Recovery of Iron from Copper Tailings Using a Combined Direct Reduction–Magnetic Separation Process

Buxin Chen, Minghong Deng, Mengjun Hu, Mengyao Dong, and Meilong Hu

Abstract Iron in the form of fayalite in copper tailings poses a challenge for traditional beneficiation methods due to its fine particle size. In this work, iron present in copper tailings was efficiently recovered by reducing fayalite to metallic iron and subsequently separating it from gangue using the low-intensity magnetic separation. Additionally, this approach prevents the agglomeration of the metallic iron during high-temperature reduction. The effects of the reduction temperature, reductant dosage, and flux dosage on iron recovery from copper tailings were investigated using a combined process of the direct reduction and magnetic separation. The results confirm that it is feasibility of iron recover from copper tailings through direct the combined process. The optimal reduction conditions are CaO to copper slag ratio of 7.5 wt% CaO, 30 wt% anthracite to copper slag ratio, 1100–1200 °C, and a duration of 3 h. The optimal experimental magnetic field current is 0.5 A. The final product obtained has an iron grade of 78%.

Keywords Copper tailings · Iron recovery · Fayalite · Direct reduction process · Magnetic separation

Introduction

As the world's largest producer of refined copper, China accounts for about 1/3 of the world's production. At present, China's refined copper is mainly produced by pyrometallurgy [1–3]. The annual discharge of copper slag exceeds 10 million tons according to the calculation of 2.2 tons of copper slag per ton of refined copper produced in the copper smelting process [4], as shown in Fig. 1. More than 120

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million tons of copper slag has been accumulated and has become a large amount of industrial solid waste produced in the metallurgical industry in China, it has brought about land occupation, environmental pollution, and many other problems [5–9]. The iron grade in copper slag is as high as 40%, which is higher than the average iron grade (35%) of iron ore in China [10]. The recovery of iron from copper slag can not only alleviate the serious shortage of iron ore resources faced by the domestic steel industry, but also alleviate the environmental pressure caused by copper slag storage.

Iron in copper slag mainly exists in the form of iron glass, fayalite and magnetite. The magnetic properties of glass and fayalite are weak, so the recovery of metal iron in fayalite is the difficulty of recovering iron from copper smelting slag. Flotation and hydrometallurgical processes are mainly used for the recovery of copper, cobalt, zinc, and other metals in copper slag, the main component iron in copper slag cannot be effectively recovered [11]. Therefore, the fire modification process is usually used to convert the iron in the copper slag into magnetite or elemental iron with strong magnetism, and then the iron concentrate is obtained by magnetic separation. In recent years, the recovery and utilization of iron in copper slag has been studied at home and abroad. Four main processes, direct magnetic separation (I), oxidation roasting-magnetic separation (II), smelting reduction–magnetic separation (III), and direct reduction–magnetic separation (IV), are proposed, as shown in Fig. 2. Part of the research is given in Table 1.

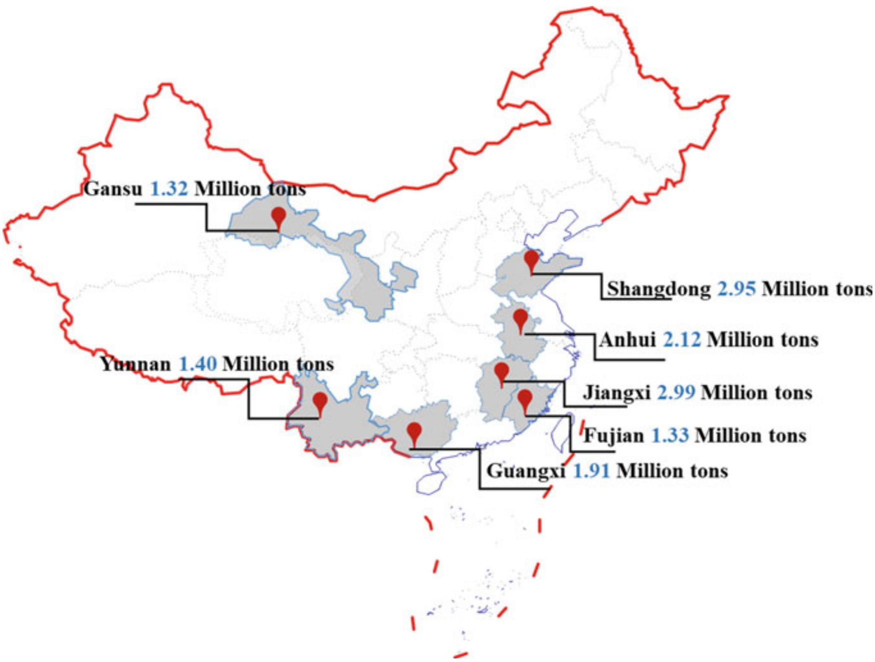


Fig. 1 Main producing provinces of copper slag from January to November 2021

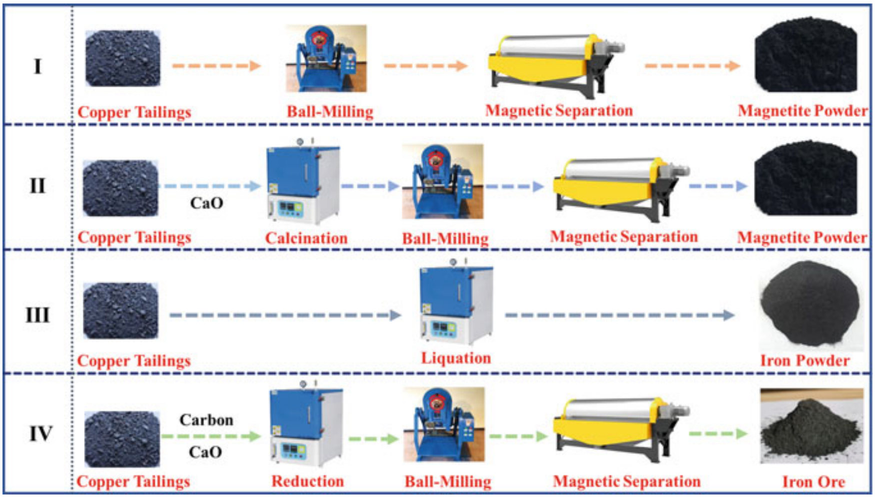


Fig. 2 Schematic diagram of four technologies for recovering iron from copper slag

Table 1 Comparison of main iron recovery technologies in copper tailings

Technology	Name	Initial iron grade (%)	Best product quality	
			Iron grade (%)	Recovery ratio (%)
I	Wang [12]	53.54	35.02	62.525
II	Cao [13]	45.34	54	90
III	Heo [14]	46.00	–	60
	Yang [15]	40.55	53.9	96–98
IV	Kim [16]	35.76	>65	85
	Li [17]	40.33	94.3	90.5
	Zhou [18]	39.85	90.68	90.49
	Li [19]	41.43	96.21	91.82

Direct reduction refers to the process of reducing iron minerals in copper slag to metallic iron particles below the melting temperature of copper slag [20]. Using direct reduction–magnetic separation technology to recover iron resources in copper slag has fair recovery effect and short reaction time, which is the development trend of comprehensive utilization and industrialization of copper slag in the future. At the same time, the product obtained by the direct reduction–magnetic separation method is metal iron powder, and the iron grade and recovery rate can reach 80–90%, which can be used as a high-quality raw material for steelmaking. Therefore, the application prospect of direct reduction–magnetic separation method in the treatment of copper slag in China is very broad. However, in actual production, too high reduction temperature will lead to the aggregation and growth of metal iron in copper tailings

Table 2 Main chemical composition analysis results of copper tailings %

TFe	FeO	Fe_2O_3	MgO	SiO_2	ZnO	S	PbO	Cu	含水率
49.14	25.01	42.8	1.87	13.92	5.09	0.12	0.5	0.3	12

during reduction, sintering with some slag, and even affecting the normal operation of industrial production.

In this paper, aiming at the problem of low stockpiling and utilization rate of copper tailings from a copper slag, the limitation of traditional beneficiation and smelting process is broken through. The direct reduction–magnetic separation process is adopted. Through experimental research, the best experimental conditions for recovering metal iron are determined, and the growth mechanism of metal iron particles is explored. The iron components in copper slag are fully utilized, which provides a certain reference for the resource utilization of copper slag.

Materials and Methods

Materials

Copper slag used in this study was the secondary tailings of a copper slag after slow cooling, crushing, grinding, and flotation. The main chemical composition of the copper slag is given in Table 2. The main ingredients of the slag are 49.14% Fe_{Total} and 13.92% SiO_2, the content of copper and harmful element sulfur is low.

The X-ray diffraction (XRD) spectrum of copper slag is shown in Fig. 3, which indicates that the main minerals phases in the slag are fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). Therefore, it is difficult to directly separate and enrich iron in the sample by physical method.

Anthracite is a reductant in the direct reduction process. The fixed carbon content is greater than 80%, and the volatile content is less than 10%. Since the copper slag is an acidic slag, in order to promote the reduction of fayalite, the alkaline oxide CaO is added in the direct reduction process.

Equipment

The main experimental equipment includes GSL-1700X horizontal furnace, JA31001 electronic balance (accuracy of 0.01 g), corundum porcelain boat (φ10 cm × 2 cm), ball mill, CXG magnetic separator, D/Max-RC X-ray diffractometer, EVO18 scanning electron microscope, etc.

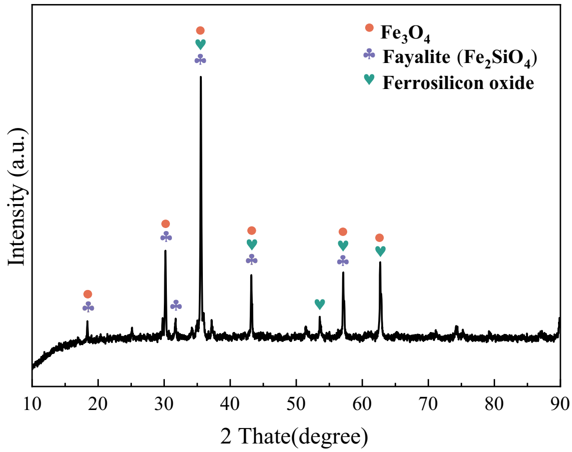


Fig. 3 XRD pattern of copper slag

Experimental Procedure

The effects of reduction temperature (System A), reductant dosage (System B) and flux dosage (System C) on the iron grade, metallization rate, and iron recovery rate of copper tailings recovery were studied. The experimental scheme is given in Table 3.

Before the experiments, 100 g copper tailings placed in a muffle furnace at a constant temperature of 100 °C for 2 h to eliminate moisture. The copper tail slag, reductant, and flux were mixed according to the composition given in Table 3 and put into the corundum porcelain boat. The flat plate was gently pressed to make the furnace charge flat and placed in a horizontal reduction furnace. After 3 h of reduction, the crucible was taken out and argon was introduced for protection. After the reduction, the temperature of the horizontal furnace is reduced to 100 °C, and

Table 3 Experimental scheme components

Item	Temperature (°C)	Anthracite (g)	CaO (g)
A1	**1150**	25	7.5
A2	**1175**	25	7.5
A3	**1200**	25	7.5
B1	1175	**20**	7.5
B2	1175	**25**	7.5
B3	1175	**30**	7.5
B4	1175	**35**	7.5
C1	1175	25	**3.0**
C2	1175	25	**5.0**
C3	1175	25	**7.5**
C3	1175	25	**10**

the reduction product is taken out and broken. The slurry is milled in a water mill for 8 min to obtain a slurry (the amount of water added is 1 mL/g), and then the magnetic separation tube is used for weak magnetic separation. The magnetic separation current is 0.5 A, and a magnetic separation concentrate dominated by metal iron is obtained. The concentrate after magnetic separation was analyzed for iron grade and iron recovery index of magnetic concentrate.

Results and Discussion

Thermodynamic Analysis

Equations (1)–(4) show the possible reactions during the reduction process of copper slag, and the Reaction module of FactSage 8.1 is used to calculate the Gibbs free energy changes of the reactions, and the results are shown in Fig. 4.

$$Fe_3O_4 + 2C = 3Fe + 2CO_2 \quad (1)$$

$$Fe_2SiO_4 + 2C = 2Fe + SiO_2 + 2CO \quad (2)$$

$$Fe_2SiO_4 + CaO + 2C = CaSiO_3 + 2Fe + 2CO \quad (3)$$

$$Fe_2SiO_4 + MgO + 2C = MgSiO_3 + 2Fe + 2CO \quad (4)$$

The fayalite is difficult to reduce by anthracite (Eq. (2)), but easier with the addition of burnt lime (CaO) and magnesium oxide (MgO) (Eqs. (3), (4)). The direct reduction

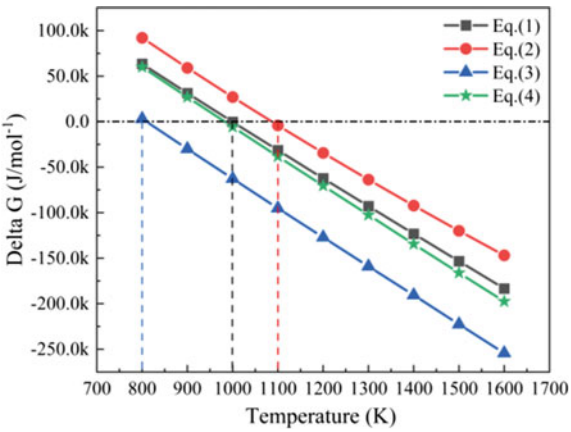


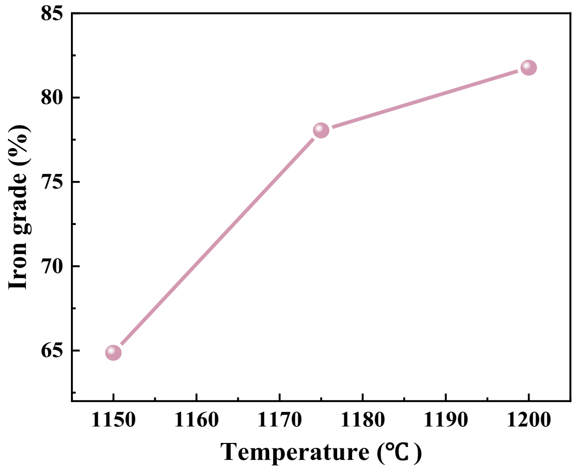
Fig. 4 Correlation of the Gibbs free energy change with temperature for Eqs. (1)–(4)

of Fe_3O_4 and Fe_2SiO_4 can be realized by controlling the reduction temperature and time and adding MgO and CaO under the premise of ensuring the reduction atmosphere.

Effect of Reduction Temperature on Iron Recovery from Copper Slag

Under the conditions of fixed anthracite to copper slag (anthracite/slag) ratio of 25 wt%, CaO to copper slag (CaO/slag) ratio of 7.5 wt%, reduction time of 3 h and magnetic separation current of 0.5 A, the effect of reduction temperature on the iron grade of magnetic separation concentrate was studied. It can be seen from Fig. 5 that with the increase of reduction temperature, the iron grade of magnetic concentrate shows an upward trend. This is because the higher the temperature, the greater the possibility of diffusion and aggregation of the generated metal iron into large particle metal iron. However, when the temperature is too high, the energy consumption and the high-temperature resistance of the equipment need to be further improved, and the generated metal iron will be mixed with some slag, thus increasing the difficulty of subsequent grinding-magnetic separation, and even affecting the normal operation of industrial production. Considering comprehensively, the reduction temperature was determined to be 1175 °C.

Fig. 5 Effect of reduction temperature on the iron grade of recovered iron from tailings



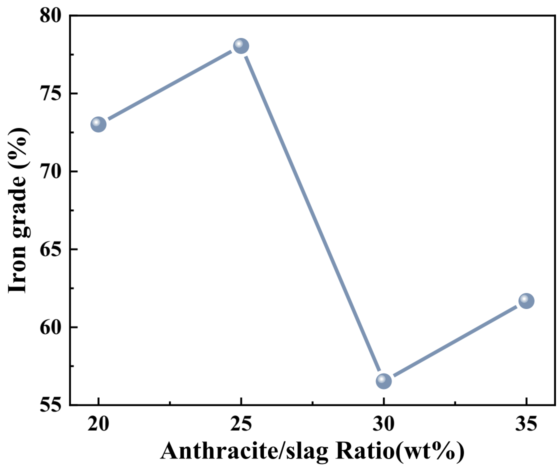


Fig. 6 Effect of reductant dosage on the grade of recovered iron from tailings

Effect of Reductant Dosage on Iron Recovery from Copper Slag

The effect of reductant dosage on the grade of magnetic concentrate was studied under the condition of fixed reduction temperature of 1175 g, CaO/slag ratio of 7.5 wt%, reduction time of 3 h, and magnetic separation current of 0.5 A. It can be seen from Fig. 6 that with the increase of the amount of reductant, the iron grade of magnetic concentrate increases first and then decreases. When the anthracite/slag ratio is 25 wt%, the iron grade is the highest, which is 78.01%. This is because with the increase of the ratio of reductant, the reduction speed is accelerated, and the yield of metal iron is increased. However, when the amount of anthracite is excessive, the solid slag phase will be loose and porous, which will hinder the aggregation and growth of metal iron particles and reduce the grade of metal iron generated by reduction. Considering comprehensively, the anthracite/slag ratio is determined to be 25 wt%.

Effect of Flux Dosage on Iron Recovery from Copper Slag

Under the conditions of fixed reduction temperature of 1175 °C, anthracite/slag ratio of 25 wt%, reduction time of 3 h, and magnetic separation current of 0.5 A, the effect of flux dosage on the iron grade of magnetic concentrate was studied. The results are shown in Fig. 7. With the increase of flux dosage, the iron grade of magnetic concentrate increases first and then decreases, and the highest point is when the flux dosage is 7.5 g. The addition of an appropriate amount of flux can replace FeO from complex compounds, which is conducive to the reduction of metal iron, and can reduce the activation energy of the reduction reaction to promote the

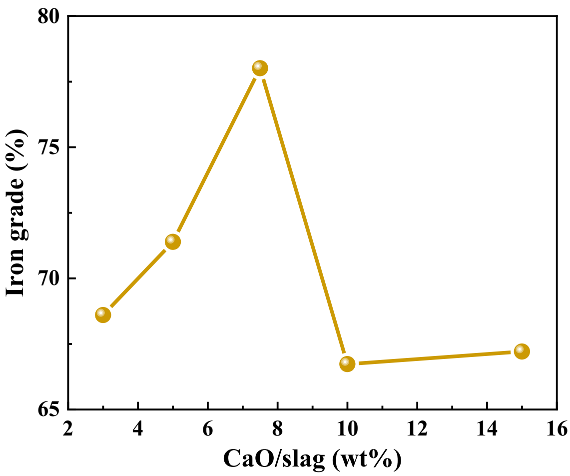


Fig. 7 Effect of flux dosage on the grade of recovered iron from copper tailings

reduction of fayalite in copper tailings. However, when the amount of flux is too large, it will reduce the fluidity of the slag, making it more difficult for the fine metal iron generated by the reduction to aggregate and grow, which is not conducive to the monomer dissociation and recovery of the metal phase iron in the subsequent grinding process. Considering comprehensively, the CaO/slag ratio was determined to be 7.5 wt%.

Optimum Condition

The optimal scheme is as follows, anthracite/slag ratio of 25 wt%, CaO/slag ratio of 7.5 wt%, reduction temperature of 1250 °C, roasting time of 3 h, magnetic separation current of 0.5 A. At this time, the iron grade of the magnetic concentrate of the reduction product was 78.01%. The appearance of the magnetic separation product calcined under the optimum conditions as shown in Fig. 8. The metal iron did not aggregate to form particles during the reduction process, indicating that sintering did not occur.

The X-ray diffraction analysis of the magnetic concentrate under the optimal scheme was shown in Fig. 9. The direct reduction iron powder obtained by reduction roasting of copper slag and then low-intensity magnetic separation is mainly composed of metallic iron. The crystalline phase substances—ferrite and magnetite, which originally existed in large quantities, no longer exist. Therefore, it is feasible to recover Fe from copper slag by direct reduction–magnetic separation method.

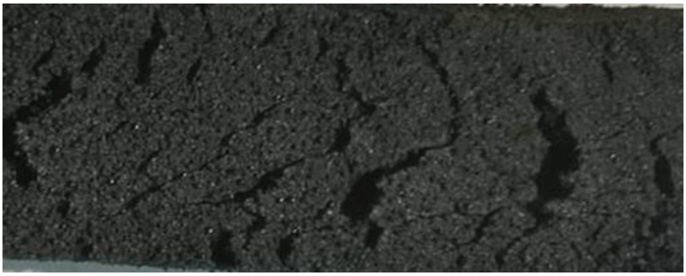


Fig. 8 Appearance of calcined products under optimum conditions

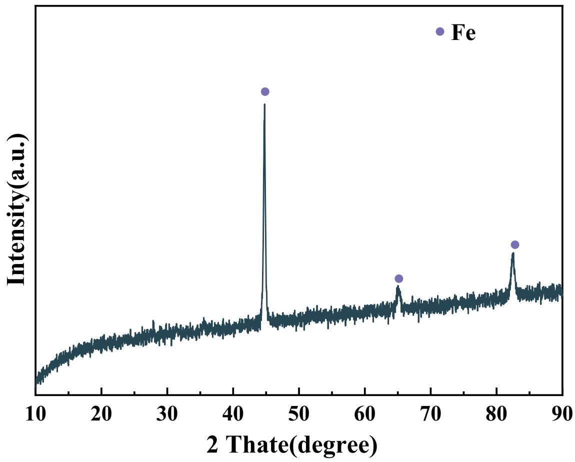


Fig. 9 XRD pattern of magnetic concentrate under optimal scheme

Conclusion

1. With the increase of reduction temperature, the iron grade of magnetic concentrate increases. With the increase of the amount of reductant and flux, the iron grade of magnetic concentrate increases first and then decreases.
2. The optimal scheme is as follows, the reduction temperature is 1175 °C, the reduction time of 3 h, anthracite/slag ratio of 30 wt%, the CaO/slag ratio of 7.5 wt%, and the magnetic separation current of 0.5 A.
3. Under the condition of the optimal scheme, there is no obvious sintering in the reduction process. The iron grade of the magnetic concentrate obtained by the reduction product is 78.01%, and the main component is metallic iron.

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