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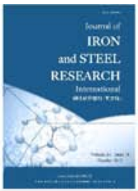

Recovery of iron and copper from copper tailings by coal-based direct reduction and magnetic separation

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ABSTRACT

A technique comprising coal-based direct reduction followed by magnetic separation was presented to recover iron and copper from copper slag flotation tailings. Optimal process parameters, such as reductant and additive ratios, reduction temperature, and reduction time, were experimentally determined and found to be as follows: a limestone ratio of 25%, a bitumite ratio of 30%, and reduction roasting at 1473 K for 90 min. Under these conditions, copper-bearing iron powders (CIP) with an iron content of 90.11% and copper content of 0.86%, indicating iron and copper recoveries of 87.25% and 83.44% respectively, were effectively obtained. Scanning electron microscopy and energy dispersive spectroscopy of the CIP revealed that some tiny copper particles were embedded in metal iron and some copper formed alloy with iron, which was difficult to achieve the separation of these two metals. Thus, the copper went into magnetic products by magnetic separation. Adding copper into the steel can produce weathering steel. Therefore, the CIP can be used as an inexpensive raw material for weathering steel.

1. Introduction

Copper is an important raw material in economic development, and increasing demands for the metal both in China and abroad have caused the copper industry to expand significantly in recent years. China is one of the most important copper producers and consumers throughout the world; the country produces a ton of refined copper for every nearly 2—3 tons of copper slag discharged. Thus, over 15 million tons of converter copper slags are produced each year[1]. The copper in these slags is preferentially recovered by flotation with a chemical agent. However, the residual solid wastes which are called copper tailings in this paper are still discarded as waste in large quantities. These copper tailings require large areas of land to store and reduce the area of usable farmland[2-4]. The construction and maintenance of copper tailing disposal sites has also increased the production cost of steelmaking plants. Even more problematic for environmental reasons is the release of chemical reagents, such as xanthate and alkaline oxides, from these storage sites, which could cause serious pollution of the soil and water[5,6].

Although the total iron content in copper tailings is relatively high, its recovery has not been developed because tailings contain large amounts of chemical reagents and are composed of a complex mixture of minerals. The particle size of ferrous minerals in copper tailings is usually small, and their compositions are also complicated[7-9]. Obtaining high-grade iron concentrate directly is difficult to achieve using traditional mineral processing techniques[10,11]. Coal-based direct reduction followed by magnetic separation has been demonstrated to be an effective method for iron recovery from solid wastes. Several researchers have investigated the production of direct reduction iron powder (DRIP) from red mud[12], iron ore tailings[13], vanadium tailings[14], cyanide tailings[15], oily hot rolling mill sludge[16], nickel metallurgical slag[17], blast furnace gas ash[18] and so on by using coal-based direct reduction followed by magnetic separation. In this process, solid wastes mixed with a reductant and additives are reduced to metallic iron, after which the roasted ores are ground and separated by mag-

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netic separation to produce DRIP. The DRIP product obtained from this process generally contains more than 90 wt. % Fe and may be used as a substitute for steel scrap in electric arc furnaces for steelmaking[19].

Adding copper to steel can produce weathering steel with improved corrosion resistance, strength, fatigue resistance, weldability, and toughness[20,21]. The content of copper in weathering steel is generally less than 0.6 wt. %[22]. Because of its good resistance to atmospheric corrosion, weathering steel is widely used in ships, bridges, railways, pipeline, and other important areas[22,23]. The present work thus aims to recover iron and copper simultaneously from copper tailings by using the coal-based direct reduction-magnetic separation technique. Here, copper and iron minerals are reduced. After grinding and magnetic separation, copper-bearing iron powders (CIP) are obtained. This CIP could be used as an inexpensive raw material for smelting weathering steels. In this study, the effects of reduction conditions, such as additive and reductant ratio, reduction time, and reduction temperature, on the quality of the CIP produced were investigated.

2. Experimental

2.1. Materials

The copper tailings used in the study were residual slags obtained after copper recovery from copper slag by flotation. Multi-element analysis results of the copper tailings are shown in Table 1. The total iron content of the slag was approximately 42.20%, and the tailings included about 0.39% Cu. The copper tailings in the experiments were ground to 80 wt. % passing 0.074 mm. The index of basicity, $R=(w_{\mathrm{CaO}}+w_{\mathrm{MgO}})/(w_{\mathrm{SiO_2}}+w_{\mathrm{Al_2O_3}})$, was 0.29, which indicated that the copper tailings could be considered as acid slag.

Table 1

Multi-element analysis of copper tailings (mass%)

TFe	Cu	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O
42.20	0.39	32.66	3.20	4.46	5.93	0.47	0.33
MnO	TiO_2	Pb	Zn	Co	P	S	As
0.071	0.22	0.22	1.55	0.011	0.074	0.39	0.07

The X-ray diffraction (XRD) pattern of the copper tailings is shown in Fig. 1. The main iron minerals in the slag include fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). Peaks of copper minerals are not detected in the tailings, likely because of their low copper content. The gangue mineral is hedenbergite. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) images of the copper tailings are illustrated in Fig. 2. Fig. 2(a) shows the SEM image of the copper tailings and Fig. 2(b−e) provides detailed EDS analyses of points 1−4 in Fig. 2(a). The main copper mineral is copper matte (Fig. 2(b)), most of which is dispersed in the fayalite (Fig. 2(c)), magnetite (Fig. 2(d)), and hedenbergite (Fig. 2(e)) as small beads. These results illustrate the difficulty of recovering copper and iron through traditional separation processes.

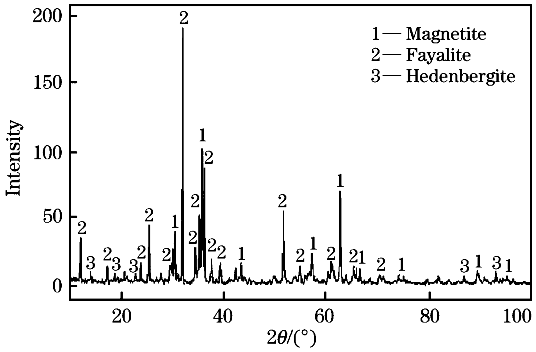


Fig. 1. XRD pattern of flotation tailings.

Bituminous coal was used as the reductant. The industrial analysis results of the bitumite show contents of 56.41% fixed carbon, 30.12% ash, 11.62% volatile matter, and 1.85% moisture. The bitumite was crushed into particles under 2 mm, and limestone, as an additive, was crushed into particles under 0.5 mm. The composition analysis of the limestone is shown in Table 2.

2.2. Principles

For copper tailings, the purpose of coal-based direct reduction is to reduce ferrous minerals and copper mattes to metallic iron and metallic copper, respectively. The reaction mechanism is expressed via the following equations[24,25]:

$$C(s)+CO_2(g)=2CO(g) \tag{1}$$

$$Fe_3O_4+CO(g)=3FeO+CO_2(g) \tag{2}$$

$$FeO+CO(g)=Fe+CO_2(g) \tag{3}$$

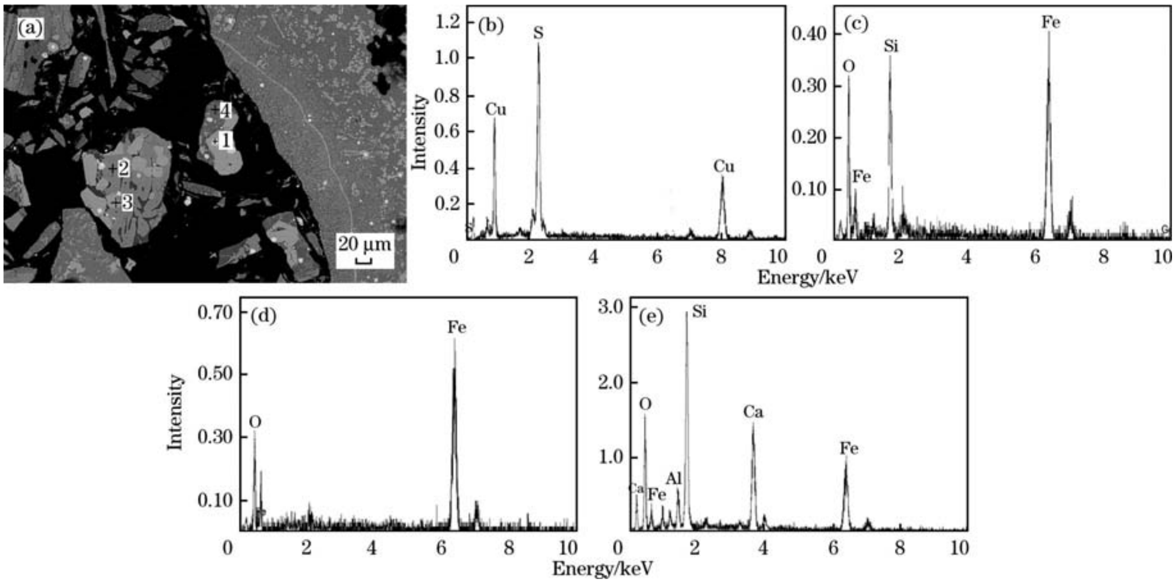
$$Fe_2SiO_4+CaCO_3+CO(g)=2Fe+CaSiO_4+2CO_2(g) \tag{4}$$

$$Fe_2SiO_4+2CO(g)=2Fe+SiO_2+2CO_2(g) \tag{5}$$

$$CuS+CO(g)+CaCO_3=Cu+CaS+2CO_2(g) \tag{6}$$

The calculated thermodynamic results for Eqs. (1)−(6) are shown in Fig. 3 to reveal the relationship between ΔG^0 and temperature. The overall reduction rate for coal-based direct reduction was revealed to be mainly controlled by the gasification reaction rate, i.e., the Boudouard reaction (Eq. (1))[26]. Taking Eq. (2) as an example, the relationship between reduction rate and other pertinent parameters is shown in Eq. (7)[25]:

$$t_R=\frac{R'}{A\exp(-E_0/RT)K\times M_c}+\frac{r_0\rho_0}{3D_e}[1/2-1/3R'-1/2(1-R')^{2/3}] \tag{7}$$

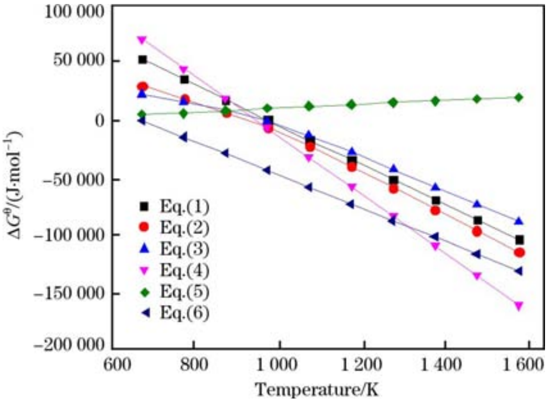


(a) SEM image of copper tailings; (b) EDS image of point 1; (c) EDS image of point 2; (d) EDS image of point 3; (e) EDS image of point 4.

Fig. 2. SEM and EDS images of copper tailings.

Table 2
Composition analysis of limestone (mass%)

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	P	S	Ignition loss
47.89	4.96	2.72	2.09	0.62	0.005	0.062	41.81



Data were obtained using HSC 6.0 software.

Fig. 3. Correlation of standard free energy (ΔG^θ) with temperature for Eqs. (1)—(6).

where, t_R is the time of Fe_3O_4 reduction, s; A is the reaction constant; R' is the reduction rate defined as the percentage of the oxides reduced, %; K is the equilibrium constant of the iron reduction reaction; M_c is the weight ratio of coal, %; E_0 is the activation energy, J · mol^{-1} · K^{-1}; R is the ideal gas constant, 8.314 J · mol^{-1} · K^{-1}; T is the temperature, K; r_0 is the grain radius when reduction rate is R', mm; ρ_0 is the oxygen contained in Fe_3O_4 initially, mol · m^{-3}; and D_e is the diffusion coefficient in the solid phase, m^2 · s^{-1}.

Eq. (7) demonstrates that the parameters influencing coal-based direct reduction are reduction temperature, reduction time, and carbon ratio. According to Fig. 2, addition of $CaCO_3$ is beneficial to the reduction of copper mattes. Furthermore, comparison with the ΔG^θ for Eq. (5) at reduction temperatures above 900 K indicated that addition of $CaCO_3$ can promote the reduction of fayalite via Eq. (4). Therefore, limestone ratio, bitumite ratio, reduction time, and reduction temperature are main factors controlling the extent of coal-based direct reduction of copper tailings, and should be experimentally determined.

2.3. *Experimental methods*

The copper tailings (20 g) were thoroughly blended with limestone and bitumite, to produce a mixture ore. The ratios of limestone and bitumite applied in this work refer to the proportion of their mass to the copper tailings and were expressed as a percentage. The mixture ore was placed in a graphite crucible that was moved into a muffle furnace chamber at a set temperature for a set time. The roasted ore was cooled to room temperature and subjected to two stages of grinding-magnetic separation. Grinding was conducted in a rod mill (RK/BM-1.0L, Wuhan Rock Crush & Grind Equipment Manufacturing Co., Ltd., China) at a speed of 289 r/min. The roasted ore was ground to about 85.00 wt. % passing 0.074 mm at the first grinding stage and then to about 90.00 wt. % passing 0.043 mm at the second grinding stage. An XCGS-73 magnetic tube with a magnetic field intensity of 111 kA/m was used to recover metallic iron. The resulting magnetic products were referred to as the CIP and the nonmagnetic products were referred to as tailings. In these experiments, the tailing yield was about 45% and the CIP yield was about 55%. A process flowsheet describing the direct reduction and magnetic separation of the copper tailings is shown in Fig. 4.

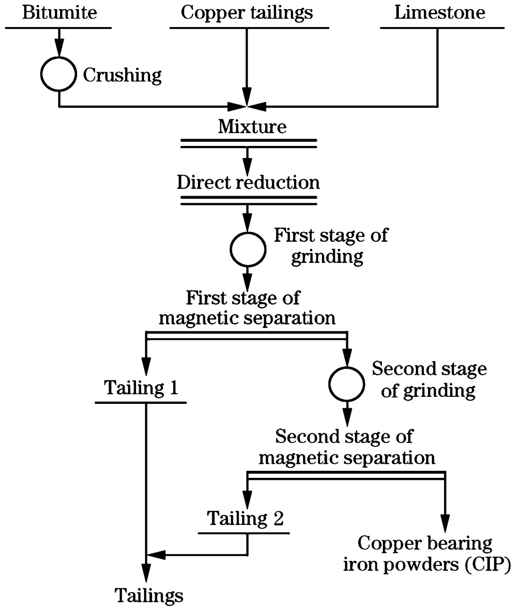


Fig. 4. Process flowsheet of direct reduction and magnetic separation of copper tailings.

The total iron content, iron recovery, copper content, and copper recovery of the CIP were used to determine the effectiveness of direct reduction followed by magnetic separation. The iron and copper recovery was calculated using Eqs. (8) and (9).

$$F_r=\frac{M_C F_C}{M_t F_t}\times 100\% \tag{8}$$

$$C_r=\frac{M_C C_C}{M_t C_t}\times 100\% \tag{9}$$

where, F_r and C_r are the Fe and Cu recoveries, respectively; M_C and M_t are the masses of CIP and the copper tailings, respectively; F_C and F_t are the iron contents of CIP and the copper tailings, respectively; and C_C and C_t are the copper contents of CIP and the copper tailings, respectively.

2. 4. *Analysis and characterization*

Multi-element analyses were conducted at the analytical laboratory of China University of Geosciences (Beijing). XRD (Rigaku DMAX-RB, Japan) using CuKα radiation and a secondary monochromator was applied to identify the phases formed in the product, and samples were scanned over the 2θ range of 10° to 100°. SEM with EDS (Carl Zeiss EVO18) was carried out on the roasted ores by mounting in epoxy resin and polishing.

3. Results and Discussion

3. 1. *Effects of limestone ratio on direct reduction and magnetic separation*

The effect of limestone ratio on the direct reduction and magnetic separation of copper tailings was investigated. The experiments were performed at a reduction temperature of 1473 K, reduction time of 90 min, and bitumite ratio of 20%. The experimental results are shown in Fig. 5.

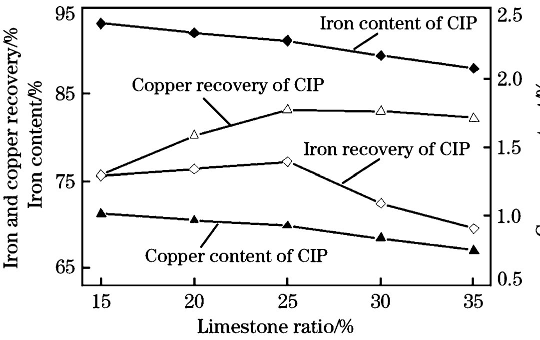


Fig. 5. Effects of limestone ratio on direct reduction and magnetic separation.

Fig. 5 demonstrates that the variation trends of the content (or recovery) of iron and copper are similar. The iron and copper recoveries of the CIP increased from 75.68% to 77.23% and from 75.73% to 83.19%, respectively, as the limestone ratio increased from 15% to 25%. As the limestone ratio was further increased from 25% to 35%, iron and copper recoveries showed slight decrease. The iron and copper contents of the CIP decreased from 93.17% to 87.97% and from 1.02% to 0.75%, respectively, as the limestone ratio increased from 15% to 35%. It is because $CaCO_3$ in the limestone can promote the reduction of iron oxide and copper mattes, FeO content in the slag will reduce and less low melting point materials will form which in turn improve the melting point and viscosity of the slag[27]. As a result, the diffusion of mass in the slag is limited, and thereby the growth and aggregation of metallic iron and copper is hindered in the reduction roasting process. This mechanism may explain why the iron and copper contents of the CIP decrease with increasing limestone dosage. Increased limestone usage can also increase the impurities in the products, thereby deteriorating the conditions required for the solid-solid reaction between minerals and the reductant in the reduction system. Thus, the iron and copper recoveries show a slight decrease at limestone ratios are beyond 25%.

The results above demonstrate that the limestone ratio exerts a great influence on the reduction of copper tailings. The optimal limestone ratio determined in this experiment is 25%.

3.2. Effects of reduction time on direct reduction and magnetic separation

The effect of reduction time on the direct reduction followed by magnetic separation of copper tailings was investigated. The experiments were performed at a reduction temperature of 1473 K, bitumite ratio of 20%, and limestone ratio of 25%. The experimental results are shown in Fig. 6.

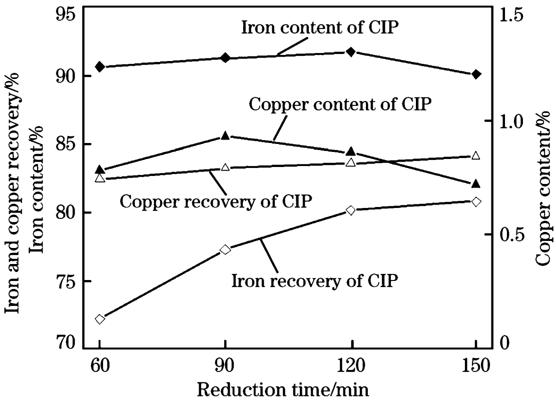


Fig. 6. Effect of reduction time on direct reduction and magnetic separation.

As shown in Fig. 6, increasing the reduction time benefits iron and copper recovery of CIP, because prolonging time is beneficial to the reduction of iron and copper minerals. Iron and copper minerals can be fully reduced when reduction lasts for 90 min. Further increases in reduction time do not significantly improve the iron and copper grades obtained and require more energy to maintain. Therefore, the optimum reduction time is 90 min.

3.3. Effects of bitumite ratio on direct reduction and magnetic separation

The effect of bitumite ratio on the direct reduction followed by magnetic separation of copper tailings was investigated. The experiments were performed at a reduction temperature of 1473 K, limestone ratio of 25%, and reduction time of 90 min. The experimental results are shown in Fig. 7.

As shown in Fig. 7, the iron and copper recoveries of CIP increased rapidly as the bitumite ratio increased from 10% to 30% but leveled off above 30%. The iron and copper contents of the CIP changed minimally during this period. When the bitumite ratio exceeded 30%, the iron and copper recoveries of CIP tended to remain stable, likely because the quantity of coal available was sufficient for direct reduction. Moreover, excess bitumite addition results in more coal ash. Thus, a bitumite ratio of 30% is optimal for the technique under study.

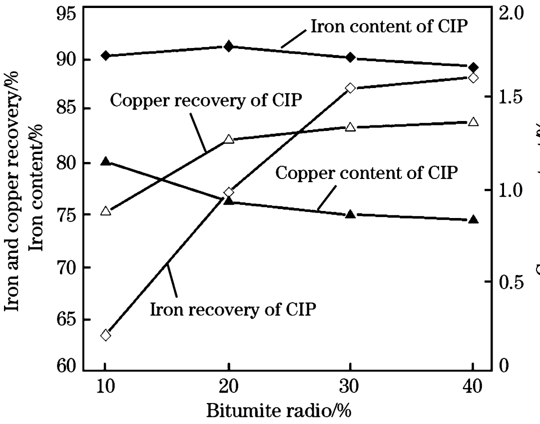


Fig. 7. Effect of bitumite ratio on direct reduction and magnetic separation.

3.4. Effects of reduction temperature on direct reduction and magnetic separation

The effect of reduction temperatures ranging from 1173 to 1573 K on the direct reduction followed by magnetic separation of copper tailings was investigated. The experiments were performed under a limestone ratio of 25%, reduction time of 90 min, and bitumite ratio of 30%, and the experimental results are shown in Fig. 8.

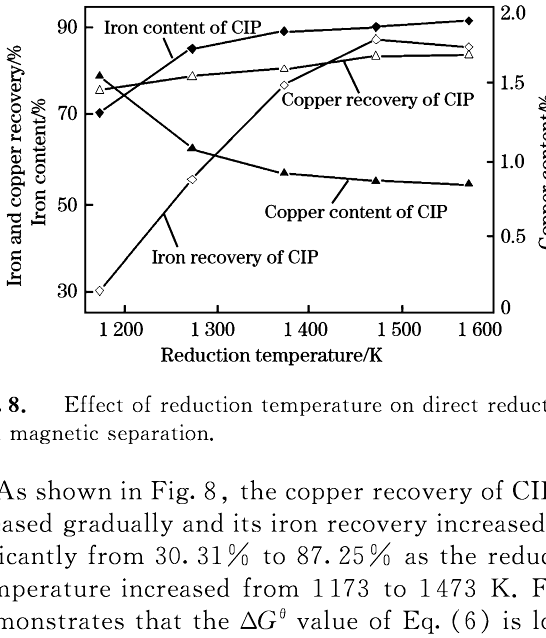


Fig. 8. Effect of reduction temperature on direct reduction and magnetic separation.

As shown in Fig. 8, the copper recovery of CIP increased gradually and its iron recovery increased significantly from 30.31% to 87.25% as the reduction temperature increased from 1173 to 1473 K. Fig. 3 demonstrates that the ΔG^0 value of Eq. (6) is lower than those of Eqs. (2)－(4) at 1173 K. Therefore, reduction of CuS is easier to achieve than reduction of Fe_2SiO_4 and Fe_3O_4 at 1173 K. Further increases in temperature decrease the value ΔG^0 in Eqs. (2)－(4), which means that the reduction of Fe_2SiO_4, Fe_3O_4, and FeO become easier. Thus, iron recovery increased sharply from 1173 to 1473 K.

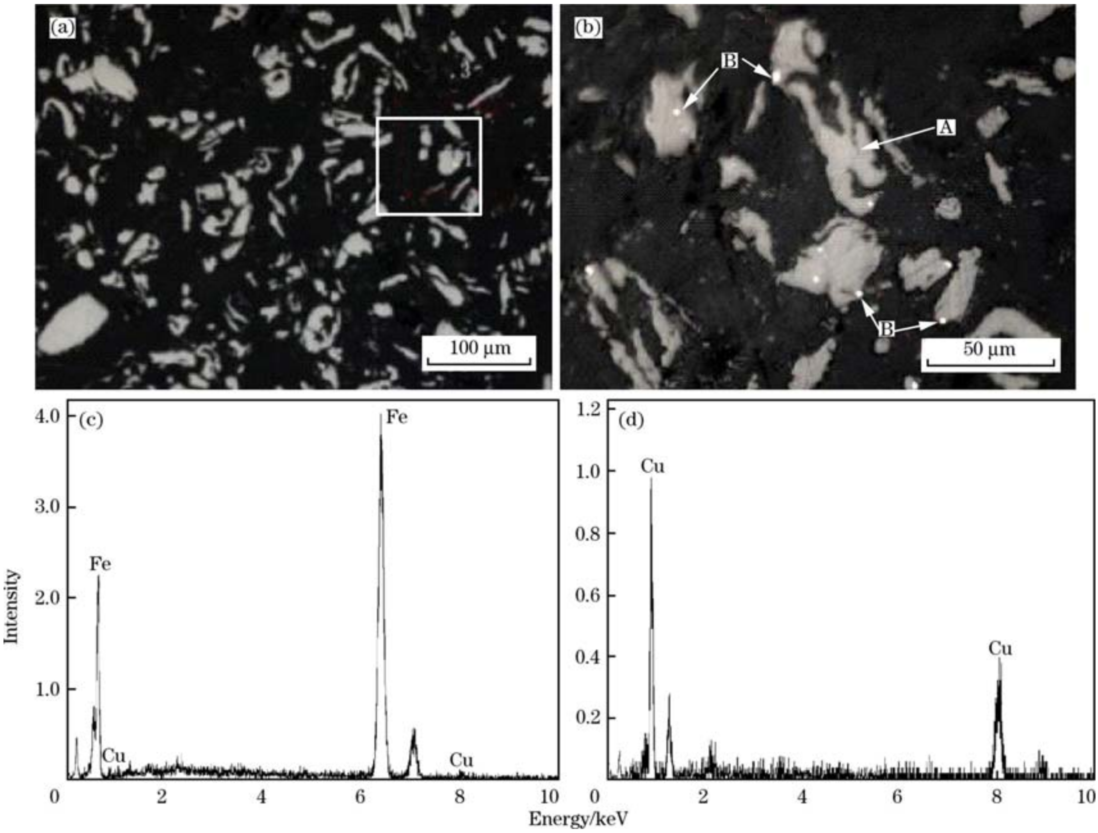
When the temperature was 1573 K, iron recovery showed a slight decrease. The copper content of CIP decreased from 1.54% to 0.84% and its iron content increased from 70.59% to 91.45% when the temperature ranged from 1173 to 1573 K. Higher temperatures are beneficial to the formation of a molten phase, and the molten structure of the roasted ore accelerates the migration rate of metallic iron and copper particles and improves particles growth[25]. After grinding, larger iron and copper particles are liberated from the tailings. The liberation copper would fall into the tailings through magnetic separation. So the iron content of CIP increases while its copper content decreases. Reduction of iron minerals is suppressed by decreases in the diffusion rate of the reductive gas in the molten phase. Thus, iron recovery decreased at 1573 K. Considering that temperatures exceeding 1473 K yield less-optimal effects and cause more energy consumption, the optimal reduction temperature appears to be 1473 K.

The optimum conditions determined by the experiments are as follows: limestone ratio of 25%, reduction time of 90 min, bitumite ratio of 30%, and reduction temperature of 1473 K. Under these conditions, CIP with an iron content of 90.11% and copper content of 0.86%, indicating iron and copper recoveries of 87.25% and 83.44%, respectively, were obtained. Results reveal that the iron and copper in the copper tailings were effectively recovered.

4. Product Examination

4.1. Microstructural analysis of CIP

The microstructure of the final CIP product obtained under optimum conditions is shown in Fig. 9; Fig. 9(b) shows a magnified view of the area marked by the box in Fig. 9(a). The coarse gray phase (point A) and the bright phase (point B) in Fig. 9(b) were observed by EDS and found to be iron-copper alloy (Fig. 9(c)) and copper (Fig. 9(d)), respectively. Thus, the CIP consisted of iron-copper alloy and copper, which illustrates that the iron and copper were efficiently recovered. The results in Fig. 9 confirm that the primary copper mattes have been reduced to metal copper, which mainly existed in the iron phase and as tiny copper particles embedded in the iron metal. The result indicated that separation of these two metals was difficult. Thus, the copper goes into magnetic products by low intensity magnetic separation.



(a), (b) SEM images of CIP; (c) EDS image of point A; (d) EDS image of point B.

Fig. 9. SEM and EDS images of CIP.

4.2. Multi-element analysis of CIP

The multi-element analysis results of CIP are shown in Table 3. The product contained 90.11% Fe, 0.86% Cu, and low traces of impurities and harmful elements. These results demonstrate that coal-based

Table 3
Multi-element analysis of CIP (mass%)

TFe	Cu	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	MnO	TiO_2	Pb	Zn	Co	P	S	As
90.11	0.86	3.12	1.90	1.92	1.38	0.04	0.26	0.20	0.055	0.002	0.007	0.025	0.087	0.026	0.002

direct reduction followed by magnetic separation can recover iron and copper from copper tailings and yield CIP. The CIP obtained can be used as an inexpensive raw material for weathering steel.

5. Conclusions

(1) The copper tailings were assayed and found to be composed of 42.20% Fe and 0.39% Cu. The main ferrous minerals in the copper tailings were fayalite and magnetite, while the main copper mineral was copper matte, most of which was dispersed in the fayalite and magnetite as small beads that were difficult to recover through traditional separation processes.

(2) Coal-based direct reduction followed by magnetic separation allows utilization of copper tailings and yields CIP as a product. Limestone ratio, reduction time, bitumite ratio, and reduction temperature were the main factors influencing CIP. The optimum conditions determined by the experiments were as follows: a limestone ratio of 25%, a bitumite ratio of 30%, and reduction roasting at 1473 K for 90 min. Under these conditions, CIP with an iron content of 90.11% and copper content of 0.86%, indicating iron and copper recoveries of 87.25% and 83.44%, respectively, were effectively obtained.

(3) The morphological characteristics of the copper and iron in the CIP revealed that some tiny copper particles were embedded in the iron and some copper formed alloy with iron, which was difficult to achieve the separation of these two metals. Thus, the copper went into magnetic products by low intensity magnetic separation. Multi-element analysis of CIP indicated that a high-quality product was obtained. This CIP could be used as an inexpensive raw material for weathering steel.

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