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A novel slag cleaning method to recover copper from molten copper converter slag

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Abstract: To recover copper from copper slag, a novel slag cleaning method was proposed. The thermodynamics and binary phase diagram of $FeO-SiO_2$ were calculated first. Then, the effects of experimental parameters on the reduction of Fe_3O_4, recovery of copper, and slag cleaning mechanism were investigated. The results showed that the addition of SiO_2 significantly reduced the initial reduction temperature of magnetite and pyrite. The contents of Fe_3O_4 and copper decreased to 2.45 wt.% and 0.39 wt.%, respectively, with copper recovery of 92.52% under the optimum conditions. More than 94% silver and 99% gold subsided into the copper matte after slag cleaning. Approximately 72% of zinc and 75% of lead volatilized in the flue gas. The viscosity of the copper slag decreased from 0.68 to 0.12 Pa·s due to the reduction of magnetite. The sedimentation of copper matte droplets could be enhanced by mechanical stirring.

Key words: copper slag; copper recovery; slag cleaning; magnetite reduction; mechanical stirring

1 Introduction

Copper slag is a solid waste in the copper smelting process [1]. At present, approximately 2.2−3.0 t of copper slag is generated per ton of copper produced [2−4]. And approximately 24.6×10^6 t of copper slag is discharged globally every year [5]. With the increase in copper matte grade and the development of copper smelting technology, the copper content in copper slag also increases [6]. The higher oxygen potential also leads to an increase in the copper content in the copper slag in either bottom blowing smelting or side blowing smelting processes [7]. Due to the existence of FeS, copper mainly exists in the form of Cu_2S, and little Cu_2O exists in the copper slag [8]. In the copper smelting process, a large amount of Fe_3O_4 is generated and enriched in copper slag due to the high oxygen potential [9,10]. And the Fe_3O_4 leads to an increase in the viscosity of the slag, which affects the sedimentation of copper matte droplets [11,12]. Copper slag also contains zinc and lead [13]. To improve the economic benefits and reduce the serious damage of copper slag to the surrounding environment [14], it is essential to extract the valuable metals contained in copper slag.

At present, the main industrial recovery method of copper from copper slag is the flotation method [15,16]. Although the copper content in slag can be reduced to 0.2−0.3 wt.% by flotation, the tailing after flotation is quite fine, which is not conducive to further utilization. Also, it is difficult to recover iron from tailings [17]. The molten copper slag needs to be cooled before flotation, resulting in the waste of a large amount of sensible heat from the molten copper slag [18,19]. On the

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other hand, the copper in copper slag could also be reclaimed by the acid leaching method and slag cleaning method [20−22]. Nevertheless, a large amount of waste acid is generated during the acid leaching process, leading to environmental pollution. Given this situation, the slag cleaning method is considered another beneficial way to extract copper from copper slag. The sedimentation and growth of copper matte droplets can be promoted by slag cleaning method due to the low viscosity of copper slag [23]. In the slag cleaning process, Fe_3O_4 is reduced to FeO, which then reacts with SiO_2 at high temperature to form the low melting point substance fayalite (Fe_2SiO_4), resulting in a decrease in the viscosity of copper slag, which is conducive to reducing the mechanically entrained loss of copper [24].

The reduction agents traditionally used for the reduction of Fe_3O_4 are natural gas and carbonaceous reductants. ZHANG et al [25] explored the moderate slag cleaning of copper slag by natural gas. The results showed that natural gas could reduce Fe_3O_4 to FeO, significantly improving the sedimentation rate of copper matte droplets. After slag cleaning by reduction, the copper content in slag decreased from 4.51 wt.% to 0.50 wt.%, and Fe_3O_4 content decreased from 16.05 wt.% to 7.36 wt.%. ZHANG et al [23] studied the reduction of Fe_3O_4 from copper slag by graphite rods. The viscosity of the copper slag was reduced, and the sedimentation of copper matte droplets could be improved. Increasing the reduction temperature and time was beneficial to decreasing the content of Fe_3O_4. The reduction of Fe_3O_4 was a second-order reaction with an apparent activation energy of 610 kJ/mol. The Boudouard reaction was the limiting step of this reduction. LI et al [26] experimented on the reduction of Fe_3O_4 in copper slag in an electric furnace by using petrol and biodiesel as reduction agents. The results indicated that increasing the reduction time and temperature could decrease the content of Fe_3O_4. The formed FeO combined with SiO_2 to generate fayalite.

Compared with carbonaceous reduction agents, the FeS agent can not only reduce Fe_3O_4 to FeO but also convert Cu_2O to Cu_2S [27]. However, the direct addition of FeS into molten copper slag will result in the problems of burning FeS, limiting the mass transfer process and long reaction time. To improve the utilization of reduction agent and reduce the raw material cost, a novel slag cleaning method of recovering copper from copper converter slag with pyrite using mechanical stirring was proposed. In the process of slag cleaning, copper, gold and silver could be recovered from the molten copper slag in the form of copper matte. Zinc and lead were volatilized and recovered from the flue gas. The tailing could be further used to prepare copper-containing antibacterial stainless steel. In this work, thermodynamics and binary phase diagram of $FeO-SiO_2$ in slag were calculated by FactSage 6.4 software. The effects of temperature, mass fraction of pyrite/slag, mass ratio of Fe/SiO_2, impeller rotation speed, and time on the slag cleaning results were investigated. The phase transition of copper converter slag and the slag cleaning mechanism during the slag cleaning process were specifically studied.

2 Experimental

2.1 Materials

The copper converter slag used in the experiments of this study was collected from Huludao Zinc Industry Co., Ltd., Liaoning Province, China. The chemical compositions of the copper converter slag were 41.83 wt.% FeO, 19.13 wt.% Fe_3O_4, 4.37 wt.% Cu, 0.72 wt.% S, 0.19 wt.% CaO, 18.53 wt.% SiO_2, 2.08 wt.% Al_2O_3, 4.82 wt.% Zn, and 2.15 wt.% Pb. The contents of Au and Ag in the copper converter slag were 14.12 g/t and 129.63 g/t, respectively. Pyrite was purchased from Jilin Daheishanmuye Co., Ltd., Jilin Province, China, and the content of FeS_2 in pyrite was 90.30 wt.%. The analytical grade reagents silica, calcium oxide, and calcium fluoride used for modifying the viscosity of the copper slag were purchased from Aladdin (Shanghai, China).

2.2 Experimental apparatus and procedure

The copper converter slag was dried in a drying oven (Nabertherm, TR1050, Bremen, Germany) at 150 °C for 24 h. Then, the dried copper converter slag was ground and milled in a rod mill (Rock, RK/ZQM(BM), Wuhan, China) to obtain a powder with a mean particle size of approximately 75 μm. The slag cleaning experiments were performed in a slag cleaning furnace, and the diagram of which is shown in Fig. 1. As shown in Fig. 1, the slag cleaning furnace

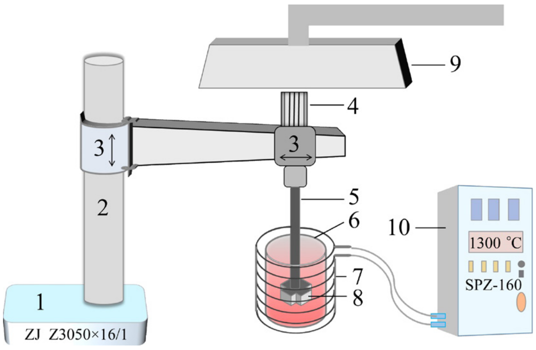

Fig. 1 Diagram of slag cleaning furnace (1−Pedestal; 2−Upright; 3−Slider; 4−Synchronous motor; 5−Impeller shaft; 6−High-purity graphite crucible; 7−Induction coil; 8−Impeller blade; 9−Smoke-dust collection system; 10−Control cabinet)

consists of three parts: mechanical stirring system (Zhongjie, Z3050×16/1, Shenyang, China), medium-frequency induction furnace (Shuangping, SPZ-160, Shenzhen, China), and a self-designed smoke-dust collection system. The raw materials consisting of 1500 g copper converter slag, 60 g calcium oxide, and 9 g calcium fluoride were mixed and added into a graphite crucible (*d*150(120) × 300 mm). Then, the temperature was raised to the predetermined value according to the thermostatic program. Temperature was measured by a high- temperature infrared temperature gun (Smart Sensor, AR892+, Hongkong, China). As the specified temperature was reached and the copper converter slag melted completely, predetermined amounts of silica and pyrite were added into the molten copper converter slag by mechanical stirring. The impeller, with a blade of cruciform structure, was made of high-purity graphite. The diameter of the impeller blade was 100 mm. The impeller rotation speed was 250 r/min, and the feeding time of silica and pyrite was 1 min to ensure that silica and pyrite were rapidly and fully mixed with the molten copper converter slag. After adding silica and pyrite, the impeller rotation speed was reduced to enhance the directional sedimentation of the copper matte droplets contained in the molten copper converter slag. After the slag cleaning was completed, the melt was cast into a high-purity graphite mold and cooled to room temperature. Owing to the large density difference, the copper matte subsided in the bottom of the melt and thoroughly separated from the tailing. The specific experimental parameters in the slag cleaning process are shown in Table 1.

Table 1 Parameters of slag cleaning experiments

Parameter	Value
Temperature/°C	1200, 1250, 1300, 1350
Mass fraction of pyrite/%	2, 4, 6, 8
Mass ratio of Fe/SiO_2	1.2, 1.4, 1.6, 1.8, 2.0
Impeller rotation speed/(r·min^{-1})	25, 40, 63, 80
Time/min	15, 30, 45, 60

2.3 Analysis method

The copper content in the samples was detected by atomic absorption spectrometry (iCE 3300 AAS). The content of Fe_3O_4 in the samples was analyzed by chemical analysis. The recovery of copper was calculated by the following equation:

$$\eta_{Cu}=(M_{slag}\alpha_{Cu}-m_{slag}\beta_{Cu})/(M_{slag}\alpha_{Cu})\times 100\% \qquad (1)$$

where η_{Cu} is the recovery of copper, %; M_{slag} and m_{slag} are the mass of the copper converter slag and tailing, respectively, g; α_{Cu} and β_{Cu} are the copper content in the copper converter slag and tailing, respectively, wt.%.

Similarly, Eq. (1) can also be used to calculate the recovery rates of gold and silver.

The phase compositions of the experimental samples were analyzed by X-ray diffraction (Bruker, D8 ADVANCE, Germany). Scanning electron microscopy (Hitachi, SU−8010, Japan) and energy dispersive spectroscopy were carried out to observe the microstructure morphology of the samples and the distribution of elements.

3 Results and discussion

3.1 Phase composition and microstructure morphology of copper converter slag

The XRD pattern of the copper converter slag is shown in Fig. 2. The main phases of copper converter slag are magnetite (Fe_3O_4), fayalite (Fe_2SiO_4), bornite ($Cu_{5.43}Fe_{1.09}S_4$), wurtzite (ZnS), and quartz (SiO_2).

From the SEM image and elemental distribution maps (Fig. 3), it can be seen that the oxygen, iron and copper are significantly enriched. The silicon is enriched in the oxygen-rich and iron-rich regions, and sulfur surrounding the copper-

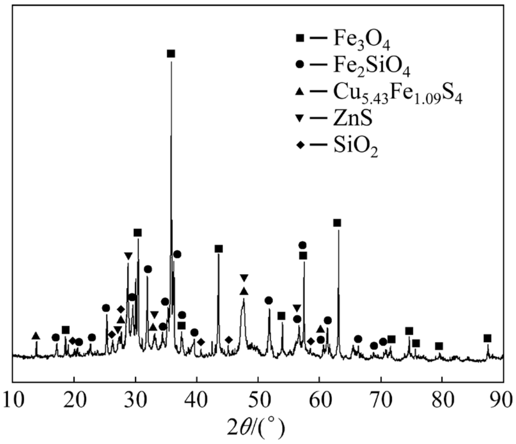

Fig. 2 XRD pattern of copper converter slag

rich phase is relatively enriched. There are three phases in the copper converter slag. The main phase components are magnetite, fayalite, and copper matte. Most copper matte particles in the copper converter slag are approximately 200 μm in diameter.

3.2 Thermodynamic of slag cleaning process

The melting point of magnetite in copper slag is high, which affects the viscosity of the copper slag and sedimentation velocity of the copper matte droplets. In the slag cleaning process, with the addition of pyrite, Fe_3O_4 is reduced to FeO, and then the formed FeO reacts with SiO_2 to form fayalite, thereby reducing the viscosity of the slag and facilitating the sedimentation of the copper matte. Also, the Cu_2O in copper slag can be converted to Cu_2S in the slag cleaning process. The main reactions in the slag cleaning process are as follows:

$$5Fe_3O_4+FeS_2=16FeO+2SO_2(g) \tag{2}$$

$$SiO_2+2FeO=Fe_2SiO_4 \tag{3}$$

$$5Fe_3O_4+FeS_2+8SiO_2=8Fe_2SiO_4+2SO_2(g) \tag{4}$$

$$5Cu_2O+3FeS_2=5Cu_2S+3FeO+SO_2(g) \tag{5}$$

FactSage 6.4 software was used to calculate the standard Gibbs free energy change of Reactions

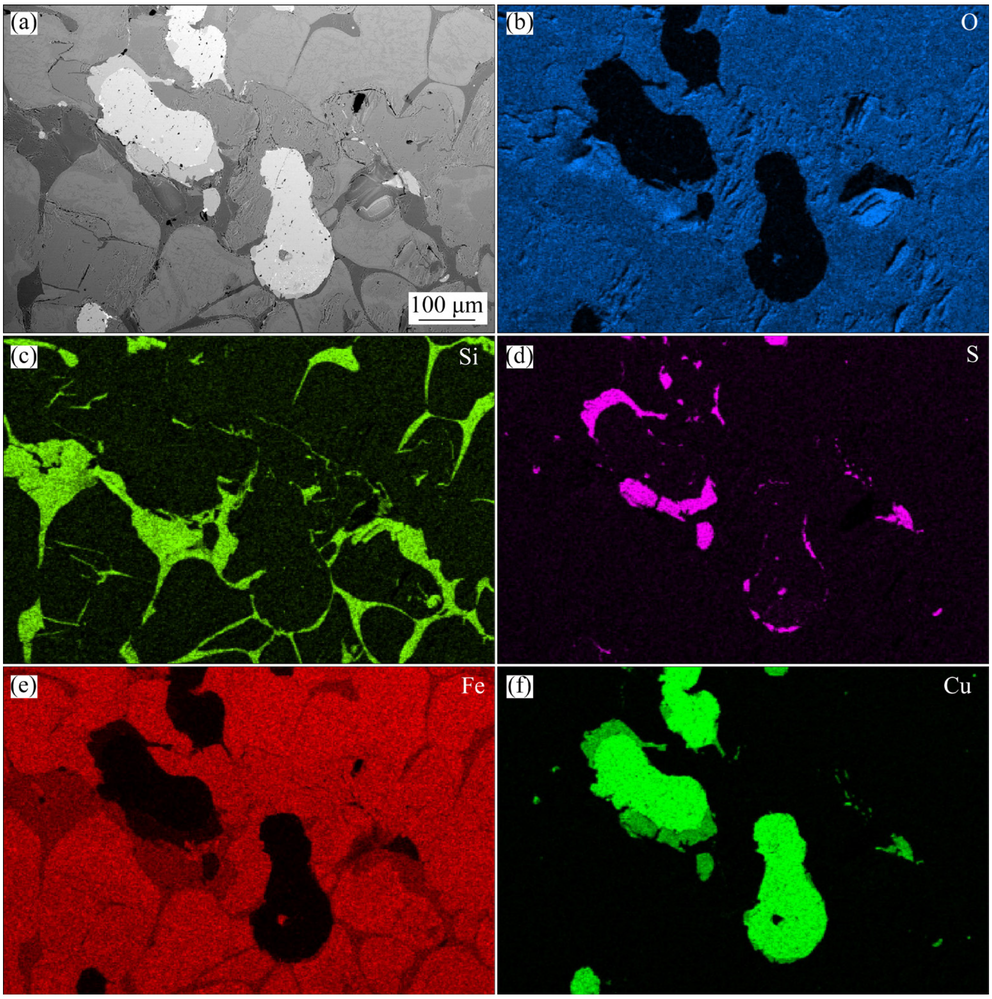

Fig. 3 SEM image (a) and corresponding elemental distribution maps (b−f) of copper converter slag

(2) to (5) at different temperatures, and the results are shown in Fig. 4. The initial reduction temperature of magnetite and pyrite (Reaction (2)) is 1267 °C. Therefore, the reduction temperature should be higher than 1267 °C to guarantee that the Reaction (2) proceeds successfully. FeO can react with SiO_2 to generate fayalite (Fe_2SiO_4) (Reaction (3)) from 800 to 1500 °C. With the addition of SiO_2, the initial reduction temperature of magnetite and pyrite reduces to 916 °C (Reaction (4)). Compared with Reaction (2), after the addition of SiO_2, the initial reduction temperature of magnetite and pyrite is significantly reduced. As a result, the addition of SiO_2 is conducive to reducing the initial reduction temperature of magnetite and viscosity of slag, so as to facilitate the sedimentation of copper matte droplets. A small amount of Cu_2O in copper slag can also be converted to Cu_2S in the slag cleaning process, and the formed small Cu_2S droplets subside to the bottom of the melt followed by large copper matte droplets.

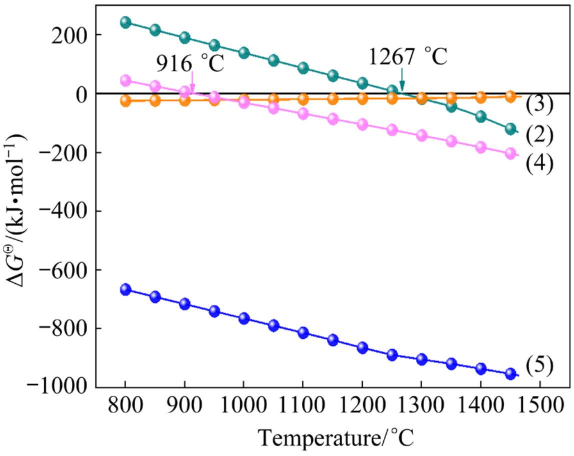

Fig. 4 Standard Gibbs free energy changes of reactions in slag cleaning process

The slag cleaning process of copper slag mainly consists of three steps. Firstly, Cu_2O in copper slag is converted to Cu_2S by FeS_2. Secondly, Fe_3O_4 is reduced to FeO by FeS_2. Then, FeO reacts with SiO_2 to form Fe_2SiO_4. The addition of SiO_2 has a great influence on the last step. Therefore, it is necessary to study the binary phase diagram of $FeO-SiO_2$. Figure 5 shows the binary phase diagram of $FeO-SiO_2$ calculated by the phase diagram module in Factsage 6.4 software. In the $FeO-SiO_2$ system, there is a stable compound Fe_2SiO_4, the melting point of which is approximately 1205 °C. There are also two eutectic points in Fig. 5. Fe_2SiO_4-FeO has a melting point of 1193 °C, and $Fe_2SiO_4-SiO_2$ has a melting point of 1189 °C. Therefore, controlling the mole ratio of FeO/SiO_2 at an appropriate value during the slag cleaning process is very important for the transition of the slag to the stable compound Fe_2SiO_4. In copper smelting production, the mass ratio of Fe/SiO_2 is an indicator to describe copper slag. Consequently, the effect of the mass ratio of Fe/SiO_2 on the slag cleaning process of copper slag should be investigated subsequently.

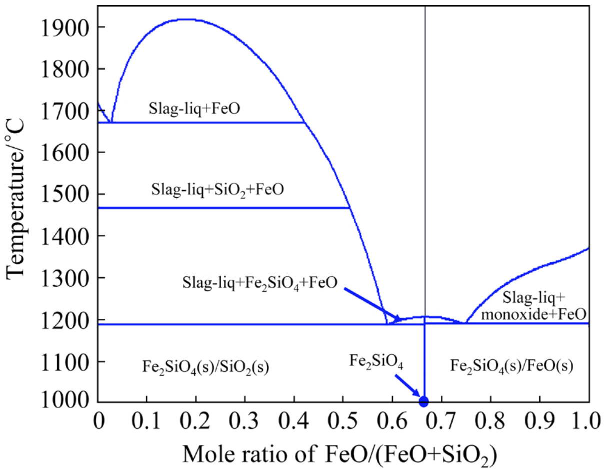

Fig. 5 Binary phase diagram of $FeO-SiO_2$ system

3.3 Slag cleaning

In this section, the effects of temperature, mass fraction of pyrite/slag, mass ratio of Fe/SiO_2, impeller rotation speed, and time on the slag cleaning results were studied systematically. The phases of the tailing and copper matte under the optimum experimental conditions were characterized by XRD, and the microstructure of the tailing was characterized by SEM–EDS.

3.3.1 Effect of temperature and time on slag cleaning

Figure 6 shows the slag cleaning results of different temperatures and time under the following experimental conditions: the mass fraction of pyrite/slag was 4%, the mass ratio of Fe/SiO_2 was 1.4, and the impeller rotation speed was 63 r/min. When the time was increased from 0 to 60 min, the Fe_3O_4 content in tailing was decreased from 19.13 wt.% to 10.53 wt.% at 1200 °C, as shown in Fig. 6(a). With the increase in temperature, the Fe_3O_4 content in tailing was gradually reduced to 2.45 wt.% at 1300 °C for 60 min. Due to the presence of silica, the reduction of Fe_3O_4 by pyrite could occur at 1200 °C, which was lower than the initial reaction

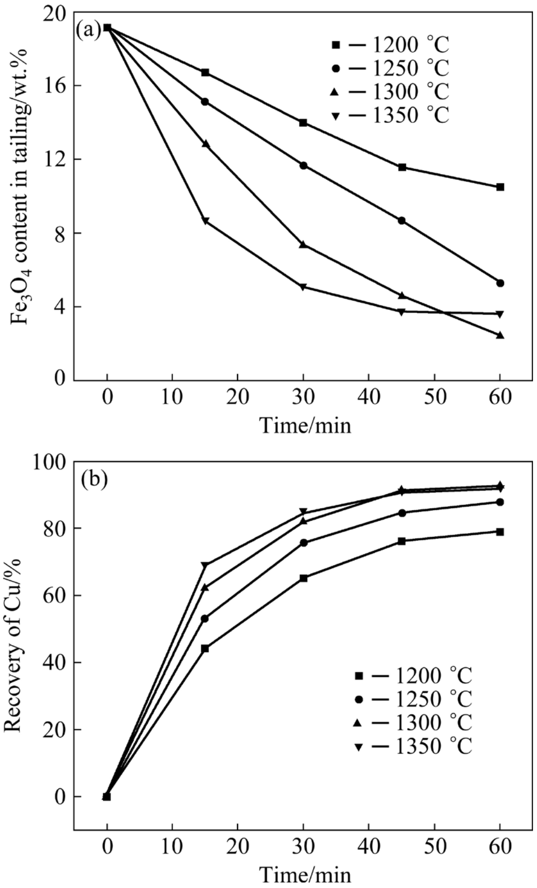

Fig. 6 Effect of temperature and time on slag cleaning: (a) Fe_3O_4 content in tailing; (b) Recovery of Cu

temperature of reduction of Fe_3O_4 by pyrite without silica (1267 °C). When the temperature increased to 1350 °C, the Fe_3O_4 content in the tailing still decreased when the time was less than 45 min. However, when the time was 60 min, the Fe_3O_4 content in the tailing increased slightly. As shown in Fig. 6(b), the variation trend of copper recovery was opposite to that of the Fe_3O_4 content in the tailing. The recovery of copper was increased from 79.11% at 1200 °C to 92.52% at 1300 °C and then decreased to 91.75% at 1350 °C for 60 min. Consequently, the content of copper decreased from 4.37 wt.% in the raw material to 0.39 wt.% in the tailing at 1300 °C for 60 min.

Due to the presence of the high melting point substance of Fe_3O_4, the viscosity of the copper slag is high at low temperatures, which affects the sedimentation velocity of the copper matte droplets and results in a high content of copper in slag. With the temperature increasing, the viscosity of copper slag decreases, accelerating the sedimentation velocity of the copper matte droplets. Additionally, increasing the temperature is conducive to the reduction of Fe_3O_4. The reduction of Fe_3O_4 could reduce the viscosity of copper slag and improve the fluidity of slag, which is beneficial to the slag cleaning process. The reduction of Fe_3O_4 by pyrite produces sulfur dioxide gas. However, the expansion of sulfur dioxide gas at high temperatures leads to a serious spatter of copper slag with good fluidity. During the spatter process, the copper slag would contact with the oxygen in the air, resulting in the reoxidation of FeO and an increase in the Fe_3O_4 content in the tailing. However, when the temperature increased to 1350 °C, the slag cleaning reactions in the molten slag were violent with serious splashing. In this case, the copper matte droplets were broken into small droplets, leading to an increase in the copper content in the tailing, which had a negative effect on the recovery of copper. Therefore, considering the recovery of copper and energy consumption, the recommended suitable temperature was 1300 °C.

3.3.2 Effect of mass ratio of Fe/SiO_2 and mass fraction of pyrite/slag on slag cleaning

As shown in Fig. 5, the mass ratio of Fe/SiO_2 had a large effect on the liquidus of the FeO−SiO_2 system. Therefore, it is necessary to investigate the effect of the mass ratio of Fe/SiO_2 on the slag cleaning results. Figure 7 shows the slag cleaning results of different mass fractions of pyrite/slag and mass ratios of Fe/SiO_2 under the following experimental conditions: the temperature was 1300 °C, the time was 60 min, and the impeller rotation speed was 63 r/min.

Figure 7(a) shows that the Fe_3O_4 content in the tailing decreased with the increasing mass ratio of Fe/SiO_2, and reached the lowest value when the mass ratio of Fe/SiO_2 was 1.4. However, when the mass ratio of Fe/SiO_2 continued to increase from 1.4 to 2.0, the Fe_3O_4 content in the tailing increased gradually. During the slag cleaning process, most of the Fe_3O_4 was reduced to FeO by pyrite. Therefore, FeO and SiO_2 were the main chemical components of the tailing. When the mass ratio of Fe/SiO_2 was 1.4, the mole ratio of FeO/(FeO+SiO_2) was 0.6. The location of the mass ratio of Fe/SiO_2 (1.4) was near the left eutectic point in Fig. 5, the melting point of which was 1193 °C.

An appropriate mass ratio of Fe/SiO_2 would decrease the melting point and improve the fluidity of slag, which was beneficial to the sedimentation

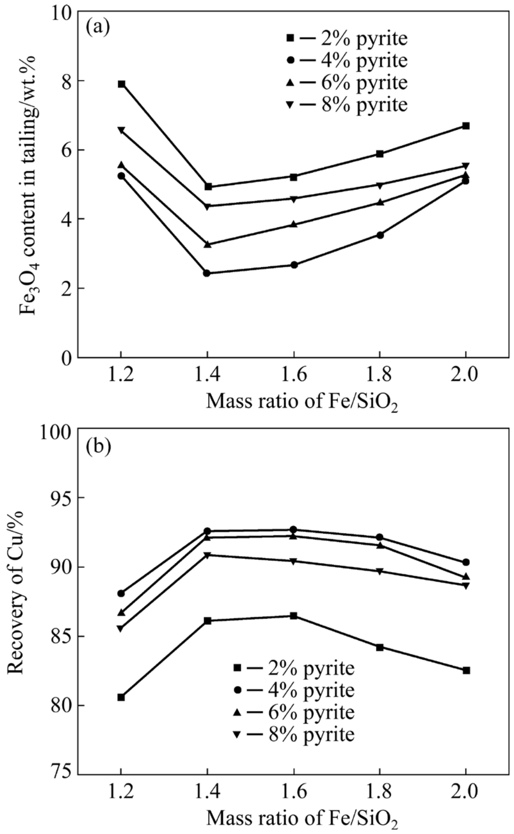

Fig. 7 Effect of mass fraction of pyrite/slag and mass ratio of Fe/SiO_2 on slag cleaning: (a) Fe_3O_4 content in tailing; (b) Recovery of Cu

of the copper matte droplets. With the increasing mass fraction of pyrite/slag, the Fe_3O_4 content in the tailing first decreased and then increased, reaching the lowest value of 2.45 wt.% when the mass fraction of pyrite/slag was 4% and the mass ratio of Fe/SiO_2 was 1.4. As shown in Fig. 7(b), with an increasing mass ratio of Fe/SiO_2, the recovery of copper first increased and then decreased. Additionally, with increasing mass fraction of pyrite/slag, the recovery of copper first increased and then decreased gradually. When the mass fraction of pyrite/slag and Fe/SiO_2 were 4% and 1.4, respectively, the recovery of copper achieved a maximum value of 91.82%. The mass ratio of Fe/SiO_2 in raw copper converter slag was 2.50 with a high copper content of 4.37 wt.%. The slag cleaning results in Fig. 7 show that reducing the mass ratio of Fe/SiO_2 appropriately had a positive effect on improving the recovery of copper and decreasing the copper content in the tailing.

The contents of Fe_3O_4 and copper in raw copper converter slag were 19.13 wt.% and 4.37 wt.%, respectively. According to the chemical Reactions (4) and (5), the theoretical addition of pyrite was required to be 4.91% (assuming that all copper in the copper converter slag existed in the form of Cu_2O because of little sulfur contained in the copper converter slag). In the slag cleaning processes, pyrite was added and sucked into the molten copper converter slag directly by mechanical stirring. Therefore, the utilization efficiency of pyrite was high. Figure 7 shows that when the mass fraction of pyrite/slag was 4%, the Fe_3O_4 content in the tailing reached the lowest point and the recovery of copper achieved the maximum value, which was lower than the theoretical addition of pyrite. This was because part of the copper in the copper converter slag existed in the form of metallic copper (see Fig. 3). In addition to the reaction with Fe_3O_4 and Cu_2O, the combustion reaction of excessive pyrite with oxygen would also occur, releasing a large amount of heat and producing a large number of SO_2 bubbles. This would cause the molten pool to splash and hinder the sedimentation of copper matte droplets. Therefore, the suitable mass fraction of pyrite/slag was 4%, and the mass ratio of Fe/SiO_2 was 1.4.

3.3.3 Effect of impeller rotation speed on slag cleaning

Figure 8 shows the slag cleaning results at different impeller rotation speed under the following experimental conditions: the temperature was 1300 °C, and the mass fraction of pyrite/slag and mass ratio of Fe/SiO_2 were 4% and 1.4, respectively. With increasing time, the Fe_3O_4 content in the tailing significantly decreased. With the increase in impeller rotation speed from 25 to 63 r/min, the Fe_3O_4 content in the tailing gradually reduced. When the impeller rotation speed increased to 80 r/min, the Fe_3O_4 content in the tailing increased again. As the impeller rotation speed increased from 25 to 63 r/min, the recovery of copper increased from 82.64% to 92.52% and then decreased to 91.12% as the impeller rotation speed increased to 80 r/min. A proper impeller rotation speed could increase the collision probability of the small matte droplets and accelerate the directional sedimentation of the copper matte droplets. However, the excessive impeller rotation speed prevents the copper matte droplets from subsiding. Therefore, the suitable impeller rotation speed was 63 r/min in this slag cleaning process.

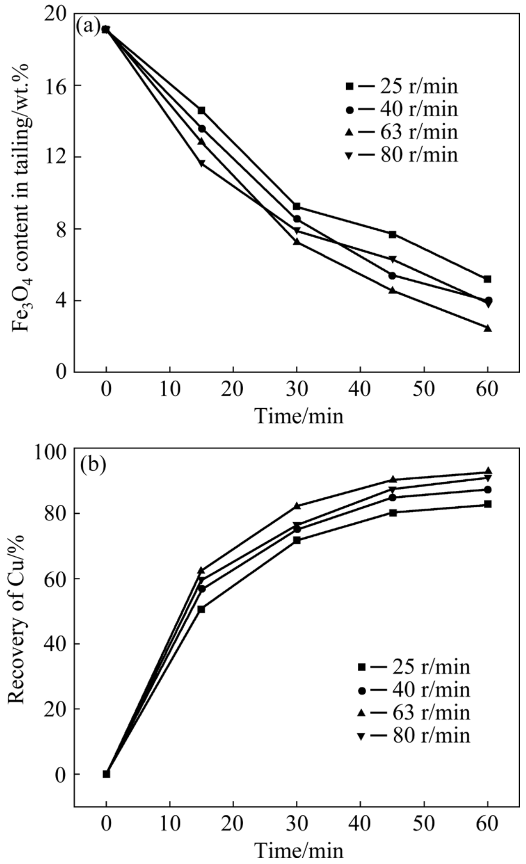

Fig. 8 Effect of impeller rotation speed on slag cleaning: (a) Fe_3O_4 content in tailing; (b) Recovery of Cu

3.3.4 Characterization analysis of slag cleaning samples

According to the slag cleaning results of the copper converter slag in Figs. 6−8, the optimal experimental conditions were as follows: the temperature was 1300 °C, the mass fraction of pyrite/slag was 4%, the mass ratio of Fe/SiO_2 was 1.4, the impeller rotation speed was 63 r/min, and the time was 60 min. Under the optimal experimental conditions, the Fe_3O_4 content in the tailing was significantly decreased from 19.13 wt.% to 2.45 wt.%. The copper content decreased from 4.37 wt.% to 0.39 wt.% with a copper recovery of 92.52%.

Figure 9 shows the XRD result of the tailing obtained under the optimal experimental conditions. Compared with the XRD result of the raw copper converter slag shown in Fig. 2, the diffraction peaks of Fe_3O_4 significantly decreased. The main mineral composition of the tailing was Fe_2SiO_4, showing that most of the Fe_3O_4 was reduced to FeO, and then FeO reacted with SiO_2 to generate the low melting point substance of Fe_2SiO_4. No copper-containing phase was detected in the tailing, indicating that most of the copper matte subsided at the bottom of the molten bath during the slag cleaning process.

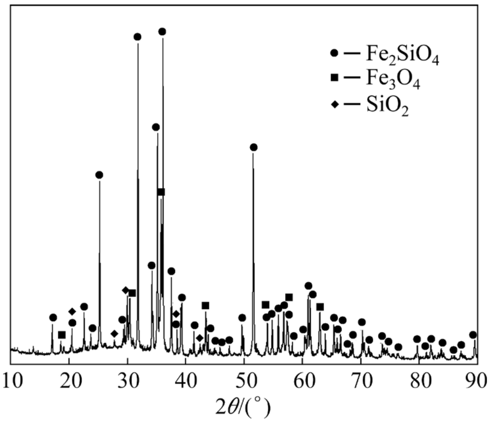

Fig. 9 XRD pattern of tailing

Figure 10 shows the SEM–EDS results of the tailing. After slag cleaning, the diameters of the copper matte particles were significantly reduced from 200 μm in raw copper converter slag (Fig. 3) to 20 μm in the tailing. There were no large particles of copper mattes in the tailing, indicating that the copper matte droplets subsided well. Only a small amount of copper matte particles was bundled with fayalite.

Figure 11(a) shows the XRD result of the obtained copper matte under optimal conditions. It can be seen that the main phases in the copper matte were Cu_5FeS_4, Cu, FeS, and Cu_2S. The formation of Cu_5FeS_4 resulted in the incorporation of iron into the copper matte, which reduced the copper grade in the copper matte.

In the slag cleaning process, zinc and lead volatilized and could be recovered from the flue gas. Figure 11(b) shows the XRD result of the condensate recovered from the flue gas. The phases of the condensate were mainly ZnO and a small amount of Pb_5O_8 and $Zn_4(AsO_4)_2O$, indicating that part of zinc, lead and arsenic was discharged and could be recovered from the flue gas.

In the process of slag cleaning, it was vital to investigate the distribution of elements in the copper matte, tailing, and flue gas. This would determine the recovery and extraction methods of these elements to realize the comprehensive recovery of valuable metals. The experimental sample under optimal conditions was analyzed to confirm the distribution of elements in the copper

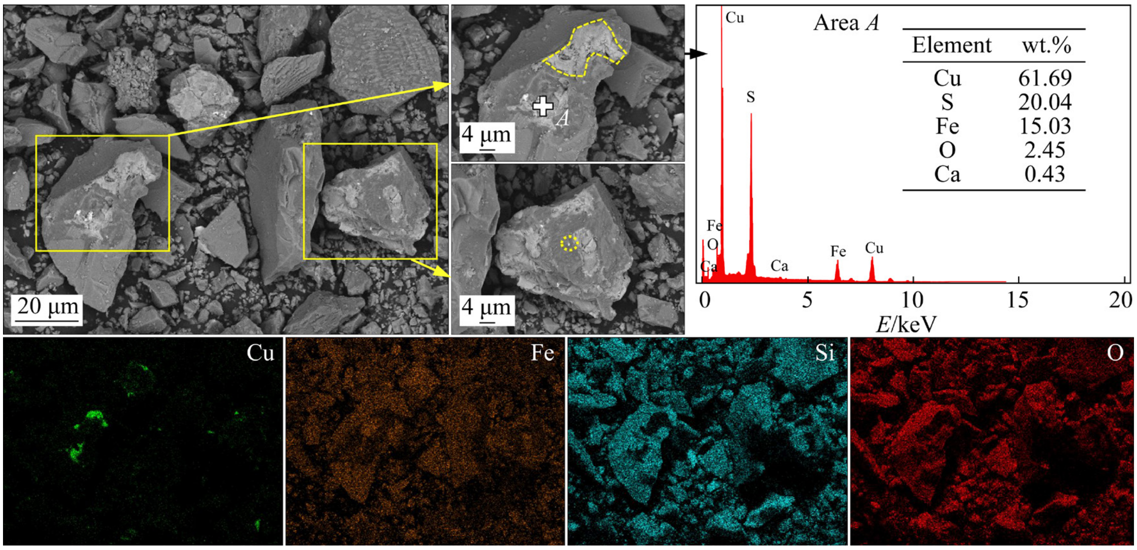

Fig. 10 SEM–EDS results of tailing

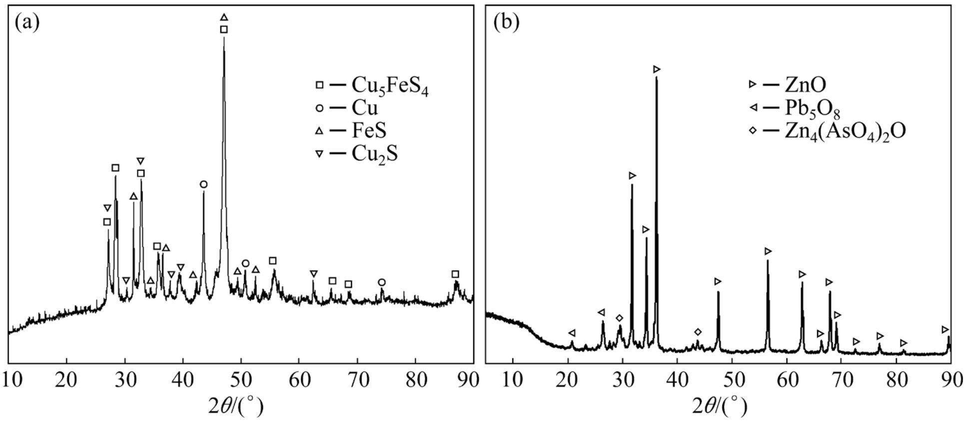

Fig. 11 XRD patterns of copper matte (a) and condensate of flue gas (b)

matte, tailing, and flue gas. The result is shown in Fig. 12. Most of the iron was retained in the tailing, and a small amount of iron entered the copper matte to form Cu_5FeS_4. Under the optimum experimental conditions, 92.52% of copper subsided in the bottom of the melt in the form of copper matte. Approximately 71.90% of zinc and 75.55% of lead volatilized in the flue gas, which could be used for extracting zinc and lead. In the slag cleaning process, 94.03% silver and 99.44% gold subsided into the copper matte and were finally recovered in anode mud to obtain greater economic benefits.

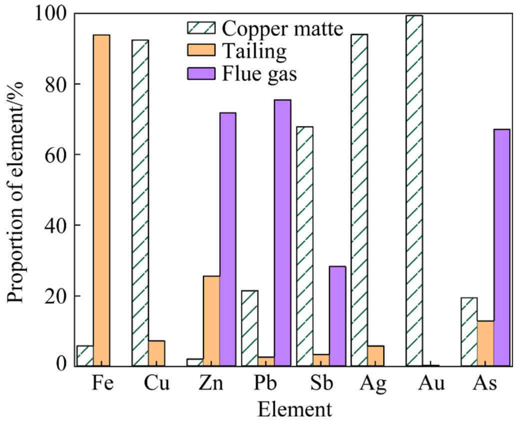

Fig. 12 Distribution of elements in copper matte, tailing, and flue gas in slag cleaning process

3.4 Slag cleaning mechanism

The main purpose of slag cleaning was to moderately recover copper from the copper slag. The precious metals of Au and Ag could be enriched in copper matte and recovered in the crude copper refining process. Therefore, whether the copper matte droplets could subside to the bottom of the melt was an important factor affecting the slag cleaning result. Copper matte droplets were affected by gravity (F_g), buoyancy (F_b) and resistance (F_d) during sedimentation.

When gravity, buoyancy and resistance were balanced, the copper matte droplets subsided down to the bottom of the melt at a uniform velocity. The uniform velocity u can be expressed by the Stokes equation as

$$u = 2gd_{\mathrm{CM}}^2\left(\rho_{\mathrm{CM}} - \rho_{\mathrm{slag}}\right)/(9\mu) \tag{6}$$

where μ is the viscosity of the copper slag.

As shown in Eq. (6), the sedimentation velocity of the copper matte droplet in the slag cleaning process is affected by three factors: (1) the density difference between the copper matte density (ρ_{CM}) and slag density (ρ_{slag}), the greater the density difference is, the faster the sedimentation velocity of the copper matte droplets is; (2) the diameter of the spherical copper matte droplet d_{CM}, the larger the diameter is, the faster the sedimentation velocity of the copper matte droplets is; (3) the viscosity of the copper slag, the smaller the viscosity of the slag is, the less the resistance of the copper matte droplets is, which is more conducive to the sedimentation of copper matte droplets.

In this work, the sedimentation velocity of copper matte droplets was mainly improved by decreasing the viscosity of copper slag. The reduction agent pyrite was used to reduce Fe_3O_4 in copper slag to FeO, and then the formed FeO reacted with SiO_2 to form the low melting point fayalite, which reduced the viscosity of copper slag. To study the effect of slag cleaning methods on copper recovery results, three experiments (Group A, without reduction agent and mechanical stirring; Group B, with reduction agent and mechanical stirring; Group C, with reduction agent and without mechanical stirring) were carried out. The temperatures were 1300 °C in three experiments with a time of 60 min and an impeller rotation speed of 63 r/min. The slag cleaning result is shown in Fig. 13.

After direct heating and melting at 1300 °C for 60 min, approximately 71.32% of the copper was recovered from the copper converter slag. However, the content of copper in the tailing was 1.42 wt.%, which needed to be recovered again. With reduction agent addition and mechanical stirring, the recovery of copper was 92.52%, and the content of copper in the tailing was decreased to 0.39 wt.%. The compositions of copper-containing molten iron reduced from the tailing could meet the requirement of copper-containing antibacterial stainless steel. Without mechanical stirring, the recovery of copper was 80.85% with a mass fraction of pyrite/slag of 4%, and the content of copper in the tailing was 0.91 wt.%. The slag cleaning result with mechanical stirring was much better than that without mechanical stirring. The content of copper without mechanical stirring was more than twice that with mechanical stirring. Therefore, proper mechanical stirring could accelerate the sedimentation of copper matte droplets and significantly improve the slag cleaning results.

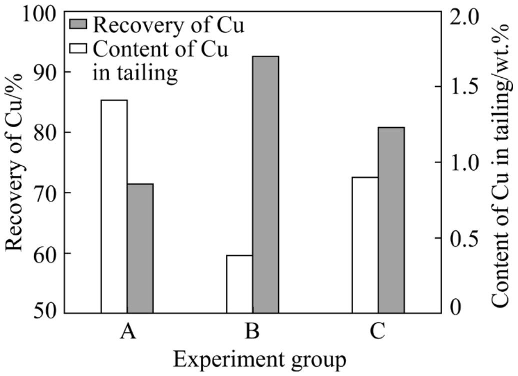

Fig. 13 Effect of slag cleaning method on copper recovery

As shown in the Stokes equation, the viscosity of the copper slag is an important influence factor for the sedimentation of copper matte droplets. Therefore, it is necessary to measure the viscosity of tailing after slag cleaning process. The tailings were crushed and put into an alumina crucible (d50(38) × 120 mm), which was then put into a comprehensive measuring instrument for melt properties (RTW−10, self-designed by Northeastern University, China). The heating power was turned on, and the crucible was heated to 1350 °C for 30 min to obtain a melt with uniform temperature and chemical compositions. The viscosity measurement probe was inserted into the molten slag and kept it 10 mm away from the bottom of the crucible. The viscosity meter began to measure, and when the viscosity value was stable, the computer began to automatically record the viscosity value of slag at the experimental temperature. After measuring 100 times at each temperature, the obtained average value was the viscosity value of the slag at this temperature. After the viscosity measurement was completed, the temperature was decreased to the next measured temperature at a cooling rate of 5 K/min. In order to ensure the accuracy of the measurement, the slag viscosity was measured at each experimental temperature after the temperature was kept constant for 20 min. The viscosity measuring probe was made of corundum. Before the viscosity measurement, the viscosity meter was calibrated with castor oil with known viscosity. The standard error of viscosity during measurement was less than ±0.002 Pa·s.

Figure 14 shows the viscosity of the tailing of Groups A, B and C. With increasing temperature, the viscosity of the tailing significantly decreased. However, the viscosity of the tailing of Group A was much higher than those of Group B and Group C. With the addition of the reduction agent pyrite, the viscosity of the tailing of Group B and Group C decreased rapidly as the temperature increased from 1100 to 1200 °C. Compared with the viscosity of the tailing of Group C, the viscosity of the tailing of Group B was lower, which was conducive to the rapid sedimentation of copper matte droplets. The viscosity of the tailing was decreased from 0.68 Pa·s without reduction agent and mechanical stirring to 0.12 Pa·s with reduction agent and mechanical stirring at 1300 °C for 60 min.

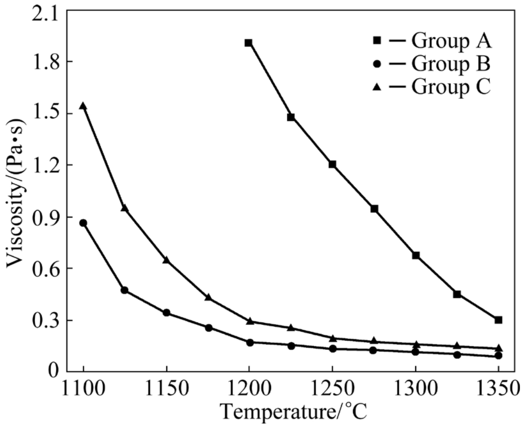

Fig. 14 Viscosity of tailing at different temperatures

4 Conclusions

(1) The addition of SiO_2 significantly reduced the initial reduction temperature of magnetite and pyrite. And Cu_2O was converted to Cu_2S in the slag cleaning process.

(2) The copper recovery was 92.52% and the content of copper was decreased from 4.37 wt.% to 0.39 wt.% in tailing under the optimum conditions.

(3) With the addition of reduction agent and mechanical stirring, the viscosity of the tailing was decreased from 0.68 to 0.12 Pa·s. And mechanical stirring was conducive to accelerating the sedimentation of copper matte droplets.

(4) This novel slag cleaning method can not only treat copper converter slag, but also be directly applied to electric cleaning furnace to significantly reduce the content of copper in tailing. The results provide a novel treatment and utilization of copper slag.

Acknowledgments

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References

[1] LI Zhi, MA Guo-jun, LIU Meng-ke, ZOU Jing-jing. Calculation model for activity of FeO in quaternary slag system SiO_2−CaO−Al_2O_3−FeO [J]. Metals, 2018, 8: 714.

[2] ZHANG Hui-bin, HE Yu-zheng, HU Jing-jing, WANG Ya-nan, CAO Hua-zhen, ZHOU Jun, ZHENG Guo-qu. Assessment of selective sequential extraction procedure for determining arsenic partitioning in copper slag [J]. Transactions of Nonferrous Metals Society of China, 2020, 30: 2823−2835.

[3] ÇORUH S, ERGUN O N, CHENG T W. Treatment of copper industry waste and production of sintered glass-ceramic [J]. Waste Management & Research, 2006, 24: 234−241.

[4] GYUROV S, RABADJIEVA D, KOVACHEVA D, KOSTOVA Y. Kinetics of copper slag oxidation under nonisothermal conditions [J]. Journal of Thermal Analysis and Calorimetry, 2014, 116: 945−953.

[5] WANG Da-wei, ZHAO Zong-wen, LIN Zhang, LIANG Yan-jie, KANG Li, PENG Bing. Interaction mechanism between arsenate and fayalite-type copper slag at high temperatures [J]. Transactions of Nonferrous Metals Society of China, 2022, 32: 709−720.

[6] BANDA W, MORGAN N, EKSTEEN J J. The role of slag modifiers on the selective recovery of cobalt and copper from waste smelter slag [J]. Minerals Engineering, 2002, 15: 899−907.

[7] WANG Qin-meng, GUO Xue-yi, TIAN Qing-hua. Copper smelting mechanism in oxygen bottom-blown furnace [J]. Transactions of Nonferrous Metals Society of China, 2017, 27: 946−953.

[8] ZHANG Bao-jing, NIU Li-ping, ZHANG Ting-an, LI Zhi-qiang, ZHANG Dong-liang, ZHENG Chao. Alternative reduction of copper matte in reduction process of copper slag [J]. ISIJ International, 2017, 57(5): 775−781.

[9] YANG Zhi-hon, LIN Qiao, LU Sheng-chun, HE Yong, LIAO Guang-dong, KE Yi. Effect of CaO/SiO_2 ratio on the preparation and crystallization of glass-ceramics from copper slag [J]. Ceramics International, 2014, 40: 7297−7305.

[10] ZHANG Jun, QI Yuan-hong, YAN Ding-liu, CHENG Xiang-li, HE Peng. Characteristics and mechanism of reduction and smelting-separation process of copper slag [J]. Journal of Iron and Steel Research, International, 2015, 22(2): 121−127.

[11] MIGANEI L, GOCK E, ACHIMOVIČOVÁ M, KOCH L, ZOBEL H, KÄHLER J. New residue-free processing of copper slag from smelter [J]. Journal of Cleaner Production, 2017, 164: 534−542.

[12] SHI Yu, WEI Yong-gang, ZHOU Shi-wei, LI Bo, YANG Yin-dong, WANG Hua. Effect of B_2O_3 content on the viscosity of copper slag [J]. Journal of Alloys and Compounds, 2020, 822: 153478.

[13] ZHANG Bei-kai, GUO Xue-yi, WANG Qin-meng, TIAN Qing-hua. Thermodynamic analysis and process optimization of zinc and lead recovery from copper smelting slag with chlorination roasting [J]. Transactions of Nonferrous Metals Society of China, 2021, 31: 3905−3917.

[14] ALTER H. The composition and environmental hazard of copper slags in the context of the Basel Convention [J]. Resources, Conservation and Recycling, 2005, 43: 353−360.

[15] KHANZADI M, BEHNOOD A. Mechanical properties of high-strength concrete incorporating copper slag as coarse aggregate [J]. Construction and Building Materials, 2009, 23: 2183−2188.

[16] EDWIN R S, de SCHEPPER M, GRUYAERT E, de BELIE N. Effect of secondary copper slag as cementitious material in ultra-high performance mortar [J]. Construction and Building Materials, 2016, 119: 31−44.

[17] TURAN M D, SARI Z A, MILLER J D. Leaching of blended copper slag in microwave oven [J]. Transactions of Nonferrous Metals Society of China, 2017, 27: 1404−1410.

[18] LI Lei, WANG Hua, HU Jian-hang. Smelting chlorination method applied to removal of copper from copper slags [J]. Journal of Central South University, 2015, 22: 59−65.

[19] KIM B S, JO S K, SHIN D, LEE J C, JEONG S B. A physico-chemical separation process for upgrading iron from waste copper slag [J]. International Journal of Mineral Processing, 2013, 124: 124−127.

[20] GYUROV S, KOSTOVA Y, KLITCHEVA G, ILINKINA A. Thermal decomposition of pyrometallurgical copper slag by oxidation in synthetic air [J]. Waste Management & Research, 2011, 29(2): 157−164.

[21] SHAMSI M, NOAPARAST M, SHAFAIE S Z, GHARABAGHI M. Synergism effect of collectors on copper recovery in flotation of copper smelting slags [J]. Geosystem Engineering, 2016, 19(2): 57−68.

[22] MOSKALYK R R, ALFANTAZI A M. Review of copper pyrometallurgical practice: Today and tomorrow [J]. Minerals Engineering, 2003, 16: 893−919.

[23] ZHANG Hai-pei, LI Bo, WEI Yong-gang, WANG Hua, YANG Yin-dong, MCLEAN A. Reduction of magnetite from copper smelting slag in the presence of a graphite rod [J]. Metallurgical and Materials Transactions B, 2020, 51: 2663−2672.

[24] ZHOU Shi-wei, WEI Yong-gang, LI Bo, WANG Hua. Effect of iron phase evolution on copper separation from slag via coal-based reduction [J]. Metallurgical and Materials Transactions B, 2018, 49: 3086−3096.

[25] ZHANG Bao-jing, ZHANG Ting-an, NIU Li-ping, LIU Nan-song, DOU Zhi-he, LI Zhi-qiang. Moderate dilution of copper slag by natural gas [J]. JOM, 2018, 70(1): 47−52.

[26] LI Bo, WEI Yong-gang, WANG Hua, YANG Yin-dong. Reduction of magnetite from copper smelting slag using petro-diesel and biodiesel [J]. ISIJ International, 2018, 58(6): 1168−1174.

[27] WANG Kun, LIU Yan, JIANG Bao-cheng, ZHANG Ting-an. Recovery of Au, Ag and Cu from copper slag by vortex dilution method [J]. Rare Metal Materials and Engineering, 2021, 50(9): 3417−3421. (in Chinese)

熔融转炉铜渣贫化法回收铜

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摘　要：为了从铜渣中回收铜，提出熔融铜渣贫化回收铜的新方法。首先计算贫化过程的热力学和 FeO−SiO_2 二元相图，然后研究实验参数对 Fe_3O_4 还原和铜回收率的影响规律，分析贫化机理。结果表明：氧化硅的加入可以明显降低黄铁矿还原磁铁矿的初始反应温度。最优条件下，铜渣中的 Fe_3O_4 和铜含量分别降低至 2.45%和 0.39%(质量分数)，铜回收率为 92.52%。贫化后，超过 94%的银和 99%的金沉降在铜锍中。大约 72%的锌和 75%的铅挥发进入烟气。由于磁铁矿的还原，铜渣的黏度从 0.68 Pa·s 降低到了 0.12 Pa·s，并且机械搅拌可以强化铜锍液滴的沉降。

关键词：铜渣；铜回收；贫化；磁铁矿还原；机械搅拌

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