



Iron and copper recovery from copper slags through smelting with waste cathode carbon from aluminium electrolysis

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Abstract: To recover metal from copper slags, a new process involving two steps of oxidative desulfurization followed by smelting reduction was proposed in which one hazardous waste (waste cathode carbon) was used to treat another (copper slags). The waste cathode carbon is used not only as a reducing agent but also as a fluxing agent to decrease slag melting point. Upon holding for 60 min in air atmosphere first and then smelting with 14.4 wt% waste cathode carbon and 25 wt% CaO for 180 min in high purity Ar atmosphere at 1450 °C, the recovery rates of Cu and Fe reach 95.89% and 94.64%, respectively, and meanwhile greater than 90% of the fluoride from waste cathode carbon is transferred into the final slag as CaF₂ and Ca₂Si₂F₂O₇, which makes the content of soluble F in the slag meet the national emission standard. Besides, the sulphur content in the obtained Fe-Cu alloy is low to 0.03 wt%.

Key words: copper slags; waste cathode carbon; oxidative desulfurization; smelting reduction; iron and copper recovery; fluoride

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1 Introduction

The copper slag is a hazardous waste which is generated from the cleaning process of copper converter slag or smelting slag in an electrical furnace. Generally, 2.0–3.0 t of copper slags are generated per ton of copper produced in the copper pyrometallurgical process, and approximately 30 million tons of slags are deposited every year in the world [1–3]. Most of them are directly discharged into the environment without treatment, causing

serious economic and environmental issues [4]. Hence, the utilization of copper slags as different value added products, such as abrasive tools, pavements, glasses, cements, roofing granules, tiles, and asphalt concrete aggregates, has been explored [5, 6]. In addition, the copper slag typically contains approximately 35 wt%–45 wt% Fe and 0.5 wt%–1.5 wt% Cu, which suggests that it is also a valuable resource for metal recovery [7]. Different methods for copper and iron recovery have been researched in recent years. These methods involve hydrometallurgical, pyrometallurgical and physical

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processes [8, 9]. A high copper recovery rate could be obtained through hydrometallurgical processes, but the waste leaching liquid presents a new form of environmental pollution [10]. Physical processes primarily include flotation to recover the copper and magnetic separation to recover the iron. The flotation process is only suitable for extracting sulphide minerals and has little effect on the recovery of copper oxides. Meanwhile, magnetic separation yields a low iron recovery rate because most iron exists in the form of fayalite (Fe_2SiO_4) in the copper slag [11]. In comparison, the pyrometallurgical processes have been widely used in previous researches given the advantages that the copper slag can be treated under molten conditions once it is discarded from the furnace before it cools down, thus achieving full use of heat value [12]. High recovery rates of copper and iron are obtained by producing Fe-Cu alloy (iron rich alloy) using a carbothermal or aluminothermy reduction process [4, 13], and this process produces low level of environmental pollution. The pyrometallurgical process is actually a slag making process, and the slag viscosity affects significantly the separation of slag and metal and the metal recovery rates. HEO et al [14] investigated the effect of CaO amount on the Fe recovery rate from copper slags by a carbothermal reduction process, and found that the Fe recovery rate reached over 90% with 20 wt% CaO added at 1500 °C for 60 min due to no formation of solid compounds with high melting point and the slag was therefore highly fluid. GUO et al [15] found that with the addition of 10 wt% Na_2CO_3 , the reduction of the fayalite, copper sulfide and copper silicate could be promoted through a phase transformation, and the metallization rate of the Fe and Cu in the reduced pellets increased from 67.78% to 93.21% and from 69.54% to 83.45%, respectively [15]. However, the S element originated from copper slags enters into the Fe-Cu alloy in the form of Cu_2S and/or FeS, reducing the alloy property obtained. This feature has received minimal consideration [16].

In addition, we have noticed that the waste cathode carbon, which is generated from the primary aluminium industry, is mainly composed of carbon, sodium fluoride and other compounds. Considerable amounts of this waste have accumulated, occupying large amounts of land in recent years [17, 18]. The fluoride and cyanide components in it cause environment pollution if exposed to air for a long

time. It is regarded as a hazardous waste by various environmental bodies. Many hydrometallurgical or pyrometallurgical processes have been used to treat waste cathode carbon to attain harmlessness and carbon separation [19–21]. Due to the difference in hydrophobic water between carbon and electrolyte, the electrolytes and carbon powder could be obtained and recovered from the waste cathode carbon [22]. However, the toxic HCN and HF would be released and precipitated during the treatment [23], which cause serious equipment corrosion and environment pollution. With the additive of fly ash or limestone, the decomposition rate of cyanide obtained 100% at temperature over 700 °C, and meanwhile most of the fluoride is solidified in the form of CaF_2 to meet the national emission standard [23, 24]. The carbon material can not be fully used through the processes above. The flotation technology is not suitable to improve the carbon purity and recovery efficiency of the leachable substance. Although thermal treatment reduces the amount of waste of some refractory components, the carbon source is not reused.

Moreover, paying attention to the fluoride component, which exists mainly in forms of NaF, Na_3AlF_6 and CaF_2 in the waste cathode carbon and can be used as a fluxing agent in the pyrometallurgical process through decreasing the slag melting point, an innovative technology that involves oxidative desulfurization and a smelting reduction process followed by the use of waste cathode carbon was proposed to produce a Fe-Cu alloy containing minimal sulphur from copper slags in this paper. In addition, most fluoride was transferred into the slag phase with low leachability, and the generated Fe-Cu alloy could be further used to produce weathering steel [25, 26].

2 Materials and methods

2.1 Materials

2.1.1 Copper slags

The copper slag in this work was obtained from Yunnan Copper Co., Ltd, China. After crushing and grinding, chemical titrimetry analysis was used to determine its composition, and the result is shown in Table 1. The slag contains 0.73 wt% Cu, 39.88 wt% Fe and 1.14 wt% S. Figure 1(a) shows the X-ray diffraction (XRD) pattern, which identifies fayalite and magnetite as the main phases in the copper slag.

The magnetite iron content was detected by a magnetic analyser, and the value is 4.90 wt%, indicating that the iron cannot be recovered effectively through a magnetic separation. In addition, the SEM-EDS analysis result in Figure 2 shows the copper is mainly distributed in the copper slag in the form of sulfide (matte).

Table 1 Chemical composition of copper slag (wt%)

Cu	TFe	S	CaO	MgO	Al ₂ O ₃	SiO ₂	Fe ₃ O ₄	FeO
0.73	39.88	1.14	5.32	3.27	4.72	28.87	4.90	46.71

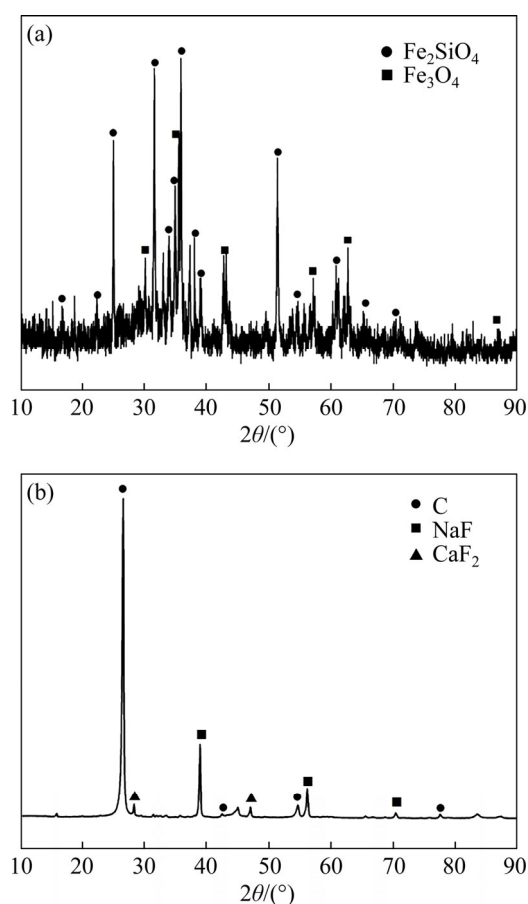


Figure 1 XRD patterns of copper slag (a) and waste cathode carbon (b)

2.1.2 Waste cathode carbon

The waste cathode carbon used, which was the first cut of the spent pot liner, was obtained from Yunnan Aluminum Co., Ltd, China. The results of the proximate analysis of the waste cathode carbon are shown in Table 2 and the chemical analysis of the ash in it is shown in Table 3. It is shown that the waste cathode carbon contains 73.24 wt% fixed carbon, 25.81 wt% ash and 0.85 wt% volatile matters. In addition, 9.49 wt% F, 8.44 wt% Na, 3.59 wt% Al₂O₃ and a small amount of CN⁻ exist in the ash.

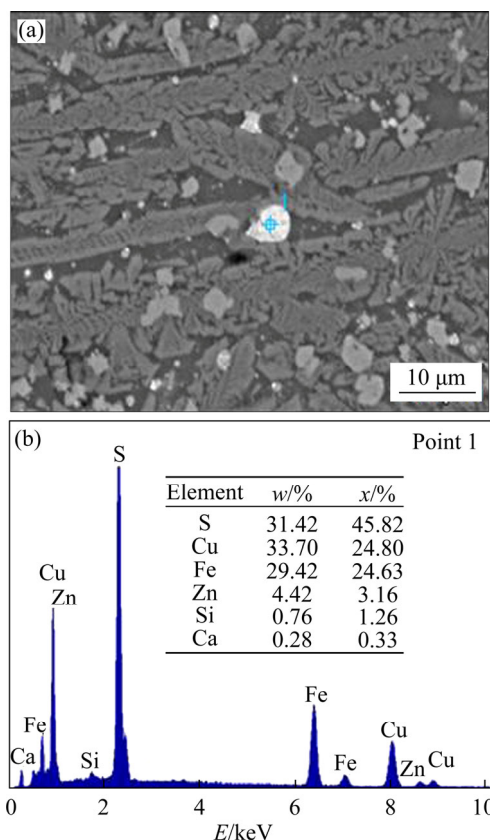


Figure 2 SEM image (a) and EDS analysis (b) of copper phase in raw copper slag

Table 2 Proximate analysis result of waste cathode carbon (wt%)

FC _{ad}	M _{ad}	A _d	V _{ad}
73.24	0.10	25.81	0.85

Note: FC_{ad}: Air drying based fixed carbon; M_{ad}: Air drying based water; A_d: Air drying based ash; V_{ad}: Air drying based volatile.

Table 3 Chemical composition of ash in waste cathode carbon (wt%)

F	Na	SiO ₂	Al ₂ O ₃	Fe	S	CaO	CN/(mg·kg ⁻¹)
9.49	8.44	1.45	3.59	0.62	0.02	1.86	<0.1

Figure 1(b) identifies C, NaF and CaF₂ as main phases in the waste cathode carbon. This waste cathode carbon is listed as a hazardous material given its levels of leachable F⁻ in Table 4. Besides, the CN leaching toxicity in this waste cathode carbon is far less than the national allowable emission concentration in China as shown in Table 4, and it was not researched in this work.

2.1.3 Additive and gas

In this study, the analytical grade CaO was used as an additive. In addition, the purity of Ar gas used in this study was higher than 99.99 vol%.

Table 4 Detection of leaching toxicity of waste cathode carbon

Toxicity	Concentration of waste cathode carbon/(mg·L ⁻¹)	National allowable emission concentration in China/(mg·L ⁻¹) [27]	Analytical approach
F ⁻	2910	<100	Ion chromatography
CN ⁻	<0.004	<5	Ion chromatography

2.2 Methods

The copper slag mainly consists of various oxides and silicates as well as sulphides. Reduction of oxides and silicates leads to recovery of various metals; however, the sulphur element simultaneously enters into the metal phase based on previous research [16], reducing the metal quality obtained. Two steps of treatment of copper slags, including oxidative desulfurization and smelting reduction, were performed in this study.

For the experimental procedure, 30 g cold copper slags with the particle size less than 149 μm were firstly placed in a corundum crucible and then located in a vertical resistance furnace for melting and oxidative desulfurization under air atmosphere. After holding for 60 min at a proper temperature, a certain amount of the mixture of CaO and waste cathode carbon with the particle size less than 149 μm was added into the corundum crucible through a feeder under high purity argon atmosphere. The CaO or waste cathode carbon amount used is expressed as the mass ratio of CaO or waste cathode carbon to copper slags. After 180 min, the sample was then cooled down to room temperature in high purity Ar gas. Once the cooling stage was completed, the sample was removed from the furnace and prepared for analysis.

2.3 Characterization

The chemical composition of the sample was detected by chemical titrimetry, and the average of three measurements was taken as the result. The magnetite iron content in the raw copper slag was measured using a saturated magnetic analyser (SATMAGAN 135), which was carried out in the conditions of voltage of 220 V, frequency of 50 Hz, and testing temperature of 25 °C. The phase composition of the sample was identified by X-ray diffraction (XRD, Rigaku, TTR-III). The diffraction was measured using Cu K_α radiation at 40 kV and 40 mA and a step size of 0.01°. A scanning electron

microscope (SEM; HITACHI-S3400 N) coupled with energy dispersive X-ray spectroscopy (EDS) and electron probe microanalysis techniques (EPMA, JXA82, JEOL) were used to determine the phase transformation of the sample in the smelting reduction process. The leachability of the F⁻ and CN⁻ in the sample was measured by Chinese standard leaching test according to the GB5085.3-2007 method. The thermodynamic data of species were given by FactSage 7.2 thermochemical software. During the smelting reduction process, the recovery rates of iron (R_{Fe}) and copper (R_{Cu}) were defined as follows:

$$R_{Fe} = \left(\frac{M_{Fe(g) \text{ slag} \rightarrow \text{metal ingot}}}{M_{Fe(g) \text{ initial slag}}} \right) \times 100\% \tag{1}$$

$$R_{Cu} = \left(\frac{M_{Cu(g) \text{ slag} \rightarrow \text{metal ingot}}}{M_{Cu(g) \text{ initial slag}}} \right) \times 100\% \tag{2}$$

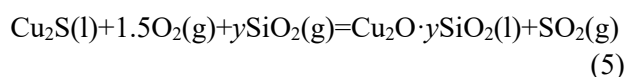
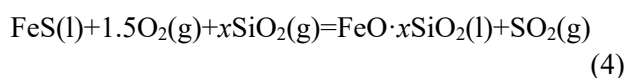
where $M_{Fe(g) \text{ slag} \rightarrow \text{metal ingot}}$ and $M_{Cu(g) \text{ slag} \rightarrow \text{metal ingot}}$ are the mass of iron and copper transferred into the metal ingot, and $M_{Fe(g) \text{ initial slag}}$ and $M_{Cu(g) \text{ initial slag}}$ are mass of iron and copper in the raw copper slags, respectively. In addition, the volatilization rate of fluoride (V_F) was defined as follows:

$$V_F = \frac{M_1 \times \alpha - M_2 \times \beta}{M_1 \times \alpha} \times 100\% \tag{3}$$

where M_1 and M_2 represents the mass of the waste cathode carbon and final slag, respectively; α and β represent the mass fraction of fluorine in the waste cathode carbon and final slag, respectively.

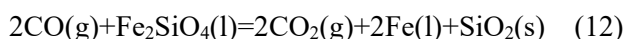
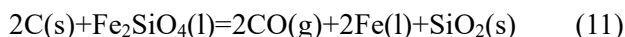
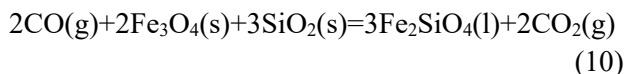
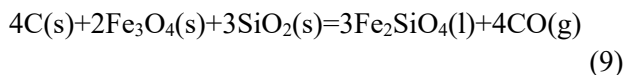
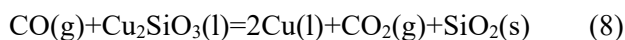
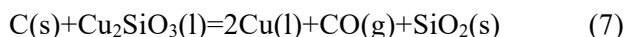
3 Theoretical analysis of metal recovery

The sulphur mostly occurs in Cu₂S and FeS in the copper slag and its content reaches 1.14 wt% as shown in Table 1, most of which enters into the metal phase in the smelting process causing the metal property to be decreased. An oxidative desulfurization process was first performed, in which the sulphur was removed in the form of SO₂(g) as [16]:



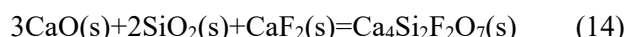
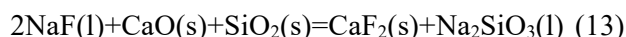
Then, with the addition of waste cathode carbon, the reduction of iron and copper compounds in the

molten copper slag occurs as follows:



During the reduction process, Figure 3(a) shows that the fluoride originated from waste cathode carbon almost volatilizes into the gas phase in forms of SiF_4 (g), SiF_3 (g) and NaAlF_4 (g) without CaO addition, which represents environmental pollution risks. Then with the addition of 10 wt%–25 wt% CaO, most fluoride is transformed into calcium fluoride (CaF_2 (s)) and/or cuspidine ($\text{Ca}_4\text{Si}_2\text{F}_2\text{O}_7$ (s)) through reactions (13) and (14) retaining in the slag

phase as shown in Figures 3(b)–(d), through which the level of leachable F^- might be decreased. Figures 3(b)–(d) also suggest that increasing the amount of CaO from 10 wt% to 20 wt% and 25 wt%, respectively, the CaF_2 (s) is almost converted to $\text{Ca}_4\text{Si}_2\text{F}_2\text{O}_7$ (s) through reaction (14), and meanwhile the fluoride amount retaining in the slag increases obviously. In addition, the increasing temperature decreases the formation amounts of CaF_2 (s) and $\text{Ca}_4\text{Si}_2\text{F}_2\text{O}_7$ (s) due to the increased formation of the gas phase of fluoride.



4 Results and discussion

4.1 Oxidative desulfurization

The raw copper slag was heated at 10 K/min to the target temperature and then held for 60 min in air atmosphere to achieve desulfurization via Eqs. (4) and (5). Figure 4(a) shows that the sulphur residual

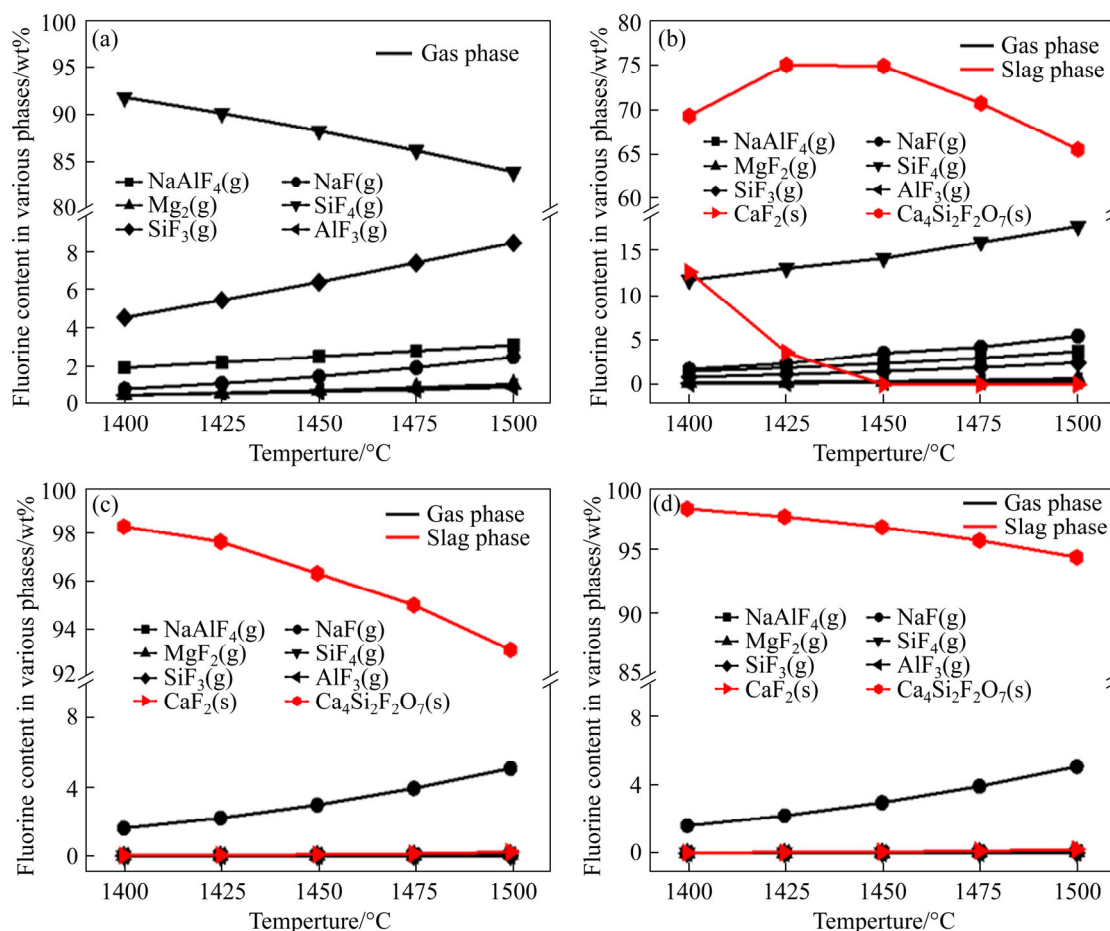


Figure 3 Effects of temperature and CaO amount on equilibrium composition of fluoride phase: (a) 30 g copper slag + 4.32 g waste cathode carbon; (b) 30 g copper slag + 4.32g waste cathode carbon+3 g CaO; (c) 30 g copper slag +4.32 g waste cathode carbon + 6 g CaO; (d) 30 g copper slag + 4.32 g waste cathode carbon + 7.5 g CaO

content decreases obviously as the temperature ranges from 1400 to 1450 °C, and then there is no significant change as the temperature continues to increase. Meanwhile, part of the fayalite (Fe_2SiO_4) phase is oxidized to Fe_3O_4 as presented in Figure 4(b). After oxidative desulfurization treatment, the diffractions due to fayalite taper off, whereas those due to magnetite are gradually enhanced.

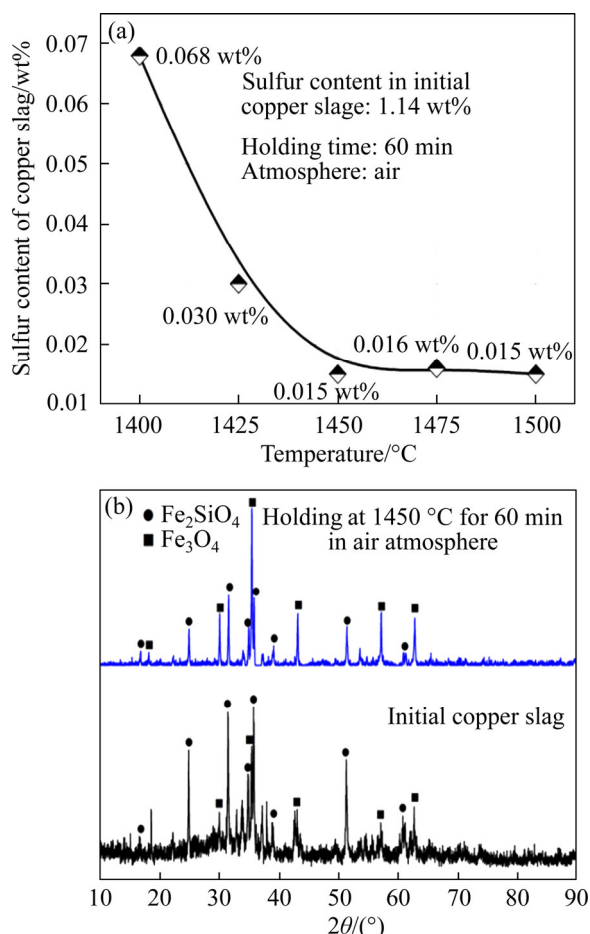


Figure 4 Sulphur content of slag after melting at different temperatures for 60 min in air atmosphere (a) and XRD pattern of raw slag and slag after oxidative desulfurization treatment (b)

4.2 Metal recovery

After the copper slag treated by the process of oxidative desulfurization, the waste cathode carbon was added into the molten slag for reduction and recovery of copper and iron. The parameters of waste cathode carbon mass, calcium oxide addition mass and smelting temperature were studied.

4.2.1 Effect of waste cathode carbon amount

The effect of waste cathode carbon on the smelting reduction process was studied without adding CaO. As the waste cathode carbon amount

increases from 12 wt% to 14.4 wt%, more iron and copper could be reduced through reactions (7)–(12) and then transferred into the metal ingot. Meanwhile, the mass of CaF_2 and NaF that originated from the waste cathode carbon introduced into the slag are also increased, causing the slag melting point to be obviously decreased as noted in Table 5 and then the metal settling separation and recovery to be further promoted. Consequently, with smelting at 1450 °C for 180 min, the iron recovery rate (R_{Fe}) increases from 54.41% to 73.91% with the increase of waste cathode carbon amount from 12 wt% to 14.4 wt% (Table 5) and then increases slightly. In addition, the changes of R_{Cu} with the waste cathode carbon amount are similar to that of R_{Fe} seen from Table 5. At the same amount of fixed carbon, it is noteworthy that the recovery rates of iron and copper with the addition of waste cathode carbon are obviously higher than that with the coke added as shown in Figure 5, which might be related to the effects of “F” component from the waste cathode carbon. Based on the solubility change of C in the Fe-Cu-C system as a function of Cu content presented in Figure 6 [28], the elements of Cu, C, and Fe exist in the state of mutual soluble in the metal ingot.

Regarding the waste cathode carbon melted with copper slags for 180 min, Table 5 and Figure 7 show that most fluoride is retained in the slag in the form of CaF_2 . Figure 7 shows the EPMA result of the final slag with the addition of 14.4 wt% waste cathode carbon, in which most F coexists closely with Ca and exists mainly in the form of CaF_2 deduced from the composition of “1” point in Figure 7. The level of leachable F^- in the final slag might be decreased due to this transformation, which will be confirmed in the subsequent detections. Meanwhile, it is noteworthy that the fluoride volatilization rate (V_{F}) decreases as the amount of waste cathode carbon increases (Table 5), which might be attributed to the fact that more SiO_2 could be released from the fayalite (Fe_2SiO_4) through Eqs. (11) and (12) and then the CaF_2 formation through Eq. (13) is promoted. In addition, all the sulphur content in the metal ingot is less than 0.1 wt% (Table 5), which is decreased by a large amount compared to that in the direct smelting reduction of copper slags as reported by previous researches [16]. Regarding the iron and copper recovery rates, the waste cathode carbon amount was fixed at 14.4 wt%.

Table 5 Effect of mass of waste cathode carbon amount, mass of calcium oxide addition and smelting temperature on smelting reduction of copper slags

Parameter		Metal ingot					Final slag		Salg Smelting Point/ $^{\circ}\text{C}$	
		wt/%				$R_{\text{Cu}}/\%$	$R_{\text{Fe}}/\%$	wt/%		$V_{\text{F}}/\%$
		Cu	Fe	S	C					
Waste cathode carbon addition/wt%	12.0	2.54	95.98	0.10	1.38	78.66	54.41	1.35	30.47	1294
	13.2	2.24	95.71	0.09	1.96	79.91	62.50	1.71	22.72	1279
	14.4	1.94	95.85	0.10	2.11	81.72	73.91	2.09	18.31	1265
	15.6	1.92	95.58	0.08	2.42	81.53	74.30	2.34	15.69	1250
	18.0	1.90	95.27	0.09	2.74	81.55	74.85	2.70	11.23	1221
CaO addition/wt%	0	1.94	95.85	0.10	2.11	81.72	73.91	2.09	18.31	1265
	5	1.88	96.30	0.09	1.73	90.82	85.15	2.12	15.36	1217
	10	1.84	96.39	0.09	1.68	94.01	90.14	2.19	11.78	1237
	15	1.83	96.42	0.07	1.68	94.89	91.52	2.09	9.62	1293
	25	1.79	96.51	0.03	1.67	95.89	94.64	1.90	7.93	1284
	30	1.80	96.52	0.03	1.65	93.96	92.23	1.80	5.67	1439
Temperature/ $^{\circ}\text{C}$	1400	1.82	96.56	0.06	1.56	96.12	93.34	1.93	6.23	—
	1425	1.81	96.52	0.05	1.62	96.23	93.93	1.92	6.57	—
	1450	1.79	96.51	0.03	1.67	95.89	94.64	1.90	7.93	—
	1475	1.79	96.56	0.02	1.63	95.29	94.09	1.77	12.77	—
	1500	1.79	96.58	0.03	1.59	95.77	94.06	1.65	18.59	—

Note: The slag melting point was predicted by Factsage.7.2 thermochemical software.

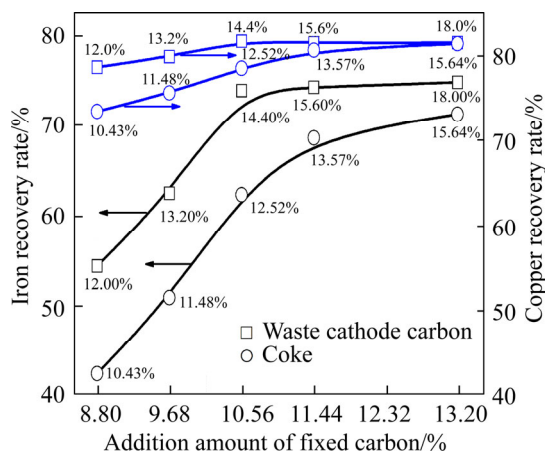


Figure 5 Changes of iron and copper recovery rates with addition of coke and waste cathode carbon respectively

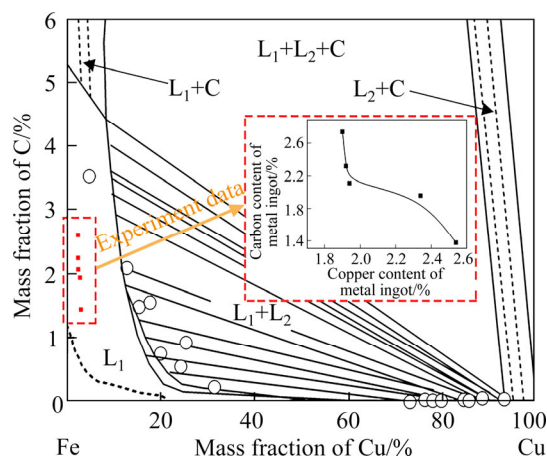


Figure 6 Solubility of C in Fe-Cu-C system as a function of Cu content at 1450 $^{\circ}\text{C}$

4.2.2 Effect of calcium oxide addition amount

In the smelting process, the slag melting point affects the obtained metal droplet settlement, aggregation, growth and subsequent metal recovery rate. Generally, a low slag melting point promotes the separation between phases of slag and metal. The phase diagram of the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ system at 1450 $^{\circ}\text{C}$ (Figure 8(a)) determined by Factsage.7.2 software shows that the composition of the slag after the Fe completely reduction without CaO added “A”

lies in the region of slag-liq + $\text{SiO}_2(\text{s})$. The appearance of $\text{SiO}_2(\text{s})$ indicates that the molten slag is a solid-containing melt due to a high melting point of SiO_2 (1723 $^{\circ}\text{C}$), which causes the slag viscosity to be increased and the separation of slag and metal to be restricted. Thus, some metal particles might be dispersed in the slag as shown in Figure 9 when the smelting reduction process carried out at 1450 $^{\circ}\text{C}$ for 180 min with the addition of 14.4% waste cathode carbon was finished. Figure 9 shows that some

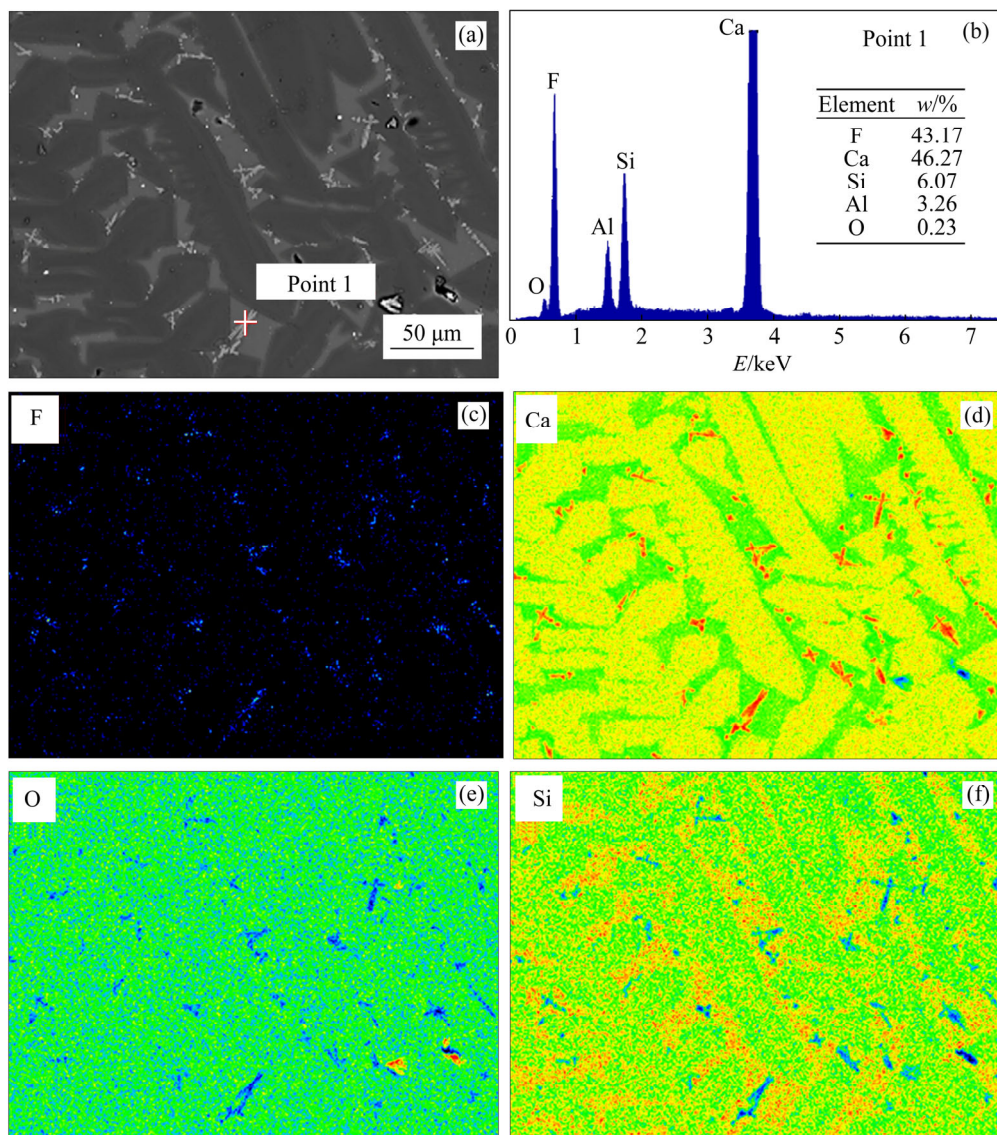


Figure 7 EPMA image of final slag with 14.4 wt% waste cathode carbon addition at 1450 °C (a) and EDS analysis of Point 1 (b–f)

particles of Fe (point 1) and Cu (point 2) are lost in the slag. Correspondingly, the recovery rates of Fe and Cu are low (Table 5). The addition of 10 wt%–25 wt% calcium oxide changes the slag composition along the indicated red arrow from the slag-liq + SiO₂(s) region to the slag-liq region in Figure 8(a). Though the slag melting point increases with the CaO amount from 10 wt% to 25 wt% as shown in Table 5, the complicated silicate structure in the slag could be simplified due to the addition of CaO [29]. As a result, the slag surface tension increases (Figure 8(b)), which promotes the separation between phases of obtained metal and slag. Consequently, the recovery rates of Fe and Cu are improved obviously (Table 5). The surface tension data in Figure 8(b) was calculated according to ion

and molecule coexistence theory of slag structure and Bulter's equation [30–32]. However, further increasing the calcium oxide amount to 30 wt%, both the recovery rates of copper and iron decrease slightly, which might be due to the generation of Ca₂Al₂SiO₇ (Figure 10(a)) of a high melting point and the subsequent increase of slag melting point (Table 5).

As more CaO is added, more sulphur will be transferred from the metal ingot to the slag phase according to Eq. (15), and correspondingly the sulphur content in the metal ingot decreases as shown in Table 5. In addition, more fluoride will also be transferred into the slag phase in the form of CaF₂ (Figure 10(a)) and Ca₄Si₂F₂O₇ (Point 1 in Figure 10(b)) by reactions of (13) and (14), and

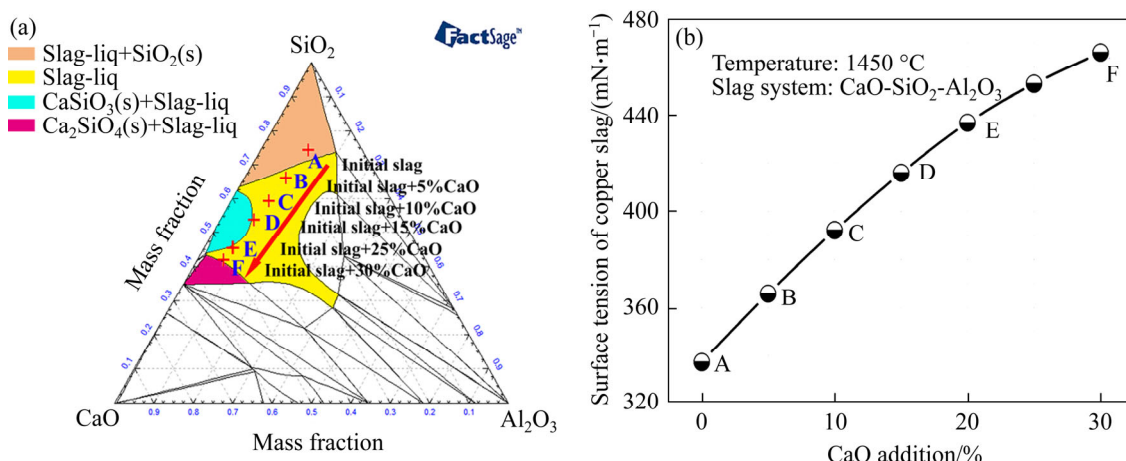


Figure 8 Phase diagram of SiO₂-CaO-Al₂O₃ system at 1450 °C (a) and effect of CaO amount on SiO₂-CaO-Al₂O₃ molten slag surface tension (b)

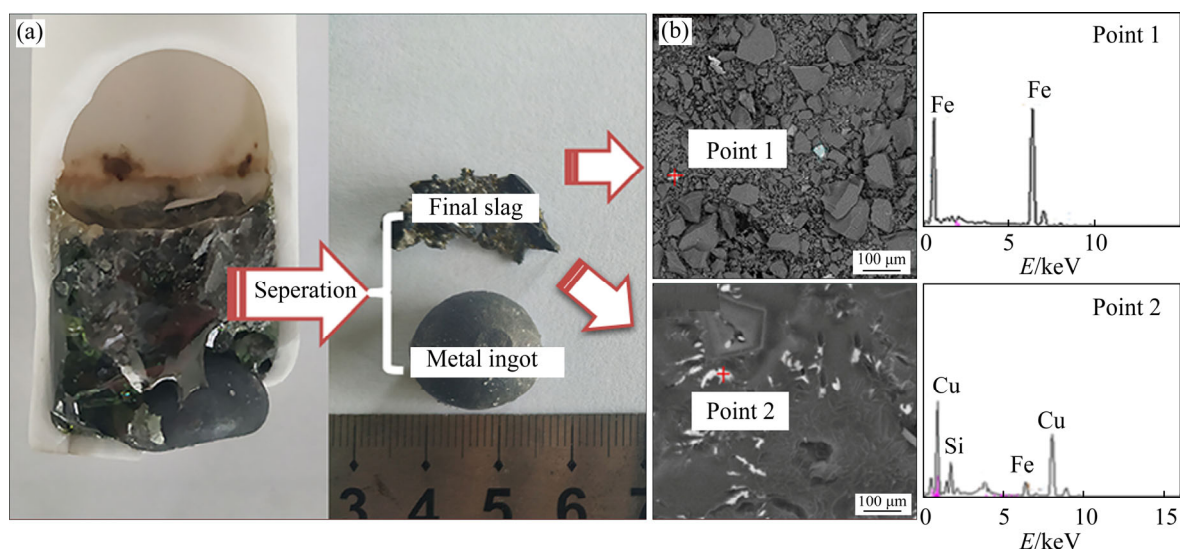


Figure 9 Photo (a) and analysis SEM-EDS (b) of final slag smelted at 1450 °C with no CaO added

V_F decreases (Table 5). Increasing recovery rates of Cu and Fe and decreasing fluoride volatilization, the calcium oxide amount should be controlled at 25 wt%.



4.2.3 Effect of smelting temperature

The effects of smelting temperature were assessed in the range of 1400–1500 °C under the condition of waste cathode carbon amount of 14.4 wt%, calcium oxide amount of 25% and smelting time of 180 min. The results are shown in Table 5. The R_{Cu} changes slightly as the temperature increases from 1400 to 1500 °C. The R_{Fe} first increases from 93.34% to 94.64% as the temperature increases from 1400 to 1450 °C and then remains almost constant around a value of 94% as the

temperature continues to increase. In addition, it is noteworthy that the increase in smelting temperature improves the volatilization rate of fluoride from Table 5, which is consistent with the calculation results in Figure 3. The temperature ranging from 1400 to 1450 °C might be a suitable smelting temperature.

After the copper slag is first treated in air atmosphere for desulfurization and then smelting reduced using 14.4% waste cathode carbon for metal recovery, a metal ingot with minimal S content (0.03 wt%) is obtained. Meanwhile, greater than 90% of the fluoride originated from the waste cathode carbon is transferred into the slag with 25 wt% CaO added at 1450 °C. Moreover, the value of leachable F⁻ in the final slag was detected via ion chromatography method and found to be 3.11 mg/L,

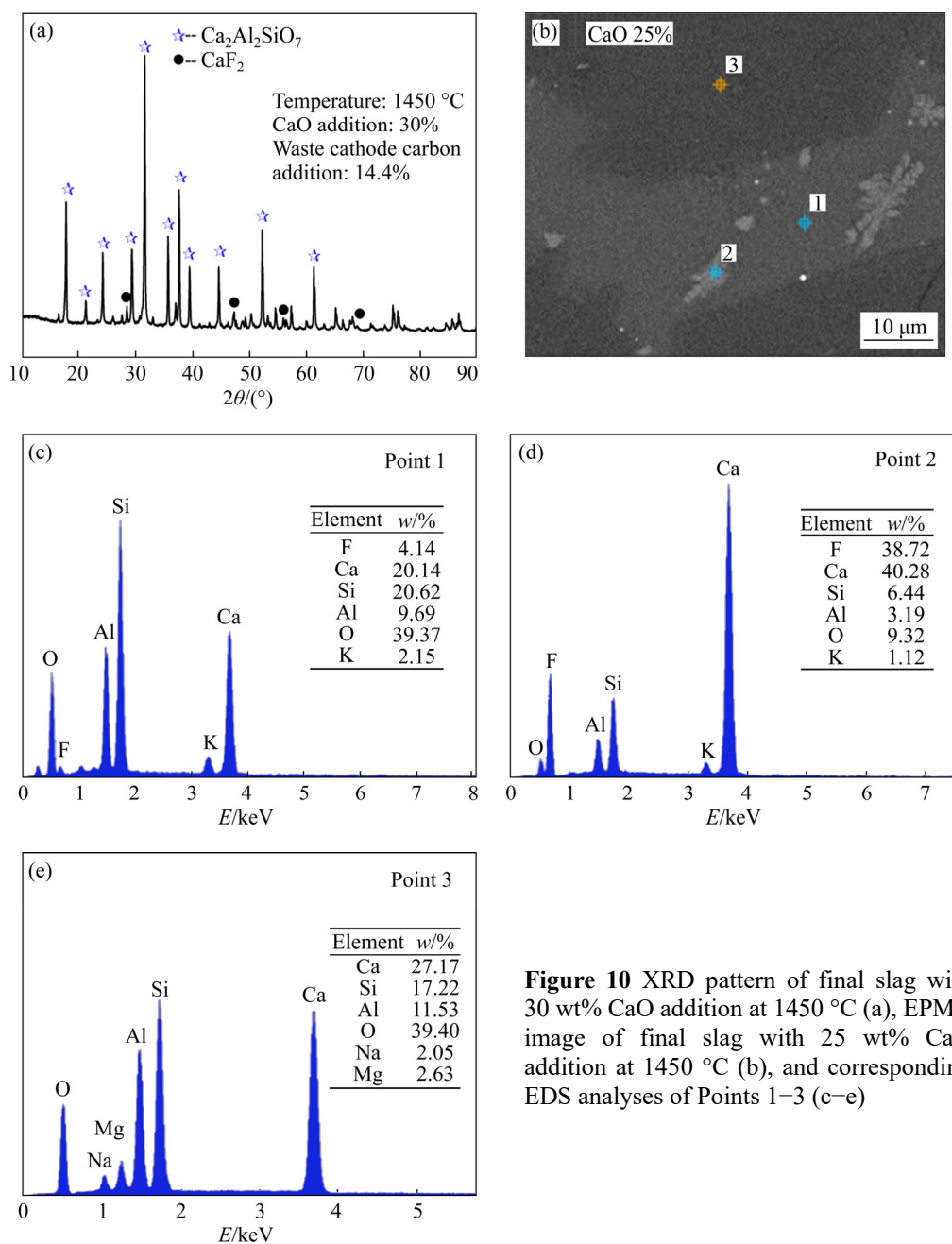


Figure 10 XRD pattern of final slag with 30 wt% CaO addition at 1450 °C (a), EPMA image of final slag with 25 wt% CaO addition at 1450 °C (b), and corresponding EDS analyses of Points 1–3 (c–e)

which is far less than the national allowable emission concentration in China as can be seen in Table 6.

Table 6 Detection of leaching toxicity of final slag

Toxicity	Final slag/ (mg·L ⁻¹)	National allowable emission concentration in China/(mg·L ⁻¹) [27]	Analytical approach
F ⁻	3.11	<100	Ion chromatography

5 Conclusions

1) A high recovery rate of iron and copper and a significant decrease in the level of leachable F⁻ can

be obtained when copper slags are smelted with waste cathode carbon.

2) The waste cathode carbon is listed as a hazardous material given its high level of leachable F⁻. When smelted with copper slags, most of this fluoride is transferred into the final slag in forms of CaF₂ and Ca₄Si₂F₂O₇, and the increase in the addition of CaO promotes this transformation. Thus, the level of leachable F⁻ decreases significantly and is far less than the national allowable emission concentration in China.

3) As the amount of waste cathode carbon increases, more iron and copper could be reduced and then transferred into the metal ingot. Meanwhile,

the amounts of CaF_2 and NaF introduced into the slag are also increased, as a result, the slag melting point is decreased and the separation and recovery of the metal is further promoted. Upon holding in air atmosphere for 60 min first and then smelting with 14.4 wt% waste cathode carbon and 25 wt% CaO for 180 min in high purity argon atmosphere at 1450 °C, the recovery rates of Cu and Fe from copper slags reach 95.89% and 94.64%, respectively, and greater than 90% of the fluoride originated from the waste cathode carbon is transferred into the final slag. Meanwhile, the sulphur content in the obtained Fe-Cu alloy is decreased to 0.03 wt%, and the elements of Cu, C, and Fe exist in the state of mutual soluble in the metal ingot. This obtained Fe-Cu alloy (low S) can be further used as the burden to produce weathering resistant steel by electric arc furnace to replace sponge iron or scrap steel.

Contributors

MAO Kai-xuan performed the data analyses and wrote the manuscript, LI Lei performed the analysis with constructive discussions and contributed significantly to manuscript preparation, XU Miao contributed to the validation of this study.

Conflict of interest

MAO Kai-xuan, LI Lei and XU Miao declare that they have no conflict of interest.

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中文导读

以铝电解废阴极炭为添加剂熔融还原回收铜渣中的铜和铁

摘要: 为了回收铜渣中的铜和铁, 本文提出了一种铜渣氧化脱硫-废阴极碳熔融还原两步处理新工艺, 在熔融还原过程中, 废阴极碳不仅可作为还原剂, 同时也可作为助熔剂降低熔渣熔点。在 1450 °C 时, 铜渣在空气气氛中保温 60 min 后, 添加 14.4 wt% 的废阴极碳和 25 wt% 的 CaO 至铜熔渣中并在高纯 Ar 气氛下进行熔融还原 180 min, Cu 和 Fe 的回收率分别可以达到 95.89% 和 94.64%。同时, 废阴极碳中 90% 以上的氟化物以 CaF_2 和 $Ca_2Si_2F_7O_7$ 形式转移至尾渣中, 炉渣中可溶性 F 含量达到国家排放标准。此外, 所得 Fe-Cu 合金中硫含量低至 0.03 wt%。

关键词: 铜渣; 废阴极碳; 氧化脱硫; 熔融还原; 铁和铜的回收; 氟化物