Original Research

Physicochemical, Mineralogical Liberation Characteristics, and Direct Recovery of Copper and Iron from Copper Electric Furnace Slag

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Abstract

Recovery of valuable metal from copper electric furnace slag (CEFS) is of great interest for saving minerals and reducing pollution. XRF, XRD, mineral liberation analysis (MLA), and batch tests were conducted to investigate the mineralogical and recovery of copper and iron from CEFS. Based on the mineralogical characteristics, a flotation and magnetic combined process was proposed and evaluated for the recovery of copper and iron. The results show that copper in CEFS main distribute in chalcopyrite, copper matte, and bornite, while iron distribute in magnetite, fayalite, and pyroxene. The proposed process involves the recovery of iron via magnetic separation from flotation tailings after recovering copper from CEFS by flotation. 72.79% of copper and 20.41% of iron were recycled from CEFS where the grades of copper and iron concentrate were 19.86% and 50.69%, respectively. This is a significant finding. Engineering application clearly proved that recycling copper and iron from CEFS by this combined process has significant economic, social, and environmental benefit.

Keywords: copper electric furnace slag, mineralogical characteristic, metal recycling, flotation, magnetic separation

Introduction

Large amount of copper smelting slag (CSS) is generated from copper pyrometallurgical process and discharged as industrial solid waste. According to the slag sources and characteristics, CSS can be classified into several categories like copper electric furnace slag, converter slag, reverberatory furnace slag and so on [1-2]. In a typical copper pyrometallurgical process, approximately 2.2 tons of waste CSS generated for every ton of copper produced [3-4]. The annual global output of CSS is an average of 25 million tons. In China, blister copper production is about 5.2 million tons, generating more than 8 million tons CSS every year [1, 5]. At present, CSS generation reaches up to more than 50 million tons [6-7]. Waste CSS still contains large amounts of copper, iron, and other valuable metals such as nickel, cobalt, and molybdenum [8-10]. However, these valuable metals are not only mineral resources, but also heavy metal contaminants. Stockpiling or disposals of such huge quantities of slag require lager areas, and the processing sites are unavailable for land utilization [11-13]. Moreover, these slags contain high concentrations of heavy metals that

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are very harmful when toxic metals is released into the environment, causing both environmental and space occupation problems. The increase in toxic metals around slag stockpiling sites has a long-term negative effect on the biosphere and potential ecological pollution risk [6, 14-16]. Therefore, the recovery of valuable metals from waste slags presents both economic and environmental incentives.

The conflict between massive demand for mineral resources and scarcity of mineral resources is becoming increasingly acute [17]. CSS contains a large of valuable metals and acts as a secondary resource of metals; therefore, it has received much attention in the recovery of valuable metals [18-22]. During the past two decades, attempts have been made to develop methods for metal recovery from CSS. Basically, these include several categories, namely, flotation [4, 23] magnetic separation [4], leaching [14, 24-28], and roasting [29-30]. Among them, physical separation including flotation and magnetic separation is one of the most simple, effective, and economical method to recover valuable metals from CSS. For copper, flotation can efficiently capture metallic Cu and sulfide minerals to provide a copper concentrate [31-32]. Iron mainly occurs as magnetite and iron silicate (fayalite) as well as silicates of other metals. Magnetic separation is the most common method for separating magnetic iron from other iron silicate minerals [5, 33].

Mineralogical morphology of valuable elements and distribution of target minerals are related to the use of CSS directly [1-2, 33]. Meanwhile, the particle size of crystallization of copper in the slag related to the cooling speed of slag closely [34]. In the CSS obtained after water quenching treatment, which is the most common CSS cooling method, the slag characteristics include stable chemical properties, compact structure and hardness, very fine granularity of embedded copper and iron, and difficult separation [1, 6]. Studies have shown that the CSS slow cooling process is advantageous for the migration and accumulation of copper particles and improvement in the grind ability [34]. The inherent composition of CSS cannot be changed; therefore, its forming process can be controlled to improve flotation and magnetic mineral processing [1, 3, 33].

In a copper-smelting plant of Yunnan Copper Co., Ltd. (Yunnan, China), approximately 0.2 million tons CEFS are abandoned annually. Metallic copper and iron contents of this slag are 0.5-0.8 wt% and 35-50 wt%, respectively. The copper content of CEFS often higher than those of copper ore grades. Thus, it worth be recovered from a perspective of both economic and environmental benefits. In this study, the CEFS of this copper-smelting plant is selected as the studied slag sample. A suitable slow cooling process, mineralogical characteristics, and recovery possibility of copper and iron from CEFS through a simple physical separation process including flotation and magnetic separation were investigated. The aim of this study was to evaluate the feasibility, economic, social, and environmental value of copper and iron recovery from CEFS by flotation and magnetic separation, thus providing guidance for the resource utilization of CEFS and other slags.

Material and Methods

Materials

The CEFS used in this study was taken from a typical copper-smelting plant of Yunnan Copper Co., Ltd. The copper smelting is pyrometallurgical process to produce blister copper from copper ore and comprises the following steps in turn: oxygen-enriched top-blown smelting, slag cleaning electric furnace and converter blowing. The studied CEFS is one of the CSS, which generate from an electric furnace for cleaning the copper slag after oxygen-enriched top-blown smelting.

Preparation and Experimental Process

A flowsheet of copper and iron recovery route developed in this study is shown in Fig. 1. After smelting, the CEFS with a high temperature (1200ºC) is released into the slag strap to cool down. To better crystallize and regrouping of metals, the optimum cooling down of CEFS involves 24 h slow natural cooling, 24 h water spray cooling, and 8 h natural cooling successively. After slow cooled in copper slag dross, the CEFS was crushed by jaw crusher (C80) and cone crusher (GP100MF) in turn to make the size of CEFS all less than 350 mm, 3 mm respectively at a crush rule of two-stage closed-circuit. Then, a
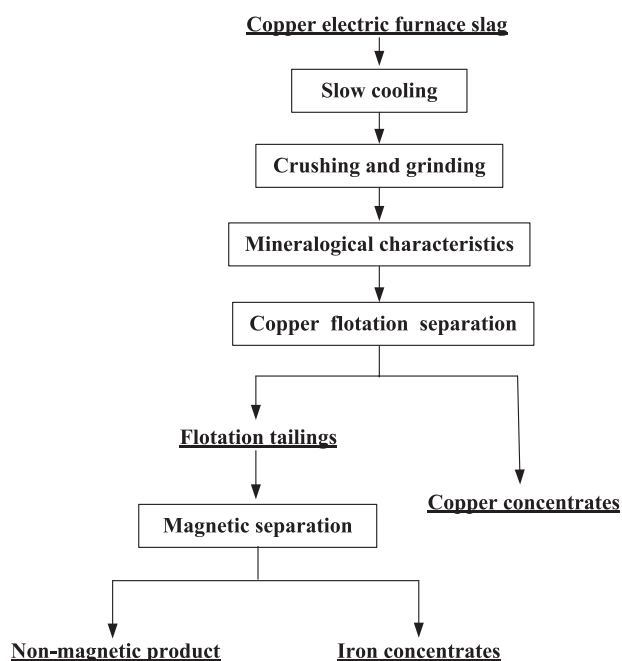

Fig. 1. Flowsheet of copper and iron recovery route developed in this study.

Table 1. Chemical composition of the CEFS sample.

Composition	Cu	Fe	Zn	Pb	As	S	SiO_2	Al_2O_3	CaO	MgO
Weight (%)	0.77	38.60	1.39	0.10	0.04	1.05	27.2	5.48	4.78	1.45

two-stage wet grinding was conducted to further make the size of 75-90% CEFS less than 48 μm (75-90%, −48 μm). The crushed and ground rate was about 0.78 t/min, 0.50 t/min respectively. The CEFS sample was well mixed and a representative samples was sampled by coning and quartering technique. These representative samples were used for the analysis of their mineralogical characteristics and recovery of copper and iron by coupling flotation and magnetic separation.

Analytical Methods

The mineralogical characteristics of minerals and chemical composition, particle size, phase distribution, mineral monomer dissociation degree, and characteristics of embedded minerals were determined by X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD, 40 kV, 150 mA), and mineral liberation analysis (MLA). MLA is a quantitative automated mineralogical analysis system, composed of one scanning electron microscope (SEM), two energy-dispersive X-ray spectrometers (EDS), and process mineralogical analysis software. MLA analysis was carried out in the XBSE measurement mode. The data processing software was MDI Jade7, and the phase retrieval database was PDF2-2004. Yield, mineral grade, and recovery rate were used to comprehensive analyze the ore dressing efficiency of copper and iron from CEFS.

Results and Discussion

Mineralogical Characteristics of CEFS

Phase and Chemical Composition

CEFS is black, and a part of clinker has obvious metallic luster, 2.0-2.4 g/mL of loose bulk density and 3.5-4.3 g/mL of weight density. CEFS is stable, has a dense texture, and hard (mohs hardness is 7-9 degrees). The results of a chemical analysis of the CEFS are shown in Table 1. There are 0.77 wt% of copper, 1.39 wt% of zinc, and 38.60 wt% of iron occurs in CEFS. It is necessary to analyze its occurrence form and the difficulty of metallic recovery.

The XRD pattern shown in Fig. 2a) showed that fayalite ($2FeO.SiO_2$), magnetite (Fe_3O_4), and pyroxene (Ca(Fe, Mg)$(SiO_3)_2$) are the main crystalline substance present in the CEFS. As shown in Table 2, the main mineral composition is pyroxene, fayalite, magnetite, and copper sulphide, and their total wt% is as high

as 98.63%. The mineral forms of copper and iron occurring in CEFS are shown in Table 3. 65.73% copper is distributed in chalcopyrite ($CuFeS_2$), copper matte, and bornite (Cu_5FeS_4). The copper grades of bornite, chalcopyrite, chalcocite, copper matte, and copper alloy are 63.31%, 29.04%, 76.14%, 7.85%, and 71.02%, respectively. Copper sulfide accounts for 85.88% of the total copper, and other 14.12% is copper oxide. Only 21.47% copper is distributed in difficultly floated minerals and gangue. This suggests that floatation is probably an effective method to recover copper from CEFS. 93.97% iron is distributed in fayalite, magnetite, and pyroxene. Magnetic iron accounts for 54.89% of total iron, but only 26.53% of iron is distributed in magnetite and ferroalloy. This shows that 26.53% of iron in CEFS can be easily recycled via magnetic separation, while others are difficult to separate.

Size Distribution

Size distributions of CEFS and target copper and iron minerals were analyzed after crushing and ground to (90%, −48 μm). As shown in Fig. 2b), the maximum and minimum particle sizes are 150.0 μm and 0.87 μm,
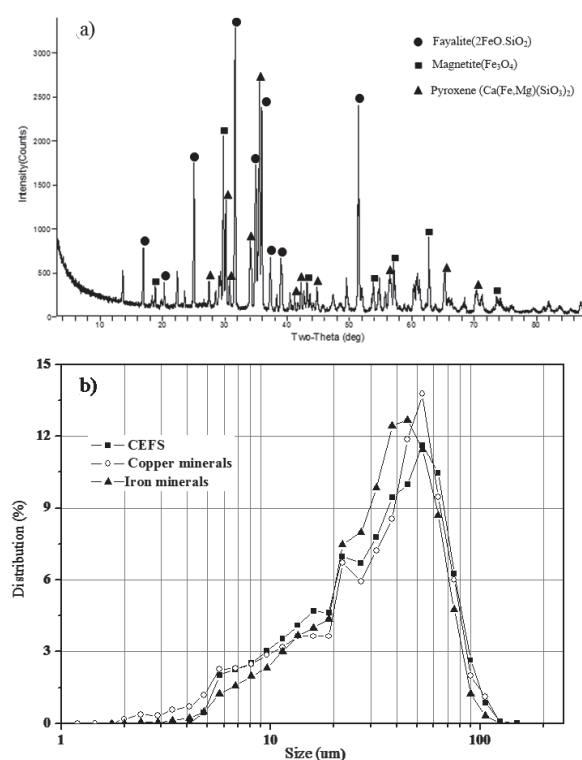

Fig. 2. a) X-ray diffraction patterns of CEFS; b) size distribution of CEFS, copper, and iron minerals.

Table 2. Principal mineral composition of CEFS.

Mineral	wt%	Mineral	wt%
Pyroxene	41.26	Copper alloy	0.039
Fayalite	38.24	Antimonide	0.005
Magnetite and Ferroalloy	15.35	Quartz and Glass	0.059
Copper matte	3.78	Oxides	0.008
Hematite	0.49	Others	0.775

Table 3. Mineral occurrence forms of copper and iron element in CEFS.

Minerals	Cu distribution (%)	Fe distribution (%)	Minerals	Cu distribution (%)	Fe distribution (%)
Copper matte	21.02	1.91	Ferroalloy	3.26	1.81
Bornite	20.89	0.09	Magnetite	2.83	24.72
Chalcocite	2.85		Hematite	2.22	0.62
Chalcopyrite	23.82	0.76	Fayalite	1.32	46.05
Copper alloy	3.90		pyroxene	11.26	23.20
Sphalerite	0.06	0.02	feldspar	0.58	0.22
Antimonide	0.07		Oxides		0.01
Galena	0.01		Others		0.02
Pyrite	5.91	0.55	Total	100	100

respectively. Compared with the size distribution of CEFS, the grains of target mineral (copper and iron) are relatively finer. Mineral granularity larger than 100 μm or smaller than 6 μm is not conducive to flotation and usually affords a lower recovery rate [35-36]. The results of size distribution indicate that the range of average particle size of copper minerals is suitable for separating copper by flotation.

Mineral Embedded and Liberation Features

The mineral embedded features of copper and iron ores in CEFS are shown in Fig. 3. As shown in Fig. 3(a-c), copper minerals (bornite, chalcopyrite, and copper matte) are the main interlocking and inclusion minerals in pyroxene, magnetite, and fayalite, and the mineral inclusion relationships are always complex. The binary and multiple inclusions of copper sulfide are 29.20% and 40.69%, respectively. Most of the magnetite is present as interlocking and inclusion minerals in pyroxene, fayalite, and copper minerals. The percentages of binary and multiple inclusions of magnetite are 46.18% and 34.11%, respectively.

Mineral liberation degrees of the target mineral of copper sulfide and magnetite are shown in Tables 4 and 5. The liberation of copper sulphide and magnetite is relatively low, only 39.02% and 34.07%, respectively, and the liberation degree is higher than 80%. The particle size (average diameter) is relatively

smaller for minerals with a lower liberation degree. This suggests that the target minerals with elaborate embedded characteristics are more difficult to liberate. For floatation, the target mineral has been effectively exposed when the liberation degree is more than 20% and vice versa. Approximately 72.42% of copper was exposed effectively when the grinding fineness is (90%, −48 μm). This indicates that most of the copper sulfide can be concentrated by floatation. Theoretical calculation shows that the copper grade of copper concentrate is 17.71% when the copper recovery rate is 72.42%. However, the average particle size distribution of 27.58% copper sulfide, exposed inadequately or not, is about 4.28 μm. Because this is not suitable for floatation, even the improvement in grinding fineness made it difficult to improve the liberation and recycling effectively. For magnetite, the recovery rate of iron is only 8.60-8.71% to qualify as iron concentrate, and the iron grade is over 60%. To improve the liberation degree of mineral, further increase in its grinding fineness is needed.

Copper Flotation Studies

Opened Circuit Flotation Tests

The open-circuit flotation experiment of copper roughing involved two-stage roughing and single-stage scavenging. The flotation times of roughing I#,
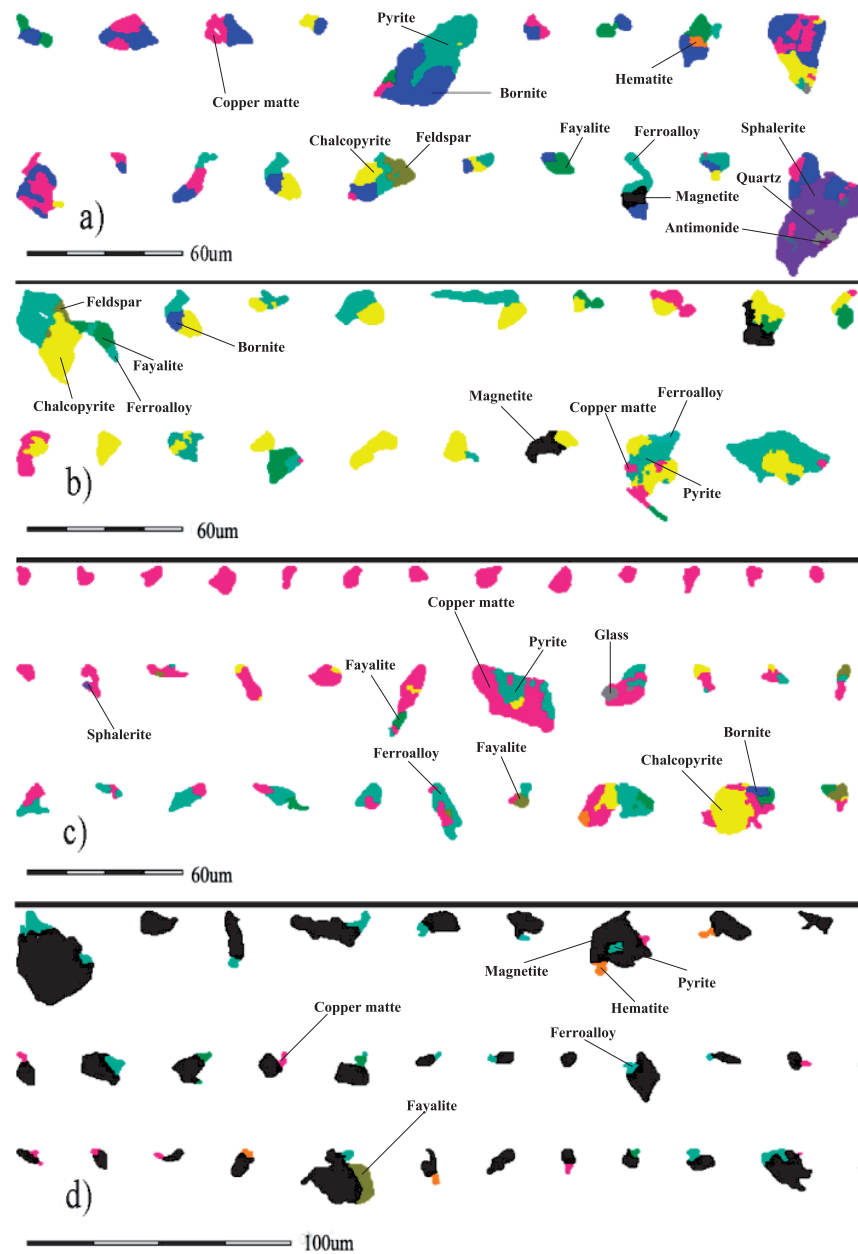
Fig. 3. Mineral interlocking and inclusions relationships and embedded features of copper and iron ores in CEFS a) Bornite, b) Chalcopyrite, c) Copper matte, and d) Magnetite.

Table 4. Mineral liberation degree of target mineral of copper sulphide.

Liberation degree (%)	Average diameter (μm)	Distribution (%)	Cumulative distribution (%)
0~20	4.28	27.58	100
20~40	7.73	12.48	72.42
40~60	11.44	10.49	59.94
60~80	17.46	10.42	49.44
80~100	26.37	9.81	39.02
100	11.98	29.21	29.21

Table 5. Mineral Liberation degree of target mineral of magnetite and ferroalloy.

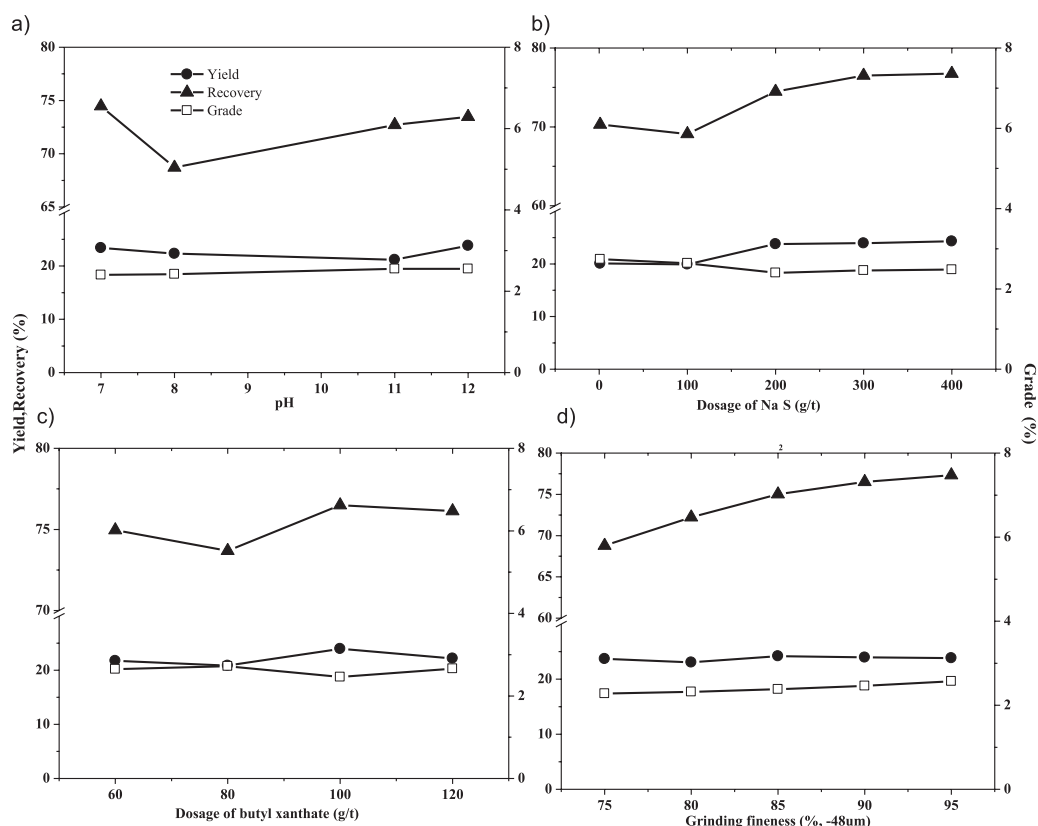| Liberation degree (%)	Average diameter (μm)	Distribution (%)	Cumulative distribution (%)
0~20	8.42	10.90	100
20~40	13.74	18.35	89.1
40~60	17.98	17.46	70.76
60~80	22.2	19.23	53.3
80~100	27.06	18.46	34.07
100	14.29	15.61	15.61

Fig. 4. Effects of main conditions and parameters for the copper roughing of CEFS flotation.

roughing II#, and scavenging I# are 8 min, 6 min, and 6 min, respectively. The effects of slurry pH, dosage of sodium sulfide (Na$_2$S), butyl xanthate (C$_5$H$_{10}$OS$_2$) (BX), and butylamine dithiophosphate ((C$_4$H$_9$O)$_2$PSSNH$_4$) (BD) on copper flotation are shown in Fig. 4. As shown in Fig. 4a), the slurry pH (adjusted by adding CaO) significantly affects the copper recovery rate and shows the optimum value at pH 7. Therefore, limestone should not be added to increase the slurry pH. Fig. 4b) shows that the copper yield and recovery rate increased by about 4% and 6%, respectively, when increasing the dosage of Na$_2$S from 0 g/t to 400 g/t. While the copper grade of rough concentrate does not decrease significantly. This shows that addition of Na$_2$S is conducive to the flotation separation of copper, and 300 g/t of Na$_2$S is an optimization index, because more Na$_2$S will increase the viscosity of bubble which is not conducive to floating. Fig. 4c) shows that the copper grade slightly changed, while the copper yield and recovery significantly increased when adding BX collector. In addition, a mixture scheme of BX and BD was investigated. The results show that the mixture of both collectors can improve the copper recovery rate. The optimum proportion of BX and BD was 1:1, and the dosages of both collectors were 50 g/t and 50 g/t, respectively. Fig. 4d) shows that both the copper recovery rate and grade increase when improving the grinding fineness of CEFS. The proposed economic grinding fineness has a better recovery rate, and the grade is (90%, −48 μm).

Similarly, the optimal conditions of flotation cleaning of copper rough concentrate were also investigated. The results show that the flotation cleaning process of copper rough concentrates needs three stages, and the flotation times of cleaners I#, II#, and III# were 6 min, 5 min, and 3 min, respectively. The optimal regulator and collector scheme was the addition of 10 g/t BX and 10 g/t BD and without Na$_2$S. The regrinding fineness of copper rough concentrates is (98%, −38 μm).

Closed Circuit Flotation Tests

Based on the open-circuit flotation conclusions, different flotation processing routes are discussed. The comparison results of different processing routes of CEFS copper flotation are shown in Fig. 5. Two-stage scavenging process can effectively reduce the losses of copper in flotation tailings even though the copper grade slightly decreased. The regrinding of copper rough concentrates can significantly improve both the copper recovery and grade. Comparing with the route of copper rough concentrates without regrinding, the copper recovery and grade increased by 2.40% and 3.45%, respectively. These results indicate that the optimal copper flotation processing routes for CEFS are two-stage roughing, two-stage scavenging, and three-stage cleaning, and copper rough concentrates needed regrinding to achieve (98%, −38 μm). The process flow diagram and parameters are shown in Fig. 8. The copper grade and recovery of copper concentrate
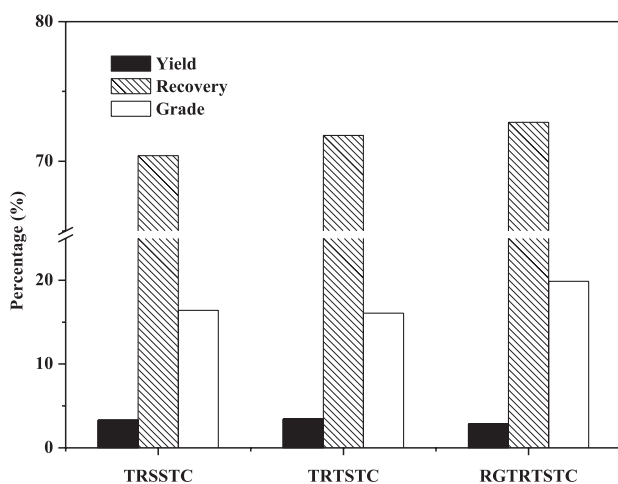
Fig. 5. Comparison result of different flotation processing routes of CEFS (in diagram, TRSSTC shows the processing route of two-stage roughing, single-stage scavenging, and three-stage cleaning; TRTSTC involves two-stage roughing, two-stage scavenging, and three-stage cleaning; RGTRTSTC involves two-stage roughing, two-stage scavenging, and three-stage cleaning after the regrinding of copper rough concentrate).

by CEFS flotation of this study were 19.86% and 72.79%, respectively. The results show Level 3 standard (20% of grade) of copper concentrate quality standard (YS/T 318-2007).

Characteristics of Copper Concentrates and Flotation Tailings

To evaluate the efficiency of this proposal on copper flotation process, the mineralogical characteristics of CEFS flotation concentrates and tailings were investigated. The results show that 98.71% copper in copper concentrates exists in the form of copper sulfide and copper alloy. However, the copper concentrates still contain a large number of impurity minerals because a part of copper sulfide is still present as interlocking or inclusion in fayalite, magnetite, and pyroxene. Most of the impurity minerals were not liberated unless the grinding degree is less than 10 μm. Magnetite (12.13%), fayalite (42.82%), and pyroxene (40.26%) are the main minerals of flotation tailings and also contain a small amount of copper sulphide (2.45%) and ferroalloys (1.02%). These indicate that the proposed flotation process is a feasible method to recover cooper from CEFS. Magnetite is difficult to
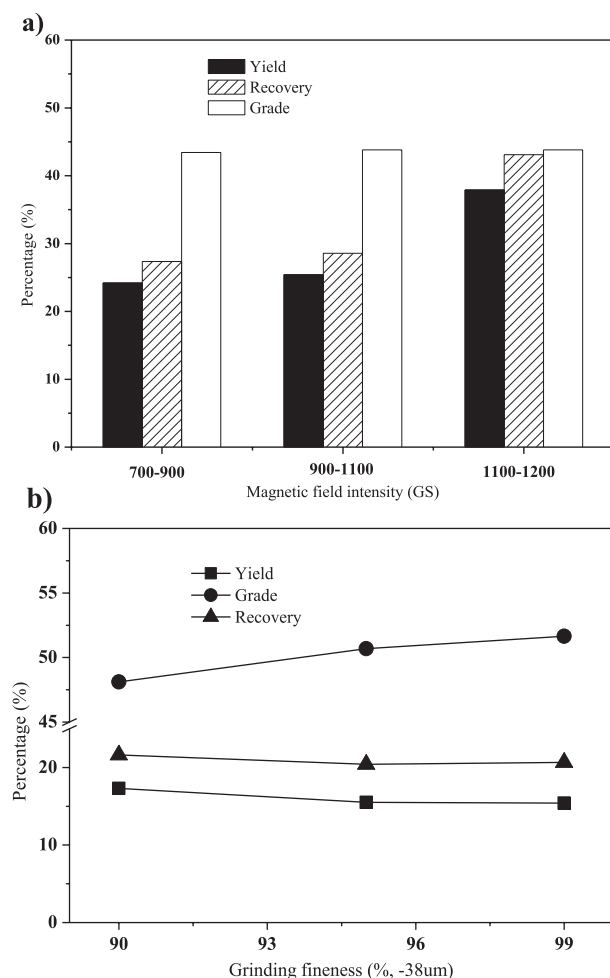

Fig. 6. Effects of condition parameters for the recovery of iron from CEFS flotation tails a) effect of magnetic intensity for iron roughing process; b) effect of regrinding fineness of rough concentrate for iron cleaning.
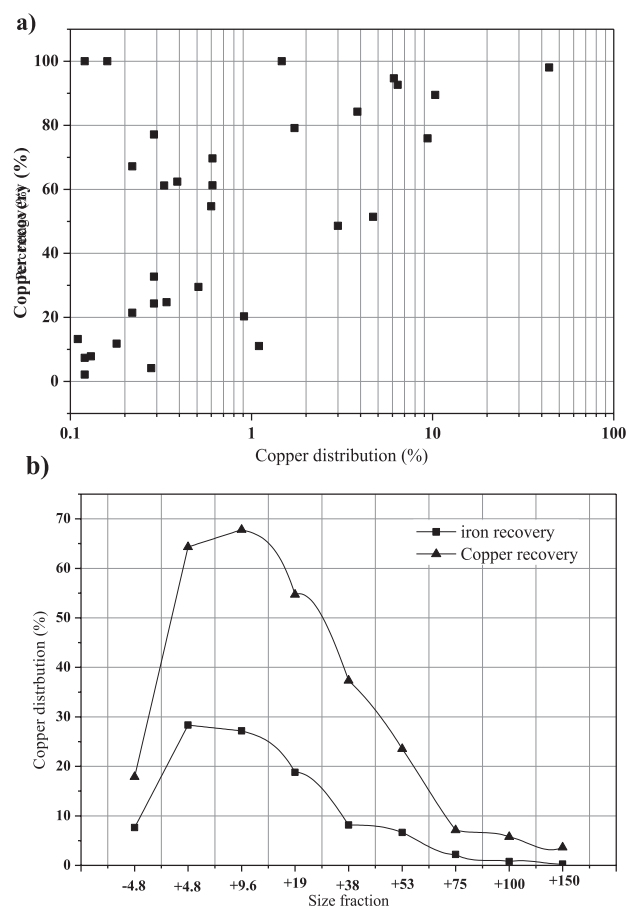

Fig. 7. a) Relationship between copper distribution and copper recovery by flotation separation; b) average size by copper and iron recovery (90%, −48 μm).

Feed (EFS)

Cu $\frac{100.00;\ 0.78}{100.00}$

grinding fineness
$P_{90\%} \leq 48um$

Na₂S 180
BX + BD: 30+30
2# oil 45

Yield%; Grade%
Recovery%
unit g/t

Roughing Ⅰ 6min

Na₂S 80
BX + BD: 15 + 15
2# oil 0

Roughing Ⅱ 6min

Cu $\frac{50.27;\ 1.65}{107.25}$ grinding fineness $P_{98\%} \leq 38um$

Na₂S 40
BX + BD: 5 + 5
2# oil 0

BX + BD: 10 + 10

Scavenging Ⅰ 6min

Cleaning Ⅰ   6min

Cleaning Ⅱ 5min

Na₂S 40
BX + BD: 5 + 5
2# oil 0

Cu $\frac{97.16;\ 0.22}{27.21}$

Flotation tailing

Cleaning Ⅲ   3min

Fe $\frac{100.00;\ 38.85}{100.00}$

Scavenging Ⅱ 6min

**Magnetic roughing
1100~1200 gauss**

Cu $\frac{2.84;\ 19.86}{72.79}$
Copper concentrate

**Cleaning I
900~1100 gauss**

**Cleaning II
700~900 gauss**

Fe $\frac{15.00;\ 50.56}{19.52}$
Iron concentrate

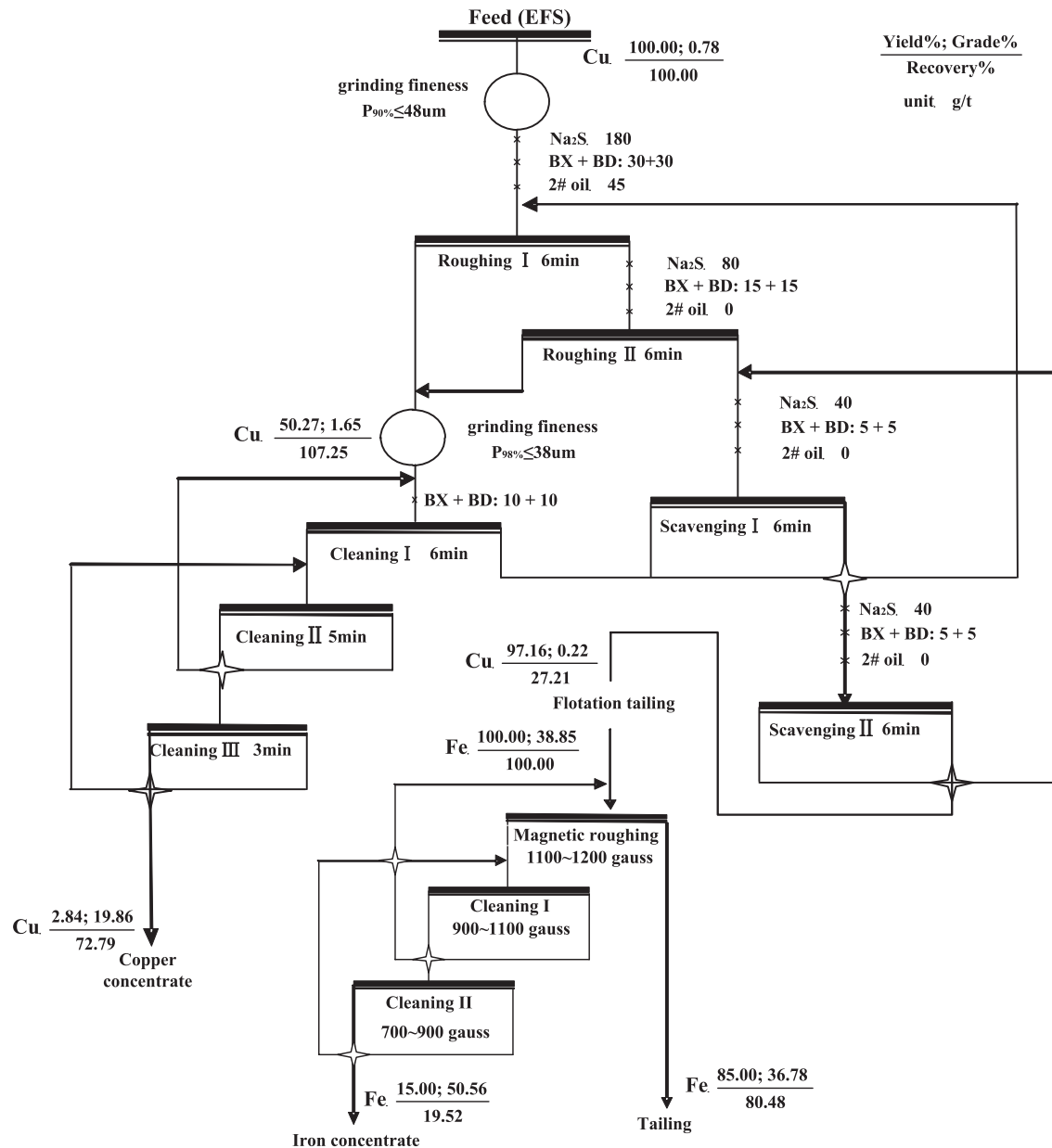Fe $\frac{85.00;\ 36.78}{80.48}$
Tailing

Fig. 8. Flowsheet and optimal process parameters of recycle copper and iron from CEFS.

float during copper floatation. Only a small amount of magnetite is added to copper concentrates because it cannot be liberated with copper sulphide. This indicates that it does not significantly affect the recovery rate and grade of recycled iron by magnetic separation followed by copper recovery by floatation.

Iron Magnetic Separation Studies

The mineralogical characteristics show that it is feasible to recycle iron from CEFS flotation tailings by magnetic separation and has a collection value. After filtration and drying, the flotation tailings act as samples for magnetic separation tests. The effect of main condition parameters for recycling iron is shown in Fig. 6. Fig. 6a) shows that increasing the magnetic intensity of roughing process of iron magnetic separation can increase the recovery rate of iron and guarantee that the iron grade does not change significantly. Fig. 6b) shows that the iron grade is affected by regrinding significantly and increases by about 5.32% when improving the regrinding fineness to achieve (95%, −38 μm). In addition, two-stage cleaning is conductive to iron recycling, and the optimal magnetic intensities of iron cleanings I# and II# were 900-1100GS and 700-900GS, respectively. This indicates that the optimal iron magnetic processing routes from CEFS flotation tailing is single-stage roughing and two-stage cleaning of iron rough concentrate after regrinding. The flowsheet and parameters are shown in Fig. 8. The iron grade and recovery of iron concentrates of this study are 50.69% and 20.41%, respectively.

Table 6. Main reference indexes of financial statistical analysis.

Index	Quantity (t/a)	Unit price (yuan/t)	Total investment (million yuan)	Unit cost (yuan/t)
CEFS	231000.00	--		
Copper concentrate	6560.40	￥6591.00	￥6.53021	￥901.7
Iron concentrate	33665.94	￥404.00		
Tailings	190773.66	￥40.00		

Mineral Balance Analysis

The relationship between copper distribution and copper recovery by flotation separation is shown in Fig. 7a). The main copper-containing minerals with copper distribution larger than 5% have a high copper recovery and vice versa. Fig. 7b) shows the average size by copper and iron recovery. Both metals show the classic size by size recovery curve as reported by Trahar et al [35-36]. The maximum recovery was achieved in the intermediate size fractions (+4.8 −53 μm), and the coarse (+53 μm) and fine (−4.8 μm) particles were recovered at a lower rate. The recovery peaks of copper are located in the 4.8 μm to 38 μm size range, while those of iron are located in the size range from 4.8 μm to 19 μm. These phenomena are consistent with the mineralogical characteristics of CEFS.

Engineering Project and Efficiency Analysis

The research achievements of this study were applied in a copper smelter of Yunnan Copper Co., Ltd., China. In each year, approximately 0.231 million tons of abandoned CEFS is generated from their copper pyrometallurgical processes. Based on this study, the design scale of slag-dressing plant is 700 tons of CEFS per day. The technological processes consist of slow cooling, crushing, grinding, copper flotation, and wet iron magnetic separation. The mineral processing flowsheet is shown in Fig. 8. The production includes copper concentrates, iron concentrates, and tailings. The main reference indexes of financial statistical analysis are shown in Table 6. The financial analysis results show that this is a profitable project, and the net profit is ￥ 19.1452 million yuan per year. After tax deduction, the finance internal return rate and investment recovery period were 34.95% and 3.86 years (including construction period of 1.0 year), respectively. In addition, it can provide about 60 new employment opportunities to alleviate the employment pressure of society and drive the development of tertiary industry, such as transportation and service. Finally, it has great environmental benefits and can reduce the discharge of copper slag (about 231,000 tons per year), recycle metallic copper (about 1300 tons per year) and iron (about 17000 tons per year), save mineral resources, and reduce about 2 hectares of land occupation due to the stacking of CEFS.

Conclusions

Recovery of copper and iron from CEFS using a physical separation process was investigated. The main mineral compositions of CEFS are pyroxene, fayalite, magnetite, and copper sulphide. Copper is mainly distributed in chalcopyrite, copper matte, and bornite, while iron is distributed in fayalite, magnetite, and pyroxene in CEFS. Copper sulfide and magnetic iron (including magnetite and ferroalloy) account for 85.88% and 26.53% of total copper and iron and can be recycled by flotation and magnetic separation, respectively. Copper sulfide and magnetite are the main interlocking and inclusion substances in pyroxene, fayalite, and each other. It is feasible to recycle iron by a combined process of magnetic separation from flotation tailings after the recovery of copper by CEFS flotation. The proposed process involves the following stages: (a) crushing and grinding CEFS to achieve (90%, −48 μm), (b) copper flotation recovery from CEFS at the optimum processing routes, and (c) iron magnetic recovery from CEFS flotation tailings at the optimal magnetic separation routes. Under the optimal conditions, the recoveries of copper and iron of this study are 72.79% and 20.41%, respectively, and the grades of copper and iron concentrates are 19.86% and 50.69%, respectively. The research achievements of this study were used in engineering applications successfully in a copper smelter of Yunnan, China. This clearly proved that it is feasible to recover copper and iron from CEFS via a combined process of flotation and magnetic separation with significant economic, social, and environmental benefits.

Conflict of Interest

The authors declare no conflict of interest.

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