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Synergistic recovery of copper, lead and zinc via sulfurization−reduction method from copper smelting slag

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Abstract: Cu, Pb and Zn were synergistically recovered from copper smelting slag via the sulfurization−reduction method. Pyrite was used as the sulfurizing agent to selectively sulfurize and recover valuable metals lost in the slag in the reductive atmosphere. Thermodynamic analysis and laboratory experiments were carried out to determine the feasibility and reliability of this process. The optimal experimental conditions were defined as follows: a dosage of sulfurizing agent (pyrite) of 26%, 6% coke addition of copper smelting slag mass, and smelting at 1350 °C for 3 h. Under the optimum conditions, Cu, Pb and Zn recoveries were 97.58%, 89.91% and 98.20%, respectively. Cu, Pb and Zn contents in the cleaned slag were 0.10%, 0.01% and 0.38%, respectively. The matte contained 7.28% copper. The proportions of Zn entering the gas, slag and matte phases were 80.93%, 10.09% and 8.98%, respectively. The proportions of Pb entering the gas, slag and matte phases were 40.12%, 1.79% and 58.09%, respectively. The matte phase mainly comprised Cu_8S_5, FeS, and some metals, such as Cu, Pb and Fe. Fe_3O_4 in the slag was reduced from 19.50% to 2.97%.

Key words: copper smelting slag; copper recovery; lead and zinc fuming; sulfurizing agent

1 Introduction

Copper is an essential primary material, and the pyrometallurgical process produces 80%−90% copper [1−4]. According to statistics released by China, the annual production of China's refined copper was 11063 kt in 2022, and 1 t of copper produced 2.2−3 t copper smelting slag [5,6]. Although the composition of copper smelting slag produced by different smelting methods varies, the principal phases are essentially fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) [7,8]. Copper slag contains valuable metals such as 0.5%−6.0% Cu, 0.2%−0.6% Pb, and 1.0%−5.5% Zn, which have high recovery. In many countries, copper smelting slag is dumped directly without treatment [3], leading to resource waste and ecotoxicity from the leakage of harmful ions such as Pb and Zn [9−11].

In recent years, extensive research has been conducted to recover valuable metals from copper slag [11−15]. They can be classified into five categories: pyrometallurgical, hydrometallurgical, pyrometallurgical−hydrometallurgical combination, flotation, and biological recovery processes [16,17]. The principle of pyrometallurgical processing is to reduce the magnetite phase in the slag, improve the fluidity of the slag, and accelerate the aggregation of tiny particles of copper and copper matte into large particles that settle into the copper matte phase [18,19].

Pyrometallurgical processing consists of three main principles. The first principle is to destroy the structure of copper slag using reducing agents or modifiers to recover valuable metals [20,21]. QU et al [22] used a 70%H_2−30%N_2 mixture to reduce copper slag. The results showed that during the reduction process, the matte precipitated in the slag,

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and the copper remaining in the cleaning slag mainly existed in the form of chemical dissolution. GUO et al [23] recycled copper and iron from copper slag by adding compound additives (a mixture of hematite, pyrite, and manganous oxide). The results showed that the synergistic action of quicklime and compound additives could improve the fluidity of molten slag. The magnetite content increased from 32.9% to 65.1%, and the metallic copper and cuprous sulfide contents rose from 80.0% to 90.3%. After slow cooling, the average particle size of the target minerals in the modified slag exceeded 50 μm, providing technical support and theoretical guidance for the beneficiation process.

The second principle involves adding modifiers (such as calcium oxide and calcium borate) and reducing agents to explore the synergistic effect [14, 18]. SHI et al [24] investigated the study of modifying copper slag with a calcium borate additive and reducing copper in the slag. Under the synergistic effect of calcium borate and ditch oil, the copper content in slag decreased from 4.49% to 0.89%. With increasing calcium borate content, the magnetic iron oxide content remained unchanged. ZHANG et al [7] explored the reduction of copper in slag using natural gas combined with calcium oxide. Under the conditions of blowing time of 20 min, temperature of 1250 °C, copper matte settling time of 60 min, and calcium oxide of 4%, copper in the slag decreased from 4.51% to 0.5%, and Fe_3O_4 decreased to 7.36%.

The third principle is adding sulfurizing and reducing agents to explore the synergy between them [25,26]. GUO et al [3] used waste ferric-oxide desulfurizer as a sulfurizing agent and coke as a reducing agent to improve slag properties, recover copper and reduce magnetite from copper slag. The results showed that the recovery of copper was 90.81%, and the produced copper matte contained 15.87% Cu, 20.25% S, and 49.56% Fe. LI et al [27] used calcium sulfate and coke as sulfurizing and reducing agents to recover Cu and Co from copper slag. The optimum conditions were a constant temperature at 1350 °C for 3 h and the addition of 12% coke and 20% $CaSO_4$, resulting in 92.04% Cu and 95.62% Co recovery in the copper−cobalt matte, with the cleaning slag contained 0.2% Cu and 0.045% Co.

At present, copper cleaning technology focuses solely on the recovery of Cu and does not consider the recovery of valuable metals such as Pb and Zn. Leaching of harmful ions such as Pb and Zn can pose potential ecological safety hazards. In this study, copper smelting slag was treated using the sulfurization−reduction method. Pyrite served as a sulfurizing agent to sulfurize and capture the metals into the matte phase or gas phase from the slag. Thermodynamic analysis and laboratory experiments were conducted to inspect and test the technical feasibility. By adding varying amounts of sulfurizing agent and a reducing agent to copper slag and controlling the reaction temperature and holding time, the distribution of various valuable elements in the copper matte phase, slag phase, and gas phase was explored. The optimal combination of additives and process conditions were investigated to achieve Cu recovery and Pb/Zn fumes.

2 Experimental

2.1 Materials

The copper smelting slag used in this study was obtained from a smelting slag dump in a smelting company in Shandong Province. The raw materials were crushed by a prototype machine (JZGJ100-10, China) for 20 s, and the samples were dried after grinding [28]. The chemical compositions of smelter slag were analyzed by inductively coupled plasma-atomic emission spectrometry (PS-6, Barid Company, USA). The results are presented in Table 1. The slag contained 3.03% Cu, 0.53% Pb, and 2.76% Zn. Pyrite mainly comprised 46.61% S and 46.62% Fe. The chemical composition and proximate analysis of coke ash (Table 2) were determined by GB/T212-2008 and GB/T219-2008.

Tables 3−6 show the chemical phase analysis results of the copper, iron, lead and zinc phase compositions, respectively. Chemical phase analysis was based on the difference in the solubility and dissolution of various minerals in chemical solvents, using the method of selective dissolution

Table 1 Chemical composition of copper smelting slag (wt.%)

Fe_{total}	Cu	Pb	Zn	As	CaO	SiO_2	S
41.65	3.03	0.53	2.76	0.11	2.62	20.70	1.20

Table 2 Industrial analysis and chemical composition of coke (wt.%)

Industrial analysis			
M_{ad}	A_{ad}	V_{ad}	FC_{ad}
0.87	14.10	7.22	77.81

Chemical composition of ash					
Fe_{total}	Al_2O_3	CaO	MgO	S	P
0.30	9.18	0.38	0.11	0.55	0.35

(M_{ad}: Moisture; A_{ad}: Ash; V_{ad}: Volatile matter; FC_{ad}: Fix carbon)

Table 3 Distribution of copper in associated minerals

Mineral	Content/wt.%	Fraction/%
Copper oxide	0.53	17.49
Metallic copper	0.19	6.27
Copper sulfide	2.21	72.94
Combined copper oxide	0.1	3.3
Cu_{total}	3.03	100

Table 4 Distribution of iron in associated minerals

Mineral	Content/wt.%	Fraction/%
Magnetite	19.5	46.82
Metallic iron	1.21	2.91
Fayalite	20.74	49.15
Hematite	0.1	0.56
Iron sulfide	0.1	0.56
Fe_{total}	41.65	100

Table 5 Distribution of lead in associated minerals

Mineral	Content/wt.%	Fraction/%
Lead sulfide	0.13	24.53
Lead oxide	0.03	5.66
Lead sulfate	0.1	18.87
Lead silicate	0.27	50.94
Pb_{total}	0.53	100

Table 6 Distribution of zinc in associated minerals

Mineral	Content/wt.%	Fraction/%
Zinc ferrite	1.24	44.93
Zinc silicate	1.42	51.45
Zinc oxide	0.02	0.69
Zinc sulfide	0.08	2.93
Zn_{total}	2.76	100

to accurately identify the mineral composition of raw material [3]. The results indicated that 72.94% of copper existed in the form of copper sulfide, 17.49% of copper was lost in the slag in oxide form, and 6.27% of copper was present in metallic copper. Pb mainly existed in the form of lead silicate and lead sulfide, while Zn primarily resided in the form of zinc silicate and zinc ferrite. A total of 49.15% of iron existed in the form of fayalite, and 46.82% of iron was present in magnetite. Figure 1 illustrates that the principal phases of copper smelting slag are Fe_3O_4, Fe_2SiO_4, and $Ca(Fe,Mg)Si_2O_6$. It can be seen from Fig. 2 that different contrasts represent different phases in which various substances exist, and copper mainly exists as the sulfide.

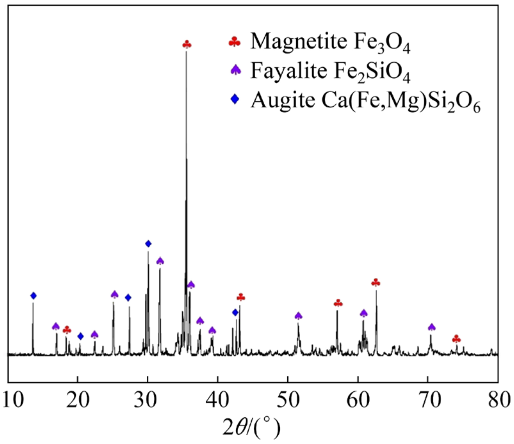


Fig. 1 XRD pattern of copper slag

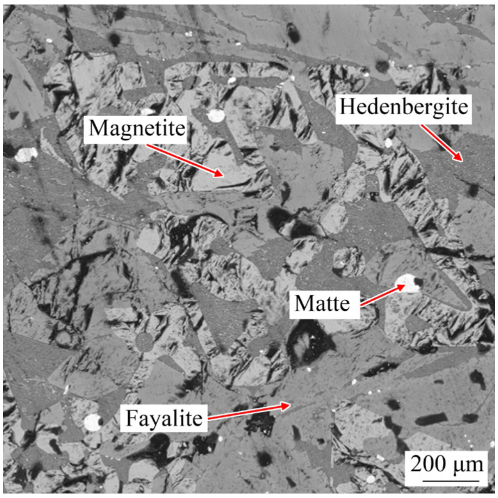


Fig. 2 SEM−EDS analysis of copper slag

2.2 Methods

In the experimental process, 200 g of copper smelting slag and a certain proportion of composite additives (pyrite and coke) were thoroughly mixed in an agate mortar and then placed into a corundum crucible. Subsequently, the corundum crucible was put into a vertical tube furnace (see Fig. 3), heated at a rate of 10°C/min under a high purity argon gas (Ar) atmosphere, and kept at a constant temperature (1250−1450 °C) for various durations (1−4 h) to ensure complete smelting. After the reaction, the sample was slowly cooled to room temperature under the protection of Ar, and then it was removed from the furnace and weighed. After the crucible was broken, the copper matte and slag phases appeared in the experimental sample. Finally, both the matte and cleaned slag were chemically analyzed by ICP-AES.

2.3 Data analysis method and characterization

(1) Copper matte and cleaned slag mass

According to the principle of copper mass conservation, it is assumed that the mass of copper matte after the reaction is X, and the mass of cleaned slag after the reaction is Y.

$$X\beta+Y\chi=M_1\alpha \tag{1}$$

$$X+Y=M_3-M_2 \tag{2}$$

where M_1 is the mass of copper slag before the reaction, M_2 is the mass of the crucible, M_3 is the mass of experimental raw materials after the reaction, α is the mass fraction of metals (Cu, Pb, Zn) in copper smelting slag, β is the mass fraction of metals (Cu, Pb, Zn) in copper matte, and χ is the mass fraction of metals (Cu, Pb, Zn) in the cleaned slag.

(2) Copper recovery

According to the mass of copper matte calculated in Eqs. (1) and (2), the Cu recovery efficiency (R_{Cu}) is presented in Eq. (3):

$$R_{\mathrm{Cu}}=\left(\frac{X\beta}{M_1\alpha}\right)\times 100\% \tag{3}$$

(3) Pb and Zn recovery

According to the mass of cleaned slag calculated in Eqs. (1) and (2), the Pb and Zn recovery efficiencies are presented by Eq. (4):

$$R_{\mathrm{Pb/Zn}}=\left(1-\frac{Y\chi}{M_1\alpha}\right)\times 100\% \tag{4}$$

(4) Three-phase distribution of Pb and Zn

The three-phase distributions of Pb and Zn are presented by Eqs. (5)−(7), which are K_1 in the gas phase, K_2 in the slag phase, and K_3 in the copper matte phase:

$$K_1=1-K_2-K_3 \tag{5}$$

$$K_2=\frac{Y\chi}{M_1\alpha} \tag{6}$$

$$K_3=\frac{X\beta}{M_1\alpha} \tag{7}$$

Samples were randomly sampled and tested by inductively coupled plasma atomic emission spectroscopy (ICP-AES, PS-6, Barid Company, USA) to determine the chemical composition. Phase

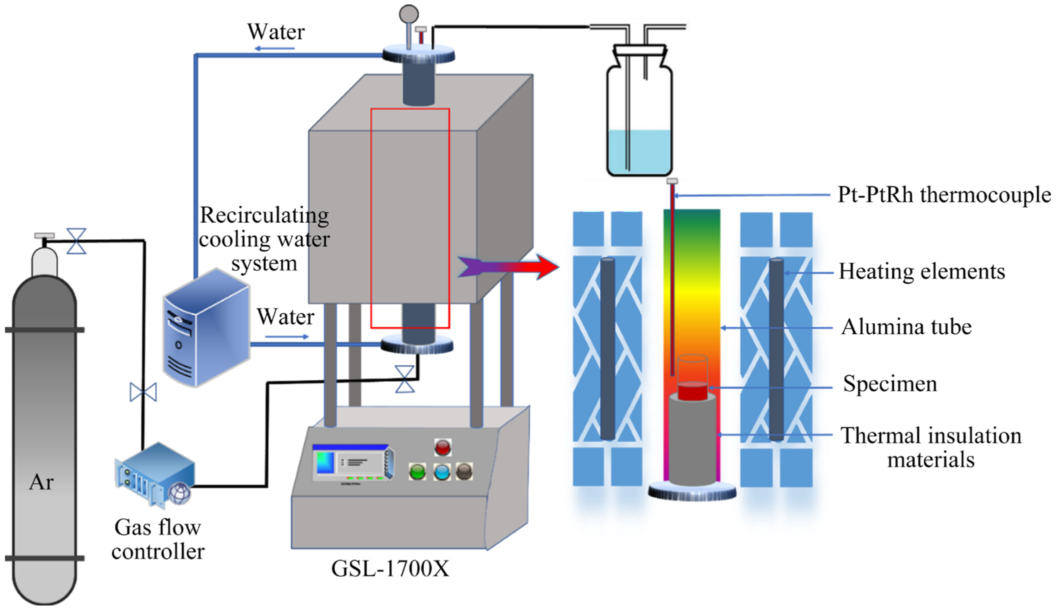


Fig. 3 Schematic diagram of experimental apparatus

identification was conducted using X-ray powder diffractometer (XRD, D/max−2550, Cu K_α radiation, from Nippon Science Co., Ltd.). Scanning electron microscope and energy dispersive spectrometer (SEM−EDS, SIRION200 from FEI Company, USA) were used to determine the elemental distribution and phase structure of sample.

2.4 Thermodynamic analysis

To accurately represent the reaction mechanism and simplify the complicated metallurgical reaction process, we used Cu_2O, $PbSiO_3$, $ZnFe_2O_4$ and Zn_2SiO_4 to represent the existing forms of Cu, Pb and Zn dissolved in the slag [29]. Figure 4 illustrates the changes in standard free energy (ΔG) with temperature during the sulfurizing−reduction process of Cu/Pb/Zn oxides. Except for Eq. (13), the standard free energy of all other reactions is negative within a specific temperature range, indicating that sulfurizing−reduction is thermodynamically feasible. Consequently, adding pyrite and coal can realize Cu recovery and Pb/Zn fuming.

$$\mathrm{Cu_2O(l)+C(s)=2Cu(l)+CO(g)} \tag{8}$$

$$\mathrm{Cu_2O(l)+FeS(s)=Cu_2S(l)+FeO(l)} \tag{9}$$

$$\mathrm{PbSiO_3+C(s)=Pb(g)+CO(g)+SiO_2(l)} \tag{10}$$

$$\mathrm{PbSiO_3+FeS(s)=PbS(g)+FeO(l)+SiO_2(l)} \tag{11}$$

$$\mathrm{Zn_2SiO_4+C(s)=Zn(g)+CO(g)+SiO_2(l)} \tag{12}$$

$$\mathrm{Zn_2SiO_4+2FeS(s)=2ZnS(g)+2FeO(l)+SiO_2(l)} \tag{13}$$

$$\mathrm{ZnFe_2O_4+2C(s)=Zn(g)+2CO(g)+2FeO(l)} \tag{14}$$

$$\mathrm{ZnFe_2O_4+FeS(s)+C(s)=ZnS(g)+CO(g)+3FeO(l)} \tag{15}$$

It is necessary to know the saturated vapor pressures for investigating the fuming of Pb and Zn. The Clausius−Klepp Lang equation is used to express the relationship between the vapor pressure of Pb and Zn and temperature as [30]

$$\lg P_{\mathrm{Zn}}=-6620T^{-1}-1.255\lg T+16.52 \quad (426-907\ ^\circ\mathrm{C}) \tag{16}$$

$$\lg P_{\mathrm{Pb}}=-10130T^{-1}-0.985\lg T+13.28 \quad (327-1740\ ^\circ\mathrm{C}) \tag{17}$$

$$\lg P_{\langle\mathrm{PbO}\rangle}=-13480T^{-1}-0.921\lg T-0.00035T+16.48 \quad (23-886\ ^\circ\mathrm{C}) \tag{18}$$

$$\lg P_{(\mathrm{PbO})}=-13300T^{-1}-0.811\lg T-0.00043T+16.93 \quad (886-1523\ ^\circ\mathrm{C}) \tag{19}$$

$$\lg P_{(\mathrm{PbS})}=-11597T^{-1}+12.57 \quad (577-827\ ^\circ\mathrm{C}) \tag{20}$$

$$\lg P_{(\mathrm{ZnS})}=-13846T^{-1}+12.7 \quad (822-1162\ ^\circ\mathrm{C}) \tag{21}$$

Figure 5 illustrates that the saturated vapor pressure of Pb/Zn increases with increasing temperature. At the same temperature, Zn volatilizes earlier than Pb and enters the gas phase. Lead sulfide exhibits better volatilization than lead oxide and lead at low temperatures. Both lead oxide and lead sulfide show superior volatilization compared with metallic lead, with lead sulfide being more easily vaporized than zinc sulfide.

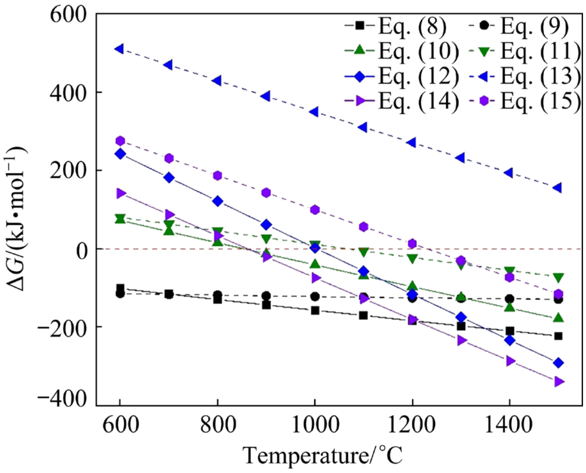


Fig. 4 Variation in standard Gibbs free energy of several reactions with temperature obtained by thermodynamic calculations using Factsage 7.1 software

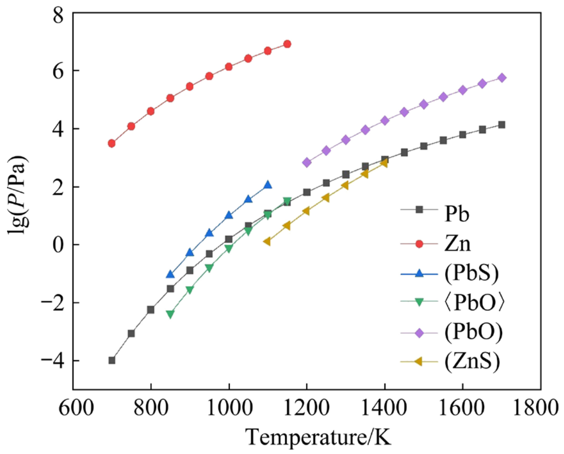


Fig. 5 Relationship between temperature and saturated vapor pressure

3 Results and discussion

3.1 Effect of sulfurizing addition

The primary purpose of the sulfurizing agent is to facilitate the reaction of Cu_2O to produce Cu_2S, which can then aggregate into large copper matte particles and enter the copper matte phase. $PbSiO_3$ is sulfided into PbS and enters the gas phase because of the high vapor pressure of lead sulfide at low temperatures. Although zinc sulfide can volatilize into the gas phase, the vapor pressure of ZnS is much lower than that of Zn. ZnS is difficult to reduce by reducing agents, so it is necessary to control the sulfurization behavior of Zn. Insufficient use of the sulfurizing agent can make it difficult for small copper matte particles to aggregate into the matte layer. It can also reduce the possibility of lead volatilization by PbS. Conversely, excessive use of the sulfurizing agent can result in a low matte grade, affecting the practical effect and leading to more Zn being sulfurized into ZnS, which affects its volatilization. Therefore, it is crucial to investigate the addition of pyrite.

The effect of sulfurizing agent addition on the recovery of Cu and the grade of Cu in the cleaned slag and matte is demonstrated in Fig. 6(a). Under the same reducing agent addition, smelting temperature, and constant temperature, the recovery of Cu increased with increasing the sulfurizing addition from 71.41% to 98.42% because S preferentially combined with Cu to form Cu_2S and then combined with FeS to aggregate into large matte particles that entered the matte phase. Cu in the cleaning slag decreased gradually and then tended to be stable. The matte grade gradually decreased from 9.63% to 7.06% due to the gradual increase in FeS.

With increasing sulfurizing addition, the recovery of Pb and Zn is depicted in Fig. 7(a_1). The recovery of Pb and Zn initially increased and then decreased. The recovery of Pb grew from 78.29% to 98.2% before dropping to 96.94%. The recovery of Zn rose from 72.21% to 89.91% and then declined to 85.83%. On the one hand, excessive sulfurizing agent reduced the iron concentration of cleaning slag due to excess S injected into the smelting system. It could be seen from the viscosity curve of the $CaO-FeO-SiO_2$ slag system [31] that the content of iron oxide was decreased, and the viscosity of slag was increased, which led to the deterioration of the cleaning slag properties and the reduction of Pb

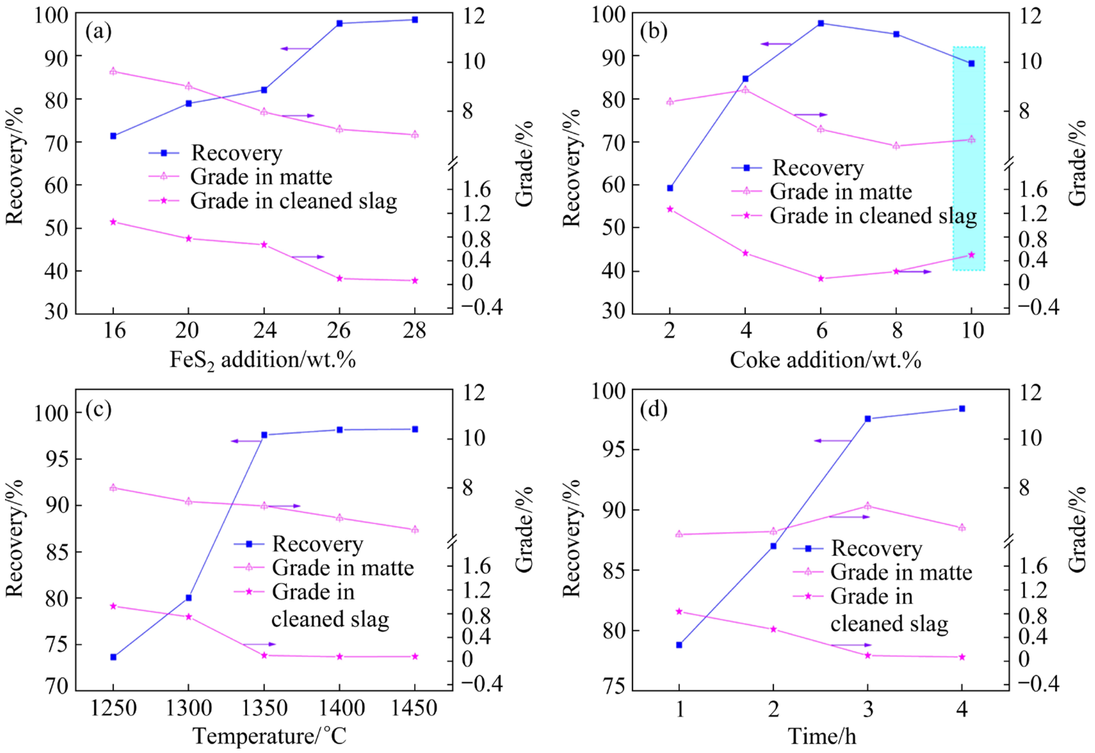


Fig. 6 Effect of process parameters on grade and recovery of Cu: (a) Pyrite dosage (at 1350 °C for 3 h with 6% coke); (b) Coke dosage (at 1350 °C for 3 h with 26% pyrite); (c) Smelting temperature (3 h with 26% pyrite and 6% coke); (d) Smelting duration (at 1350 °C with 26% pyrite and 6% coke)

and Zn recovery. On the other hand, Zn began to form more sulfides that were difficult to volatilize, which affected the recovery of Zn.

From the three-phase distribution of Zn, as shown in Fig. 7(a_2), the proportion of Zn entering the gas phase increased from 67.41% to 80.93% with increasing sulfurizing before declining to 76.23%. When the sulfurizing agent was used excessively, the proportion of Zn entering the gas phase declined, while the proportion entering the slag phase grew due to the production of additional ZnS. Figure 7(a_3) showed that with increasing sulfurizing agent addition, the proportion of Pb entering the gas phase increased from 34.96% to 42.43%. Based on the previous theoretical analysis, the vapor pressure of lead sulfide is lower than that of lead oxide, making it easier to volatilize. Therefore, when the sulfurizing agent was used excessively, it resulted in a deterioration of the slag properties. It is challenging to volatilize from the system, which increased the fraction of entering the slag phase and confirmed the above findings. According to the three-phase distribution of Pb and Zn, Pb entered the matte phase more easily than Zn [32]. In summary, the optimum amount of sulfurizing agent was 26% of the total mass of copper slag. When the addition of sulfurizing agent was 26%, the proportions of S entering the gas, slag, and copper matte phases were 25.91%, 4.72%, and 69.37%, respectively.

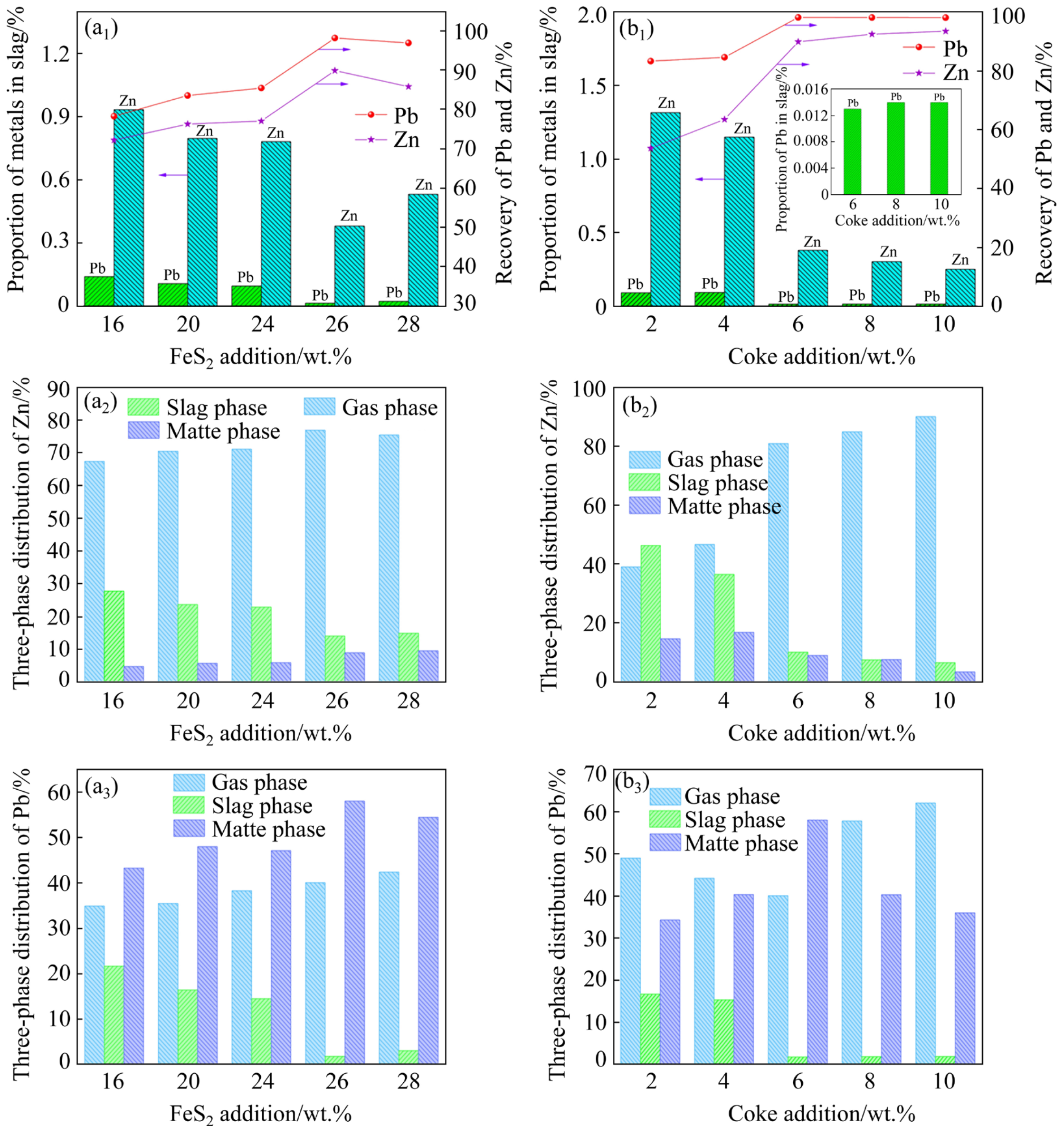
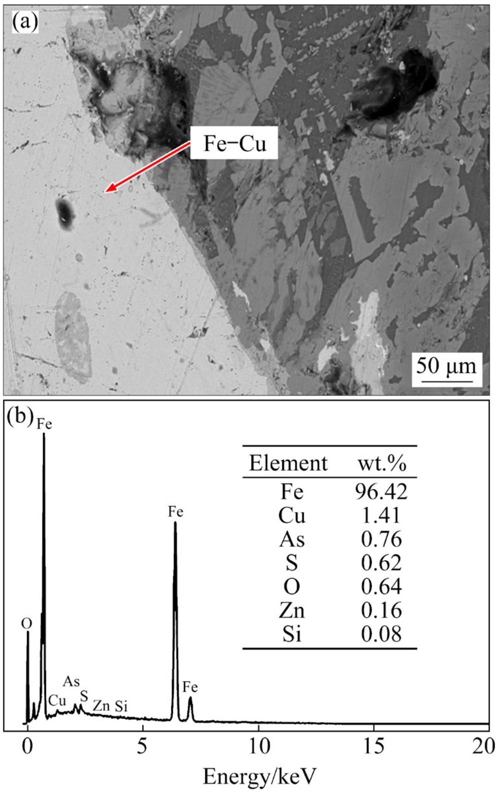


Fig. 7 Influence of process parameters on recovery and three-phase distribution of Pb and Zn: (a_1, a_2, a_3) Pyrite addition (at 1350 °C for 3 h with 6% coke); (b_1, b_2, b_3) Coke addition (at 1350 °C for 3 h with 26% pyrite)

3.2 Effect of reducing agent addition

The primary purpose of reducing agents is to reduce high-valent iron oxide (Fe_3O_4) to low-valent oxide (FeO). Inadequate addition of reducing agent results in the insufficient reduction of Fe_3O_4, leading to suboptimal volatilization of Pb and Zn. Hence, it is essential to investigate coke addition.

The effect of reducing agent addition on the recovery and grade of copper in the cleaned slag and matte is illustrated in Fig. 6(b). With the same amount of sulfurizing agent, smelting temperature, and constant temperature time, the copper recovery increased from 59.28% to 97.58% before dropping to 88.21% with the addition of the reducing agent. The copper content in the cleaned slag declined from 1.27% to 0.1% before rising to 0.44%. The copper content in the matte decreased from 8.87% to 6.86%. With 6% addition of reducing agent, the matte grade was 7.28%. Excessive use of reducing agent resulted in the reduction of iron oxide to metallic Fe (see Fig. 8), leading to high viscosity and poor fluidity of the molten slag [3].



Element	wt.%
Fe	96.42
Cu	1.41
As	0.76
S	0.62
O	0.64
Zn	0.16
Si	0.08

Fig. 8 SEM−EDS results with excess reducing agent (smelting sulfurization−reduction at 1350 °C for 3 h with 26% pyrite and 10% coke)

With increasing coke addition, the recovery of Pb and Zn is demonstrated in Fig. 7(b_1). The recovery of Pb grew from 83.32% to 98.2% with increasing coke addition (2%−6%). When the reducing agent was used excessively, the recovery of Pb remained unchanged, while the recovery of Zn gradually increased from 53.68% to 93.5%. Although the high-reducing atmosphere could enhance the recovery of Zn, it resulted in a decrease in copper recovery.

From the three-phase distribution of Zn, as shown in Fig. 7(b_2), the proportion of Zn entering the gas phase increased from 39.04% to 90.11% with increasing coke. The proportion of Zn entering the slag phase gradually decreased from 46.32% to 6.49%. It can be seen from the three-phase distribution of Pb (Fig. 7(b_3)) that with increasing coke addition, the proportion of Pb entering the slag phase decreased from 16.68% to 1.89%. The proportion of lead in the gas and matte phases changed when the reducing agent was used excessively. Under a weak reducing atmosphere, Pb was primarily volatilized in the form of lead sulfide or lead oxide. With the enhancement of reducibility, Pb generated by the lead element was captured by the matte, leading to a decrease in the proportion of Pb entering the gas phase and an increase in the proportion entering the matte phase. Excessive enhancement of the reductive atmosphere would impact the coalescence and settling of the matte, resulting in a reduction of matte grade and the ability to capture Pb. This was consistent with the distribution law observed in previous studies on copper smelting, which verified the experimental reliability [33].

3.3 Effect of smelting temperature

In the process of cleaning copper slag, increasing the temperature can accelerate the reaction rate in the system, thereby shortening the reaction time. Additionally, high temperatures can improve the properties of the slag, such as reducing its viscosity and improving its fluidity. On the one hand, it is convenient for small copper matte particles to gather into large particles and enter the copper matte phase. On the other hand, it is also convenient for Pb and Zn to volatilize into the gas phase. However, if the temperature is too high, it can lead to the reduction of high-valent iron oxide to Fe. Moreover, higher temperatures also result in increased heat energy consumption, which can lead to a waste of resources.

The impact of smelting temperature on copper recovery and copper grade in the cleaned slag and matte is shown in Fig. 6(c). Under the same sulfurizing agent, reducing agent, and constant temperature time, the copper recovery increased from 73.64% to 97.58% in the temperature range of 1250−1350 °C, and then stabilized with further temperature increasing. The copper content in the cleaned slag decreased from 0.93% to 0.1%. The copper content in the matte remained relatively stable in the temperature range of 1250−1450 °C. As the temperature increased, the polymeric ions in the slag system disintegrated, facilitating the movement of particles and reducing the slag viscosity. Tiny particles of the copper matte quickly coalesced into large particles, which facilitated the settling of matte into the copper matte.

The impact of increasing temperature on the recovery of Pb and Zn is depicted in Fig. 9(a). The recovery of Pb gradually increased from 83.27% to 98.20% before stabilizing, while the recovery of Zn initially rose from 69.91% to 89.91% before decreasing to 85.52%. With increasing temperature, the possibility of generating metallic iron increased, resulting in a poor recovery of Zn [34].

Figure 9(b) illustrates that with increasing temperature, the proportion of Zn entering the gas phase increased from 58.35% to 80.93% before decreasing to 72.87%. The proportion of Zn entering the matte phase decreased from 11.56% to 8.98% and then increased to 12.64%. When the temperature was too high, iron oxide was more easily reduced to metallic iron, leading to the precipitation of the metal phase in the system, forming a solid metal solution and entering the matte phase. Therefore, 1350 °C was selected as the optimum temperature.

3.4 Effect of smelting time

The duration of smelting has an impact on the extent of the reaction. A shorter smelting time can result in an insufficient reaction, affecting the recovery of valuable metals from copper smelting slag. Conversely, a longer smelting time can lead to resource wastage and an increase in process costs.

The effect of smelting time on copper recovery and the grade of Cu in the cleaned slag and matte is shown in Fig. 6(d). Under the same sulfurizing agent, reducing agent, and smelting temperature, the recovery of Cu increased from 78.83% to 97.58% as the smelting time extended from 1 to 3 h. Within the range of 3−4 h, the recovery of Cu increased from 97.58% to 98.42%. When the reduction time continued to increase, the recovery of Cu increased slowly. It was implied that insufficient smelting time could not guarantee the thorough sulfurization reaction of Cu_2O, leading to poor cleaning efficiency of the smelting slag. Moreover, it also took enough time for the complete set of matte. The copper content in the cleaned slag decreased from 0.84% to 0.1% within 1−3 h and then stabilized. Matte grade had minimal change in the span of 1−4 h. Thus, the optimal smelting time should be 3 h.

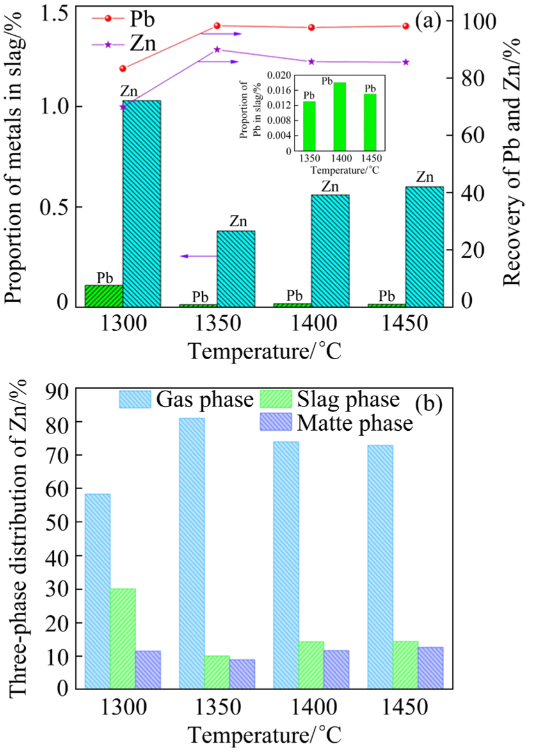


Fig. 9 Influence of process parameters on recovery of Pb and Zn (a) and three-phase distribution of Zn (b) (for 3 h with 26% pyrite and 6% coke)

3.5 Optimizing conditions

By investigating the effects of pyrite addition, reducing agent addition, smelting temperature, and smelting time on the recovery of Cu, Pb and Zn, the optimal experimental conditions were as follows: the mass of sulfurizing and reducing agents was 26% and 6% of the total mass of copper slag, respectively, and the temperature was 1350 °C for 3 h. Under these conditions, the recoveries of Cu, Pb and Zn were 97.58%, 98.20% and 89.91%, respectively. The cleaned slag contained 0.10% Cu, 0.01% Pb, and 0.38% Zn. The matte grade was 7.28%. The proportions of Zn entering the gas, slag and matte phases were 80.93%, 10.09% and 8.98%, respectively. The proportions of Pb entering the gas, slag and matte phases were 40.12%, 1.79%, and 58.09%, respectively. Figure 10 shows that Zn more easily entered the gas phase than Pb. The cleaned slag was layered with matte and exhibited poor wettability with the crucible. Iron phase analysis and XRD analysis were conducted on the cleaned slag to clearly understand the iron phase in the cleaning slag under optimized conditions.

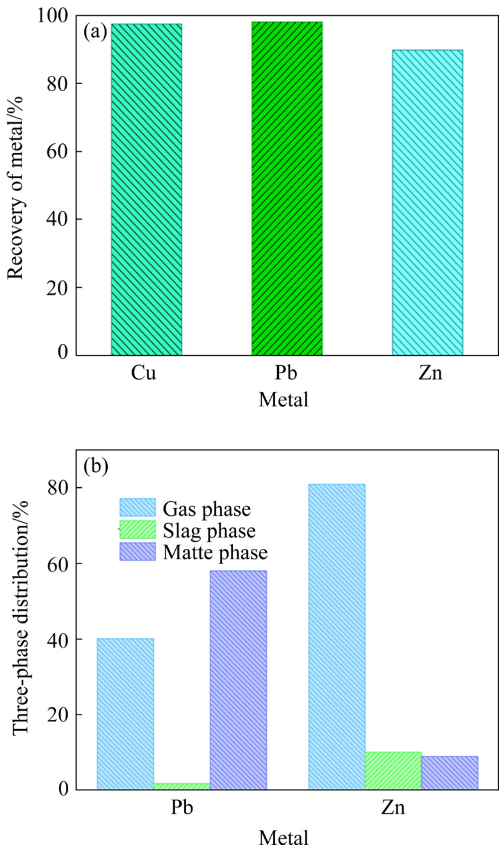


Fig. 10 Optimization conditions of Cu, Pb, and Zn recovery (a), and three-phase distribution of Pb and Zn (b) (at 1350 °C for 3 h with 26% pyrite and 6% coke)

3.6 Characterization of cleaned slag and copper matte

The cleaned slag and copper matte were slowly cooled to room temperature under the protection of Ar. It can be seen from Table 7 that Fe_3O_4 in the slag was reduced from 19.50% to 2.97%, and there was no Fe detected in the cleaned slag, indicating that it was reduced at this time. Fe mainly existed in the cleaned slag in the form of fayalite (Fe_2SiO_4) and ferrous oxide (FeO), accounting for 55.46% and 32.27% of the total iron, respectively. The cleaned slag contained 0.78% S and 0.04% C, suggesting the absence of residual reductant coal in the cleaning slag.

Combined with XRD and SEM−EDS (Fig. 11), it can be seen that the main phases of cleaned slag mainly contained Fe_2SiO_4 and $CaSi_2O_5$. Fe mainly existed in the cleaned slag in the form of fayalite, which improved the slag structure. Sulfide existed in the cleaned slag. The sulfide contained small amounts of Cu and Zn. After cleaning treatment, the cleaned slags containing FeO, CaO and SiO_2 mixtures are quality raw materials for cement, which can avoid potential ecological safety hazards.

Figure 12 shows that the matte phases primarily comprised geerite (Cu_8S_5) and troilite (FeS). It can be seen from Fig. 13 that Area *A* was

Table 7 Phase analysis of iron in cleaned slag

Mineral	Content/wt.%	Fraction/%
Iron sulfide	0.4	1.45
Magnetite	2.97	10.82
Fayalite	15.23	55.46
Iron(II) oxide	8.86	32.27
Fe_{total}	27.46	100

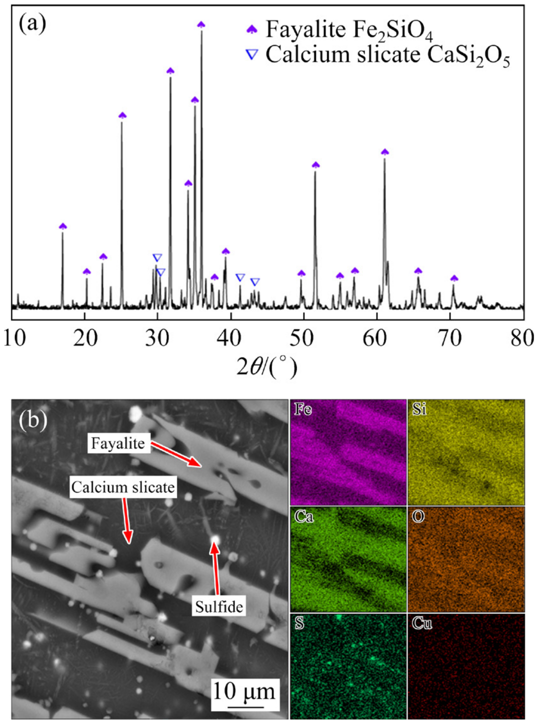


Fig. 11 XRD pattern (a), and SEM−EDS results (b) of cleaned slag (at 1350 °C for 3 h with 26% pyrite and 6% coke)

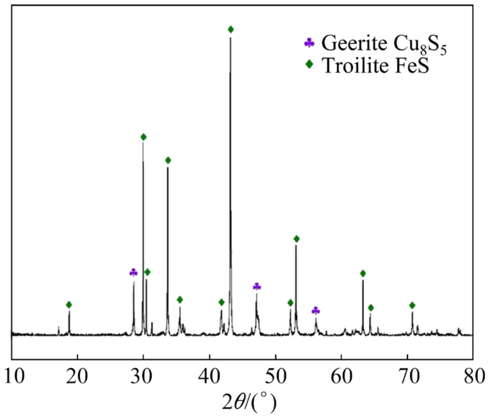
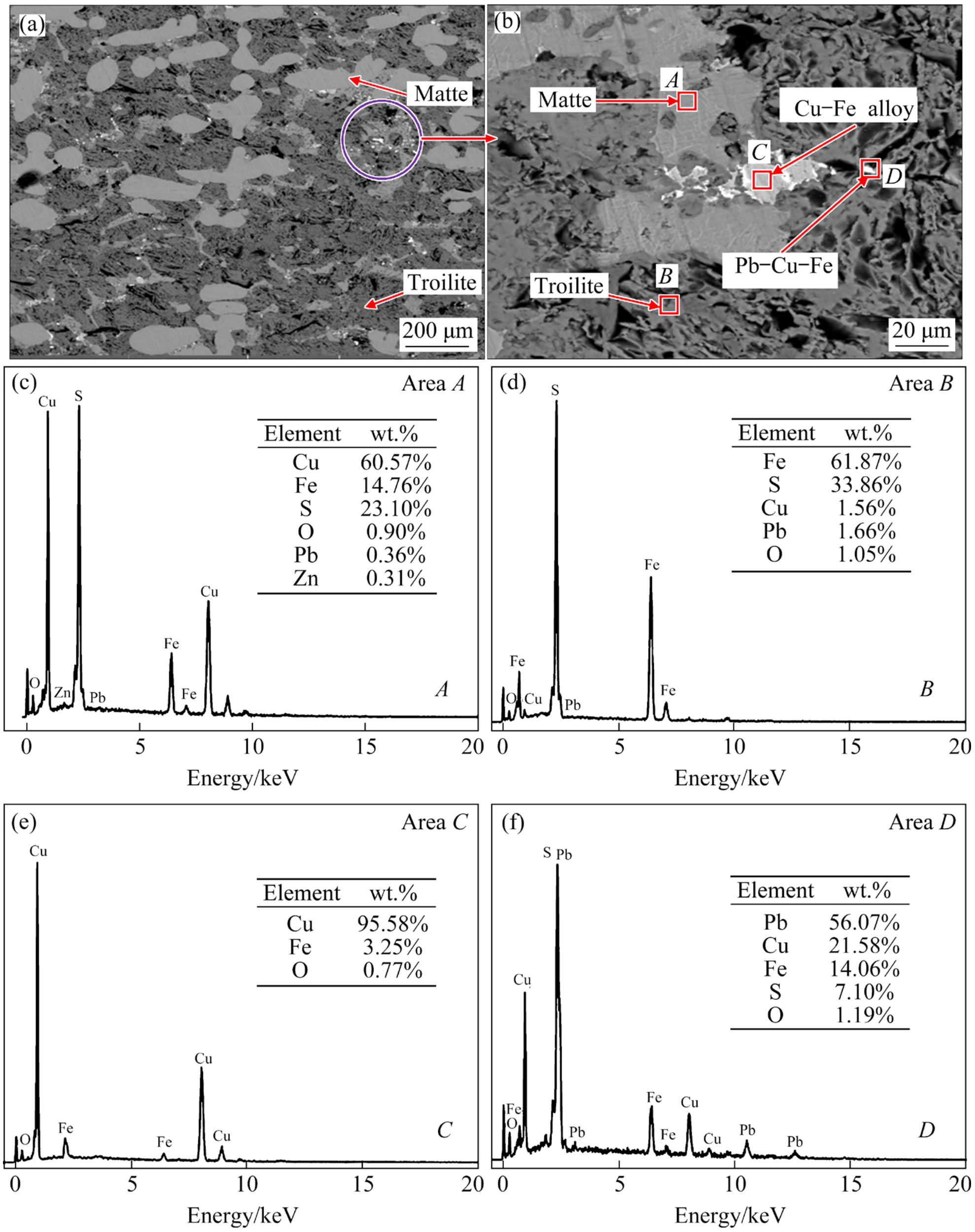


Fig. 12 XRD pattern of copper matte (at 1350 °C for 3 h with 26% pyrite and 6% coke)

especially the matte phase, and the contents of Cu, Fe and S were approximately 60.57%, 14.76% and 23.10%, respectively. Area *B* was mainly the FeS phase, containing a small amount of Cu and Pb, with Cu, Fe and S contents of approximately 1.56%, 61.87% and 33.86%, respectively. Area *C* was mainly the copper metal phase, containing a small amount of Fe, and the contents of Cu and Fe were approximately 95.58% and 3.25%, respectively. Area *D* was mainly the Pb phase. Pb was trapped by matte, and the contents of Pb, Cu, Fe and S were 56.07%, 21.58%, 14.06% and 7.10%, respectively. Therefore, this sulfurization−reduction method effectively cleans the copper smelting slag.



(c) Area *A*

Element	wt.%
Cu	60.57%
Fe	14.76%
S	23.10%
O	0.90%
Pb	0.36%
Zn	0.31%

(d) Area *B*

Element	wt.%
Fe	61.87%
S	33.86%
Cu	1.56%
Pb	1.66%
O	1.05%

(e) Area *C*

Element	wt.%
Cu	95.58%
Fe	3.25%
O	0.77%

(f) Area *D*

Element	wt.%
Pb	56.07%
Cu	21.58%
Fe	14.06%
S	7.10%
O	1.19%

Fig. 13 SEM−EDS results of copper matte (smelting sulfurization−reduction at 1350 °C for 3 h with 26% pyrite and 6% coke)

4 Conclusions

(1) By investigating the effects of the sulfurizing agent, reducing agent, smelting temperature, and smelting time on the recovery of Cu, Zn and Pb, the optimal experimental conditions were as follows: the mass of sulfurizing and reducing agents was 26% and 6% of the total mass of copper slag, respectively, and the temperature was 1350 °C for 3 h.

(2) Under the optimal conditions, the recoveries of Cu, Zn and Pb were 97.58%, 89.91%, and 98.20%, respectively. The contents of Cu, Zn and Pb in the cleaned slag were 0.10%, 0.01% and 0.38%, respectively. The matte grade was 7.28%. The proportions of Zn entering the gas, slag and matte phases were 80.93%, 10.09% and 8.98%, respectively. The proportions of Pb entering the gas, slag and matte phases were 40.12%, 1.79% and 58.09%, respectively. The copper matte phase was mainly comprised Cu_8S_5, FeS and some metals, such as Cu, Pb and Fe. Fe_3O_4 in the slag was reduced, and the content of Fe_3O_4 was decreased from 19.50% to 2.97%. Iron mainly existed in the cleaned slag in fayalite (Fe_2SiO_4) and ferrous oxide (FeO).

Acknowledgments

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硫化还原法协同回收铜冶炼渣中的铜、铅和锌

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摘 要：采用硫化还原法从铜冶炼渣中协同回收铜、铅和锌。以黄铁矿为硫化剂，在还原气氛下选择性硫化回收渣中有价金属。通过热力学分析和实验，确定该工艺的可行性和可靠性。确定了最佳的实验条件：硫化剂黄铁矿添加量为铜冶炼渣质量的 26%，焦炭添加量为铜冶炼渣总质量的 6%，温度 1350 ℃，熔炼时间 3 h。在优化条件下，铜、铅和锌回收率分别为 97.58%、89.91%和 98.20%。清洁渣中铜、铅和锌含量分别为 0.10%、0.01%和 0.38%。铜锍相含铜 7.28%，锌在气相、渣相和铜锍相中的分布比例分别为 80.93%、10.09%和 8.98%，铅在气相、渣相和铜锍相的分布比例分别为 40.12%、1.79%和 58.09%。铜锍相主要由 Cu_8S_5、FeS 和 Cu、Pb、Fe 等金属组成，渣中 Fe_3O_4 含量由 19.50%降至 2.97%。

关键词：铜冶炼渣；铜回收；铅锌烟化；硫化剂

(Edited by Xiang-qun LI)