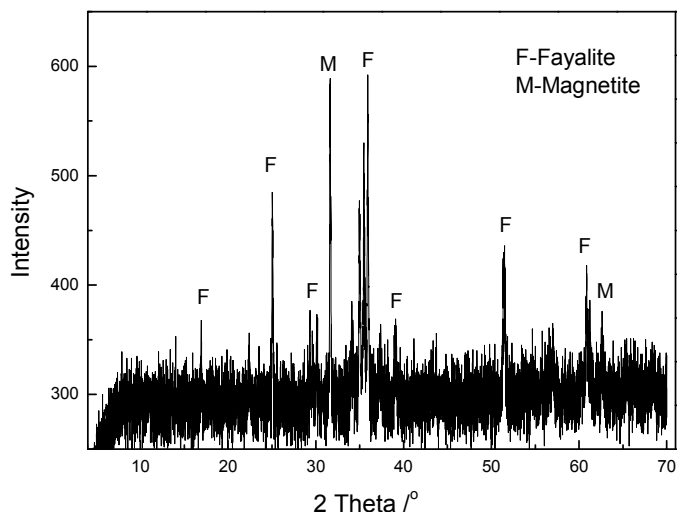


Fig.1 X-ray diffraction pattern of the copper slag

The analytical reagent of calcium carbonate ( $\text{CaCO}_3$ ) was employed as the additive during the experiment. The coke fines was used as the reductant with the fixed carbon on air-dry basis (FCad) of 87.15%, volatile matter on dry ash-free basis (Vdaf) of 1.88%, ash on air-dry basis (Aad) of 10.46%, S content of 0.38%. The size distribution of coke fines is 85% passing 0.074 mm.

## 2.2. Experimental methods

The experimental process includes briquetting, high temperature reduction of briquettes and magnetic separation of reduced briquettes, as shown in Fig. 2.

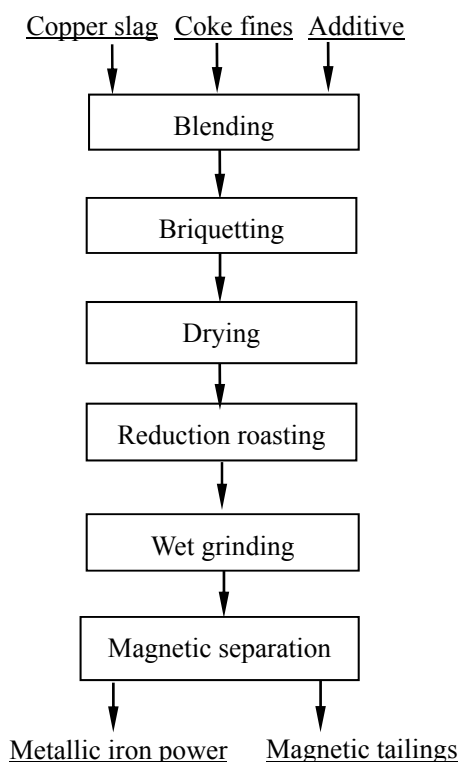


Fig. 2. The flowsheet of the whole processes

Cylindrical briquettes with 10 mm in diameter and 10 mm in height were produced by pressing 2.5 g of the mixture of copper slag, calcium carbonate and coke fines with 8% water (based on dry basis) into a cylindrical mold for 1min. The sketch of the briquettes is shown in Fig. 3. The pressure of 8 MPa was made by a vertically loading piston. Then the briquettes were dried at 105°C for 4 h in the oven. The graphite crucible with 100 mm in diameter and 100 mm in height, containing 50 g dried briquettes, was put into the muffle furnace when temperature was elevated to the target value. After the crucible had stayed in the furnace for the desired time, nitrogen with flow rate of 1 L/min was introduced to cool down, which could protect the reduced briquettes to avoid re-oxidization [14]. The magnetic separation was performed in the magnetic tube after the reduced briquettes being ground in the cone ball mill. The final iron concentrate (metallic iron powder) was obtained after magnetic separation at the grinding fineness of 90% powder passing 0.074 mm and the magnetic intensity of 0.08 T. After carbothermic reduction, the iron oxides were reduced into metallic iron, so the low intensity magnetic field was used to recover the metallic iron. During our previous research, the iron grade decreased at the magnetic intensity higher than 0.08T, and the iron recovery dropped at the magnetic intensity lower than 0.08T [17]. Therefore, the magnetic intensity of 0.08 T was chose in this experiment. The model of cone ball mill is XMQ240×90 and the laboratory magnetic equipment is Davis tube of XCGS-73.

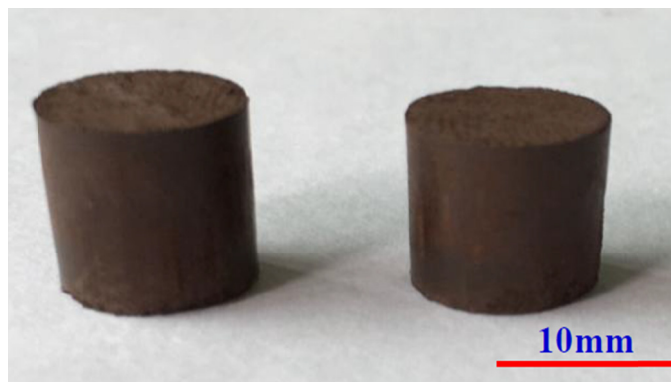


Fig. 3. The sketch of the briquettes

The crystalline phase of copper slag was investigated by XRD (powder X-ray diffraction) technique, using Ni-filtered  $\text{Cu K}\alpha$ , operated at 40 kV and 100 mA and at the scanning rate of  $4^\circ \text{ min}^{-1}$  from 5 to  $80^\circ$ . The structures and element distribution of reduced briquettes were analyzed by SEM (scanning electron microscope) with EDS (energy dispersion system). The total iron ( $\text{Fe}_{\text{total}}$ , wt%) content and metallic iron (MFe, wt%) content in iron concentrate (metallic iron powder) were analyzed by chemical methods, and the metallization degree ( $\lambda = \text{MFe} \times 100 / \text{TFe}$ , %) was calculated. The iron recovery was calculated as  $\varepsilon = \gamma * \beta_{\text{Fe}} / \alpha_{\text{Fe}}$ , %; where  $\gamma$  is the yield of iron concentrate after the magnetic separation, wt%;  $\beta_{\text{Fe}}$  is the  $\text{Fe}_{\text{total}}$  content of the iron concentrate, wt%;  $\alpha_{\text{Fe}}$  is the  $\text{Fe}_{\text{total}}$  content of the reduced briquettes, wt%.

### 3. Results and discussion

#### 3.1. Basicity

Fig. 4 illustrates the effect of binary basicity ( $\text{CaO}/\text{SiO}_2$ ) on the qualities of the iron concentrate. The iron grade dropped from 93.36% to 85.30%, while the iron recovery increased sharply from 64.43% to 88.70% when basicity was increased from 0.06 (without adding calcium carbonate) to 0.90. The more liquid phase was generated in the absence of CaO, because of the high content of  $\text{SiO}_2$  in the copper slag, leading to the growth of metallic iron grain, which increased the iron grade. But more iron still exist in the form of  $2\text{FeO}\cdot\text{SiO}_2$ , which can not be recovered by the following magnetic separation, resulting in the low iron recovery. When basicity was increased, FeO was liberated and reduced to metallic iron because CaO could react with  $\text{SiO}_2$  and formed calcium silicate, which led to the high iron recovery.

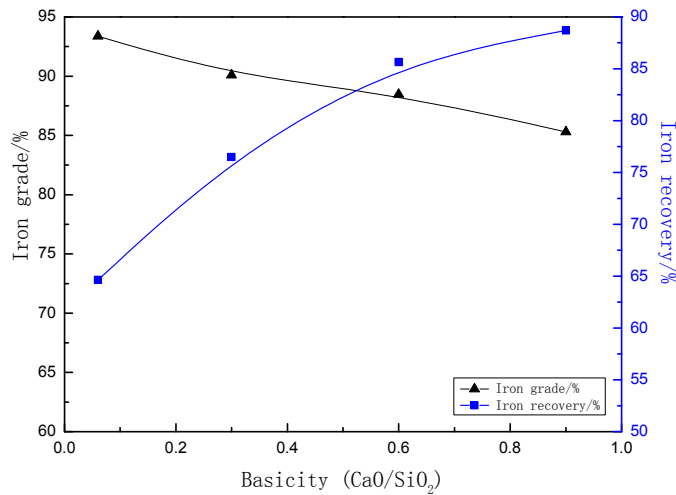
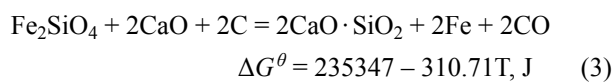
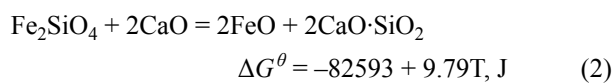
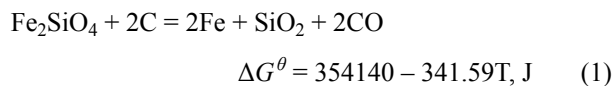


Fig. 4. Effect of basicity on the qualities of the iron concentrate (briquettes with 12% coke fines roasting at 1250°C for 30 min)

When the coke fines are introduced to the carbothermic reduction process,  $\text{Fe}_2\text{SiO}_4$  in the copper slag can be reduced to metallic iron by the reactions with carbon. Additive CaO reacts with  $\text{Fe}_2\text{SiO}_4$  during the reduction roasting. The possible reactions can be expressed with the following equations.



The relationships of  $\Delta G^\theta$  and temperatures for reactions (Eqs. (1-3)) are illustrated in Fig. 5, and these reactions are easy

to occur according to thermodynamic calculation. As shown in equation (1), the starting temperature for the reaction between  $\text{Fe}_2\text{SiO}_4$  and C is 1037 K. It is noted that CaO can promote the decomposition of  $\text{Fe}_2\text{SiO}_4$ , improve the activity of FeO and reduce the starting temperature from 1037 K down to 757 K (as shown in equation (3)).

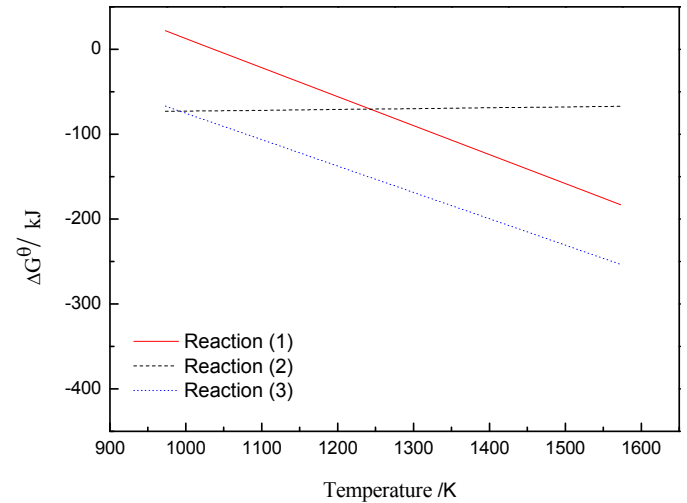


Fig. 5. The correlation of standard free energy ( $\Delta G^\theta$ ) with temperature for Eqs. (1-3)

Fig. 6 shows the macrostructures of reduced briquettes at the different basicity. With the increase of basicity, the content of liquid phase was decreased. The briquettes were melted after reduction roasting at the basicity of 0.06, while the briquettes at the basicity of 0.60 and 0.90 still kept the shape unchanged.

Figs. 7 and 8 shows the SEM-EDS of reduced briquettes at the basicity of 0.06 and 0.60, respectively. The metallic iron grains are pure and embrace some of metal Cu (Point 1 in Figs. 7 and 8). The size of metallic iron grains is small and dispersive in the reduced briquettes at 0.06 basicity, while the size of metallic iron grains is large and interconnecting at 0.60 basicity. The compositions of slag were very complicated at 0.06 basicity, and the Fe, Si and O elements are still 38.73%, 25.85% and 21.63%, respectively (Point 2 in Fig. 7), which indicated that the iron can not be recovered during the following magnetic separation because iron presented in the form of nonmagnetic ferro-silicate.

By contrast, increasing the basicity can significantly promote the growth of metallic iron grains. Compared with the reduced briquettes at the basicity of 0.06, and the content of ferro-silicate was decreased, which also confirmed the high iron recovery at the basicity of 0.60 (Point 2 in Fig. 8). The calcium silicate content was increased as increased the basicity (Point 3 in Figs. 7 and 8), which indicated that CaO replaced FeO from fayalite to form new phases of calcium silicate during the reduction roasting. The surface charging of non-conductive sample effected the SEM images in Figure 7 and 8 because of the equipment, but it had no affect on the testing results.



Fig. 6. Reduced briquettes after reduction roasting at the different basicity (briquettes with 12% coke fines roasting at 1250°C for 30 min)

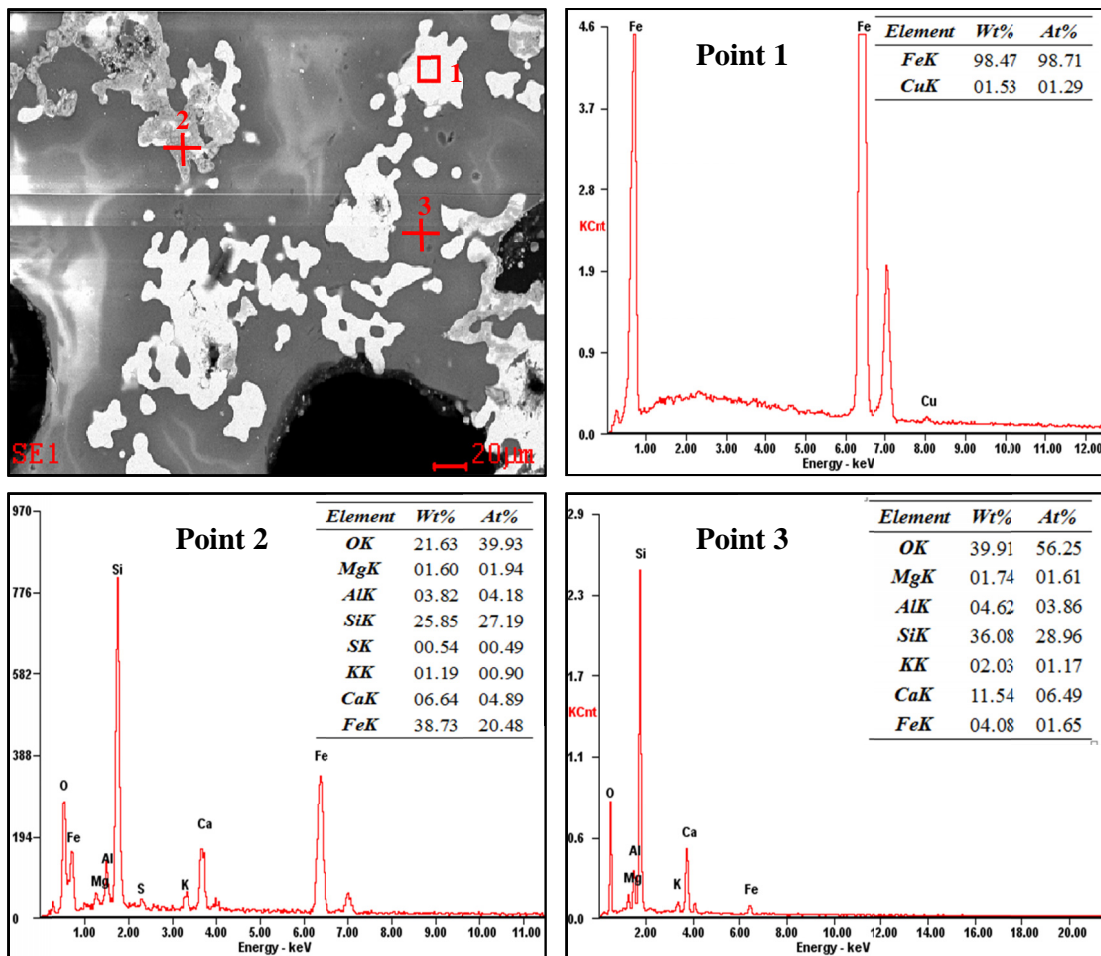


Fig. 7. SEM-EDS of reduced briquettes at the basicity of 0.06 (briquettes with 12% coke fines roasting at 1250°C for 30 min)



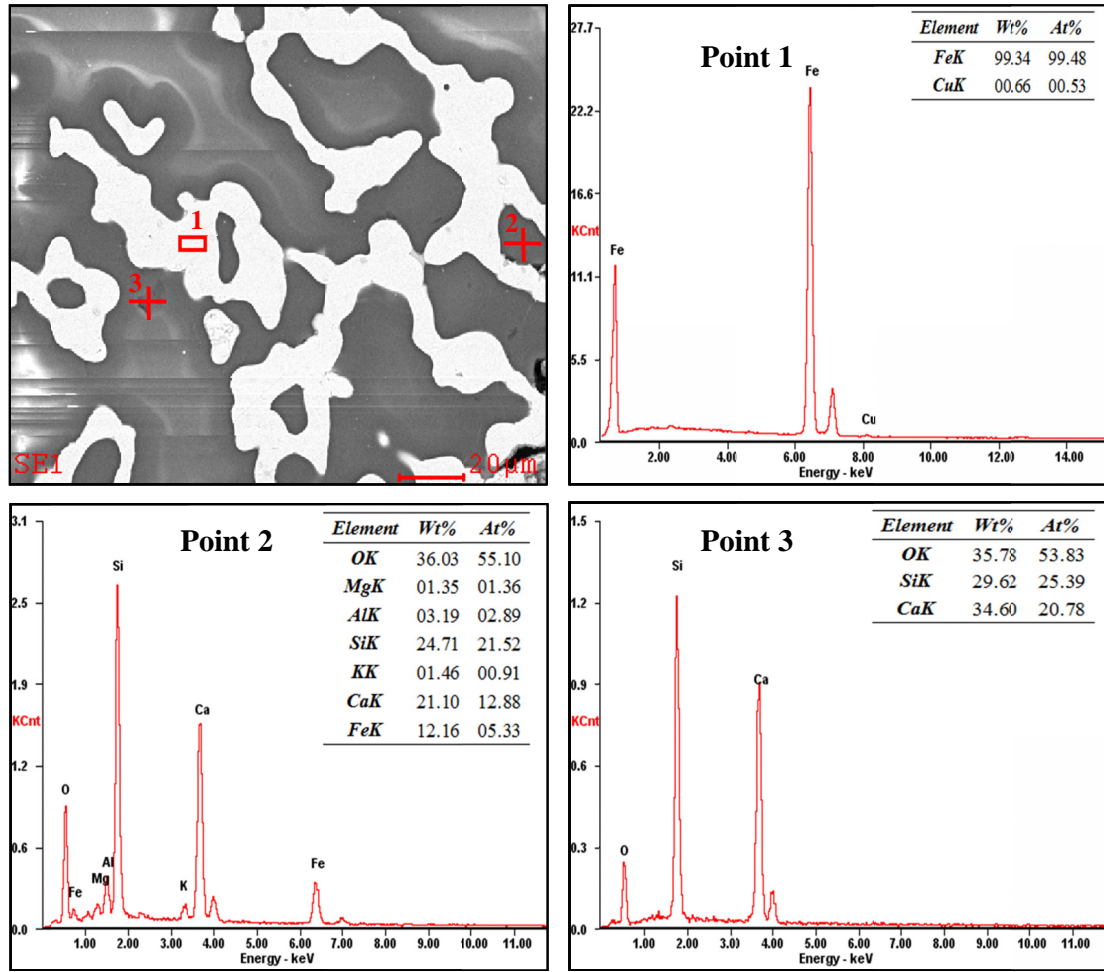


Fig. 8. SEM-EDS of reduced briquettes at the basicity of 0.60 (briquettes with 12% coke fines roasting at 1250°C for 30 min)

### 3.2 Reduction temperature

Fig. 9 shows the effects of reduction temperature on the qualities of the iron concentrate. Due to the fact that carbothermic reduction is an endothermic reaction, increasing temperature is an effective way to improve the reduction of iron oxides. The higher the reduction temperature is given, the higher iron grade and iron recovery of iron concentrate are obtained. In addition, increasing the temperature also promotes the reactions between CaO and SiO<sub>2</sub>. When reduction temperature was elevated from 1200°C to 1300°C, the iron grade of iron concentrate increased from 83.39% to 90.23%, and the iron recovery increased from 80.32% to 87.70%. The iron grade and iron recovery increased slightly when the temperature was enhanced into 1350°C. In consideration of the more energy consumption at higher roasting temperature, 1300°C is recommended.

### 3.3. Reduction time

The effect of reduction time on the qualities of the iron concentrate is presented in Fig. 10. When reduction time was extended from 20 to 30 min, the iron grade upgraded from 84.32% to 90.23%, and then leveled off. The iron recovery also

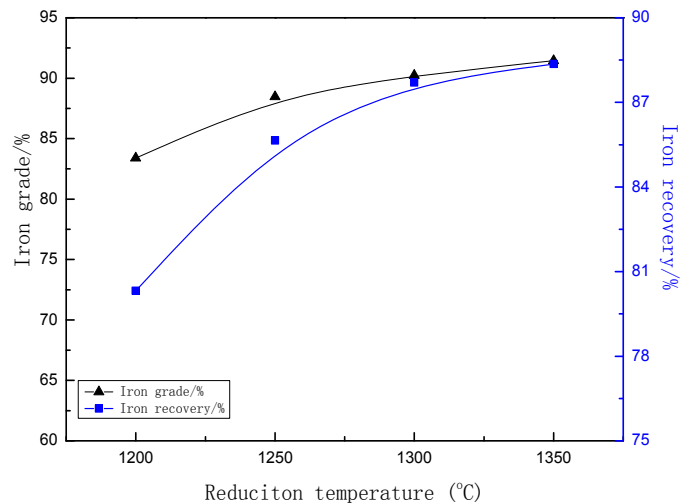


Fig. 9. Effect of reduction temperature on the qualities of the iron concentrate (briquettes with 12% coke fines and 0.60 basicity roasting for 30 min)

increased significantly when reduction time was prolonged. It was inferred that the suitable reduction time was 30 min, when the reduction reactions of iron oxides, and reactions between CaO and SiO<sub>2</sub> were mostly completed at 1300°C for 30 min.

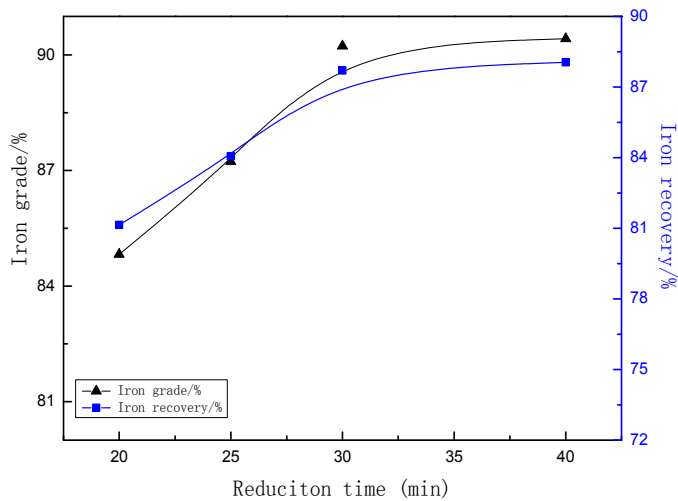


Fig. 10. Effect of reduction time on the qualities of the iron concentrate (briquettes with 12% coke fines and 0.60 basicity roasting at 1300°C)

### 3.4. Dosage of coke fines

Fig. 11 presents the effect of coke fines dosage on the qualities of iron concentrate. Dosage of coke fines is also an important factor during high temperature reduction. The more the dosage of coke fines is, the higher the reducing atmosphere is, which can improve the reduction reaction of iron oxides. However, the cost would be increased when more coke fines is used. Therefore, 12% coke fines was suitable during this experiment.

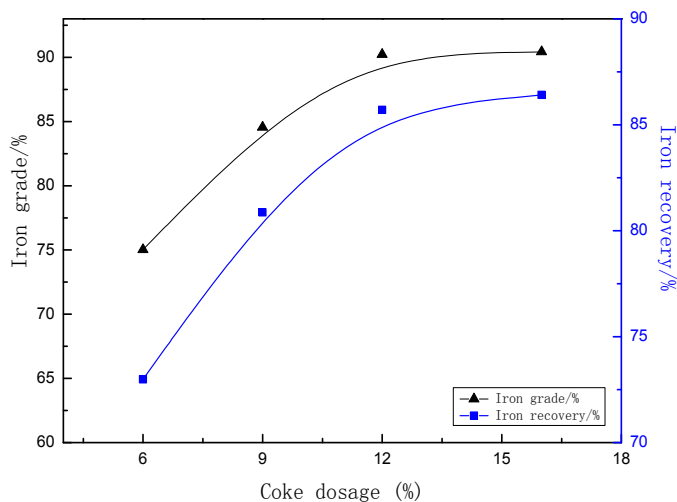


Fig. 11. Effect of coke dosage on the qualities of iron concentrate (briquettes with 0.60 basicity roasting at 1300°C for 30 min)

### 3.5. Analysis of final product

The final product, assaying 90.23%  $Fe_{total}$  (representing a metallization degree of 93.94%) at the iron recovery of 85.70% was achieved under the conditions of adding 12% coke fines and 0.60 basicity, reducing at 1300°C for 30min. The chemical composition of final metallic iron powder obtained is shown in Table 2. The iron grade of metallic iron powder was higher than 90% and other impurities, such as the contents of sulfur and phosphorus were low. During the carbothermic reduction, the copper oxides, zinc oxides and lead oxides were reduced into metallic copper, zinc and lead. The zinc and lead were vaporized in the gas, while the metallic copper was kept in the metallic iron. The Zn and Pb content in the final product are low with 0.01% and 0.02%, respectively, but the Cu content is higher with 0.58%. Because of the requirement of adding copper to manufacture the weathering resistant steel (0.15-0.75% Cu) [18], the final product after briquetting can be used as the burden for weathering resistant steel making by electric arc furnace.

### 4. Conclusions

The principal findings of the study can be summarized as follows:

- (1) Most iron exists in the form of fayalite and magnetite in the copper slag. The technology of carbothermic reduction and magnetic separation is an effective way to recover iron from the copper slag in the presence of CaO. During the reduction roasting, CaO reacted with  $SiO_2$ , forming the calcium silicate, improving the size growth of metallic iron particles, which improved the iron grade and iron recovery.
- (2) The metallic iron powder, assaying 90.23%Fe (representing a metallization degree of 93.94%) obtained at the iron recovery of 85.70% was achieved under the optimum conditions. The metallic iron powder obtained can be briquetted as a burden material for weathering resistant steel making by electric arc furnace.

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TABLE 2

Chemical composition of the final product wt%

Item	TFe	MFe	$SiO_2$	CaO	$Al_2O_3$	Cu	Pb	Zn	S	P
Content	90.23	84.76	3.58	0.42	0.36	0.58	0.02	0.01	0.04	0.07

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