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Reprocessing of copper by flotation *via* mineralogical characteristics from a copper slag case study

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Copper slag (CS), a prominent industrial by-product derived from copper sulphide concentrate smelting, contains valuable copper minerals. Mineralogical analysis revealed 0.56% arsenical copper/chalcopyrite, 1.29% chalcocite, 0.25% cuprite, and 0.24% bornite as the primary copper-bearing phases. Given the rapid depletion of readily exploitable copper resources, CS has emerged as a significant source for copper production. A systematic investigation was conducted to establish optimal operational parameters for classification, grinding, and flotation. This study encompassed diverse scenarios and laboratory tests, with a particular focus on reagent application, including types and consumption rates. The findings demonstrated that Na₂S is used to activate copper oxide minerals that are difficult to recover after a period of grinding, increasing the recovery rate of CS from 53.92% to 87.58%, and the two-stage grinding process is beneficial for precise control of the particle size, considering both energy efficiency and mineral recovery rate. Upon conducting a comprehensive investigation into the closedcircuit flotation process for copper recovery from CS under optimal conditions, it was determined that the copper concentrate achieved a grade of 21.24% and a recovery rate of 36.31%. Additionally, the grade of copper in the flotation tailings was diminished to 0.20%. The synchronous enrichment of copper significantly curtails total emissions in pyrometallurgical processing, mitigating pollution from CS flotation tailings. This study offers a scientific foundation for sustainable CS tailing management, promoting resource recovery and reduced environmental impact.

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1. Introduction

Worldwide, approximately 80% of copper is generated via the pyro-metallurgical processing of sulfide ores. Copper slag is predominantly produced during the smelting of copper sulfide ores and the refining of blister copper. The generation of slag is typically in the range of 2.2 to 3.0 tons for each ton of metal that is produced.2 In China, the accumulated CS inventory surpasses 300 million tons, with an annual generation rate of approximately 20 million tons that continues to increase.3 Classified as industrial solid waste, CS contains highly toxic metallic elements (e.g., copper, lead, and mercury) in their fine particulate form. Long-term stockpiling and atmospheric exposure can trigger the migration of these metals into soil, sediment, and groundwater/surface water, posing significant environmental risks. 4,5 Consequently, advancing low-carbon processing technologies for copper slag valorization becomes

Research has been carried out on the recovery and use of valuable metals in copper smelting slags, which can be summarized as pyro-metallurgy,6 hydro-metallurgy7 and flotation.8 Maximizing copper recovery necessitates mineralogydriven flotation design, where elemental occurrence forms, size distribution, and liberation behavior constitute fundamental determinants.9,10 Maintaining molten copper slags during pyrometallurgical dilution entails substantial energy consumption, while flux additives complicate the slag composition, hindering subsequent resource recovery. Hydrometallurgical processing necessitates oxidizing Cu₂S to CuO, enabling ionic copper enrichment via leaching agents.11 Employing oxidizing agents enables copper recovery rates exceeding 90%. 12,13 Flotation emerges as the optimal copper recovery method from slags, combining environmental friendliness, cost-effectiveness, and high efficiency (>90%), outperforming pollutant-prone hydrometallurgy (requiring expensive corrosive agents) and energyintensive pyrometallurgy.14-16

Flotation is a commonly used process in which valuable minerals can be separated from gangue minerals because of the differences in the surface properties of different minerals. In principle, CS flotation is quite similar to the flotation of Cu-

environmentally imperative, given copper tailings' dual economic function in compound recovery and risk reduction.

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bearing sulphide minerals.¹⁷ Xanthates serve as primary collectors, supplemented by auxiliary collectors (e.g., dithiophosphates, mercaptans, thionocarbamates, xanthates, fuel oil, or kerosene) to enhance copper surface hydrophobicity. Frothers of varying types complete the reagent system. 18 In many plants, a combination of two or more frothers is used to increase the recovery of copper. Most copper slags (CS) are derived from water-quenched processes, yielding finely dispersed metallic copper/sulfide particles intricately interlocked with magnetite, olivine, and gangue minerals. This morphology impedes mineral liberation during grinding, limiting flotation recovery to 50-75%. 19,20 Moreover, copper oxide's inherent floatability challenges are compounded by mineral oxidation during slow cooling and comminution, further compromising slag flotation efficiency. This renders valuable mineral recovery from slag markedly more problematic than from comparable ores.21,22 Na2S sulfidizes copper oxide mineral surfaces to CuS compounds, enabling xanthate collection and establishing its role as a primary activator for oxide copper recovery.23,24 This method is known as the sulfidization-xanthate method. Therefore, it is necessary to identify its potential mechanisms and provide theoretical guidance for the recovery of CS.

To enhance copper recovery from CS, this study investigates flotation-affecting factors through mineralogical and grinding characterization (including liberation analysis). We have investigated a practical flotation approach for copper extraction from CS. Leveraging insights from CS mineralogy, a tailored flotation flowsheet was designed and comparatively assessed. Systematic optimization examined the influence of grinding time, rougher circuit design, and reagent type/dosage on flotation efficiency. Finally, a closed-circuit flotation for the copper slag was proposed and tested. Consequently, this study establishes a sustainable framework to enhance copper recovery from CS and analogous low-grade sulfide ores.

Experimental 2.

Materials and reagents

The copper slag (CS) sample, sourced from China Copper Southeast Copper Co., Ltd (Fujian Province, China), was processed through crushing and homogenization prior to bag storage for experimental analysis. The chemical reagents used in this study include the following: Z200 (95% purity, Qingdao Xinyuan Chemical Co., Ltd, China), butyl xanthate (90% purity, Kunming Luder Chemical Co., Ltd, China), KM6 (85% purity), KM3 (92% purity), and F5b (90% purity), all sourced from Kunming Metallurgical Research Institute Co., Ltd (China). Additionally, terpineol (96% purity, Jiangxi Hongxing Flavor & Fragrance Factory, China), 24 K (90% purity, Huainan Kedi Chemical Technology Co., Ltd, China), and sodium sulfide (65% purity, Jinan Huijinchuan Chemical Co., Ltd, China) were employed.

2.2 Sample characterization and methods

The copper-chemical-phase composition and primary components of the CS were analyzed using the selective chemical dissolution method. Mineralogical characterization of copper slag (CS) and flotation products employed MLA-650 (FEI Quanta

650 SEM-EDS) for particles <2 mm, with concentrate/tailings sourced from closed-circuit flotation tests. Crystalline phases were analyzed by XRD (D/Max-2500, Cu-Kα, 40 kV/40 mA), while chemical composition was determined using XRF (AxiosmAX).

2.3 Selective grinding

The CS raw ore sample was mixed evenly, shrunken, and ground to -2 mm after roller treatment, and then sampled for testing. Here, 500 g of raw ore and 500 mL of water were rod-ground for 5, 7, 9, and 11 minutes, respectively, and then passed through a 45 µm mesh sieve. The samples positioned above and beneath the screen were subjected to drying and subsequent weighing procedures to ascertain their proportions. Subsequently, the pulverized samples were utilized for conducting flotation tests. CS grinding can analyze the particle size of the mineral and also consider the mineral's degree of dissociation and beneficiability, so after each group of grinding experiment results, the flotation experiment was used to analyze the grinding effect, to obtain the required grinding conditions.

2.4 Grinding tests

Fig. 1(a) shows that the ratio of -45 μm increased with the increase of grinding time. At a grinding time of 9 minutes, the ratio of -45 µm reached 84.24%. On further extending the grinding time to 11 minutes, the ratio of $-45 \mu m$ was 93.05%. Grinding tests demonstrate high grindability, generating excessive ultrafine particles under equivalent durations. This may adversely affect flotation kinetics and overall copper recovery.25 As depicted in Fig. 1(b), copper recovery rises progressively with grinding time under consistent flotation conditions. Beyond 9 minutes of grinding, however, this recovery growth rate plateaus. Further increase in grinding time will cause higher grinding energy consumption. As the grinding time increased from 9 to 11 minutes, the copper concentrate grade exhibited a slight decrease from 6.29% to 6.28%. This indicates that with the increase of grinding time, the increase of fine particles will deteriorate the selectivity of flotation. Therefore, the grinding time was fixed at 9 minutes, and after grinding, the CS samples were used for the flotation process.

Flotation tests on the laboratory scale

Representative samples underwent rougher-cleaner flotation tests to evaluate circuit configurations, reagent schemes, and dosage parameters to optimize the process performance. Impurity separation from CS was performed using an XFD III-3L flotation machine. The specific test conditions are detailed below. Flotation parameters: 80 g L⁻¹ pulp density, 2000 r min $^{-1}$ impeller, 40 r min $^{-1}$ wiper, 0.2 m 3 h $^{-1}$ aeration. After the sequential addition of collector (3 min conditioning) and frother (1 min conditioning), the foam collected over 4 min constituted tailings, while pulp solids formed concentrates. Products were filtered, dried, and weighed for Cu grade analysis via chemical methods, with recovery calculated using eqn (1).

$$\varepsilon = \frac{m_1 \beta}{m_1 \beta + m_2 \theta} \times 100\% \tag{1}$$

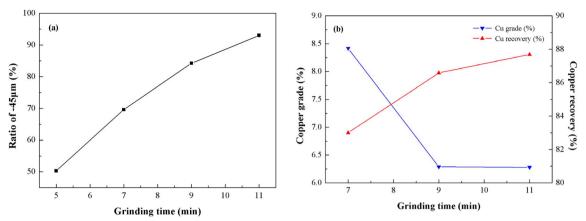


Fig. 1 Results of the grinding tests: (a) effect of grinding time on the $-45~\mu m$ ratio and (b) effect of grinding time on the copper grade and recovery.

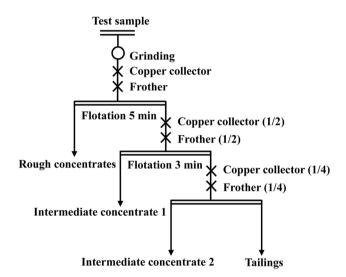


Fig. 2 Flotation process for screening the reagents.

where ε is the Cu recovery, m_1 and m_2 are the dry weights of the concentrate and tailing (g), respectively, β and θ are the Cu grades of the concentrate and tailing (%), respectively.

In the flotation experiments for screening the reagents, the flotation process, as shown in Fig. 2, was adopted. The reagent for the first stage of scavenging was 50% of that for the rough flotation, while the reagent for the second stage of scavenging was 25% of that for the rough flotation.

Based on CS physical property analysis, two flotation processes were compared in order to obtain higher copper recovery. As shown in Fig. 3, two principal processes are selected: the flotation process of oxygen and sulfur mixing (Fig. 3(a)) and the flotation process of preferential mixing of sulfur and then oxygen (Fig. 3(b)).

2.6 Batch flotation tests

Table 1 shows the chemical reagents utilized in nine series of distinct flotation tests. Collectors included Z200, butyl xanthate (BX), KM6, KM3, and F5b. Terpineol and 24 K were used as a frother, and sodium sulphide was used as an activator. The

selection of collectors in the oxidized copper flotation process is primarily determined by the degree of ore oxidation. Based on process mineralogy results, this study chose five collectors for comparative analysis, evaluating their performances with various frothers. Based on the previous studies, $^{26-28}$ in order to compare the efficiency of these reagents, the dosage of the collector was selected as 20 g t⁻¹ and 40 g t⁻¹, and the dosage of the frother was set at 10 g t⁻¹ and 20 g t⁻¹.

Results and discussion

3.1 Materials characterization

The multi-element composition of the CS was determined, and the results are presented in Table 2. The SiO_2 content was 29.68%, metallic elements such as Cu constituted 2.26%, while other metallic elements included Zn at 1.50%, Fe at 43.82%, $\mathrm{Al}_2\mathrm{O}_3$ at 4.50%, and minor quantities of sulfur, arsenic, silver, magnesium, and calcium. Consequently, the particulate impurities in CS are predominantly composed of iron and silicon.

The morphology and distribution of elements in the material were determined, and the test results for CS are shown in Fig. 4. As the primary target mineral, copper-bearing phases exhibited distinctive optical properties: higher reflectance than gangue minerals under incident light, with internal reflections displaying cloudy light-yellow brown hues. The nonmetallic minerals are mainly olivine, silicate mixtures, etc., and the metal minerals are mainly magnetite, chalcocite, arsenite/ metallic copper, bornite, chalcocite, iron copper, etc. Copper minerals and chalcocite are closely associated. From the crosssection, many particles are encapsulated by copper minerals around chalcocite. The nonmetallic minerals mainly display tabular and columnar structures, whereas the metallic minerals are chiefly composed of subhedral-anhedral granules, inclusions, and reaction rims. Key challenges in CS beneficiation include: (i) developing efficient copper concentration circuits; (ii) designing integrated metallic by-product recovery flowsheets with minimized copper losses; and (iii) reconciling disparate liberation sizes of magnetite and co-products. Furthermore, the fine-grained nature of metallic by-products necessitates

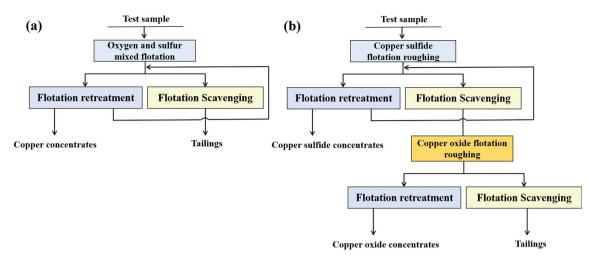


Fig. 3 Preliminary flotation process route: (a) flotation process of oxygen and sulfur mixing and (b) flotation process of sulfides prior to oxides.

Table 1 Type and amount of chemical reagents consumed

Test series	Chemical reagents	Dosage (g t ⁻¹)	Concentration		Tailing			
			Cu grade (%)	Cu recovery (%)	Cu grade (%)	Cu recovery (%)		
1	Z200	40	8.39	83.53	0.31	10.48		
	Terpineol 20							
2	Xanthate	20	8.98	80.14	0.44	15.23		
	Terpineol							
3	Butyl xanthate	40	8.55	84.40	0.34	11.70		
	Terpineol	10						
4	Butyl xanthate	40	7.31	86.19	0.30	9.94		
	Terpineol	20						
5	Butyl xanthate	40	7.34	89.73	0.35	6.07		
	24 K	10						
6	Butyl xanthate	20	8.77	83.84	0.33	12.21		
	24 K	10			0.33			
7	KM6	40	7.40	86.40	0.28	8.31		
	Terpineol	20						
8	KM3	40	7.80	86.02	0.31	10.45		
	Terpineol	20						
9	F5b	40	7.95	81.46	0.46	15.03		
	Terpineol	20						

optimized size fractionation strategies, requiring specific grinding protocols.

To better understand the occurrence state and dissociation degree of copper minerals in CS, MLA (FEI MLA650, America) was used to analyze the dissociation degree, and the results are shown in Fig. 5. The independent minerals of copper include arsenic copper/copper, chalcocite, cuprite, bornite, chenevixite, copper and iron alloy, chalcopyrite, with contents of 0.56%, 1.29%, 0.25%, 0.24%, 0.19%, 0.03%, 0.01%, and 0.004%, respectively. Other minerals are mainly olivine, silicate mixture, and magnetite, the contents of which are 45.49%, 30.53% and 21.22%, respectively. There are also small amounts of trapezite, muscovite, quartz, potassium feldspar, albite, galena, sphalerite, and so on.

The dissociation characteristics of major minerals were analyzed, and the results are shown in Fig. 6. The dissociation characteristics of arsenic copper/copper are shown in Fig. 6; it is

mostly in other granular, spheroidal granular, or star point forms and is closely associated with chalcocite, chalcopyrite, olivine, silicate mixture, and magnetite. Most forms are pelletized in chalcocite; some are associated with olivine and silicate mixtures and some are associated with chalcocite and magnetite, and occasionally with chalcopyrite. The distribution size is between 0.01 and 0.3 mm. Fig. 6(b) shows the dissociation characteristics of chalcocite. Here, chalcocite is in the other granular or pelletized form and has a close symbiotic relationship with arsenite/ metallic copper, olivine, silicate mixtures, and magnetite. Copper arsenide forms multi-coated pellets, some of which are associated with magnetite. Alternatively, it also appears as dissociated monomer particles or solid solution separations in bornite. The distribution size is in the range 0.004-0.4 mm. Generally, the optimal particle size range for flotation is usually in the range 0.01-0.15 mm.^{29,30} Thus, particles that are too fine **RSC Advances**

Table 2 Multi-element analysis results of the sample

Elements	Cu	Zn	Fe	S	Ag^a	As	CaO	MgO	$\mathrm{Al_2O_3}$	SiO_2
Contents (%)	2.06	1.50	43.82	0.37	2.50	0.12	2.60	1.79	4.50	29.68
^a Indicates g t ^{−1} .										

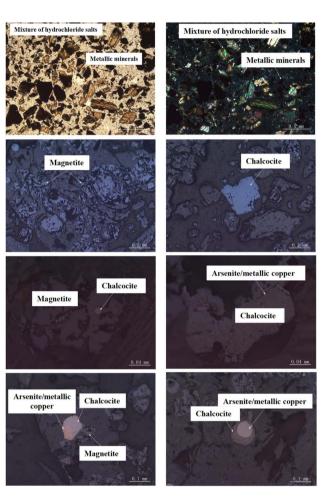


Fig. 4 Polarizing microscope micro-analysis of CS.

are prone to form slime, increasing the viscosity of the pulp, reducing the probability of collisions between bubbles and mineral particles, and at the same time, the slime will adsorb flotation reagents, increasing the consumption of reagents.31 Coarse particles often encapsulate useful minerals due to incomplete dissociation, thus increasing the grade of flotation tailings.32,33 In addition, the results of the material analysis indicate that the copper slag has a high oxidation rate. According to previous research results, 34,35 with traditional flotation, it is difficult to achieve the desired effect for copper slag with a high oxidation rate. Usually, the sulfidation method is needed to enhance the flotation to recover copper from the slag.

3.2 Flotation behavior

3.2.1 The effects of flotation factors on copper recovery. Fig. 7 demonstrates the effects of key parameters (activator Na₂S dosage, collector types, and reagent additions) on copper slag flotation. As seen in Fig. 7(a), copper recovery rose from 53.92% to 87.58% with Na_2S increasing from 0 to 150 g t^{-1} , but declined to 65.54% at 200 g t⁻¹. However, compared with not adding Na2S, the grade of copper decreased significantly when it was added. When the Na2S dosage was increased from 0 g t-1 to 200 g t⁻¹, the recovery of copper increased from 18.25% to 9.22%. According to the physical property analysis results of CS, it contains malachite, hematite, and other copper oxide minerals. Oxidized copper minerals often exhibit hydrophilic hydroxyl (-OH) or carbonate coatings. Substances containing sulfur (HS/S²) displace these groups via ion exchange or complexation, exposing fresh sulfide-like surfaces. The activation mechanism comprises the following: (i) sulfide ion adsorption forming CuS; (ii) sulfide oxidation; (iii) oxidized compound desorption via ion exchange.36,37 The net sulphidisation for sodium sulphide can be represented by eqn (2):38,39

$$M^{2+}A^{2-} + 2Na^{+} + S^{2-} \rightarrow M^{2+}S^{2-} + 2Na^{+} + A^{2-}$$
 (2)

where M2+ and A2- denote surface metal ions and anions, respectively. Pulp chemistry dictates whether HS or S2-serves as the active species. Freshly formed sulfide surfaces enable flotation via standard sulfide collectors.40 Therefore, sodium sulfide is used to activate copper oxide minerals that are difficult to recover after a period of grinding, increasing the recovery rate of CS. Malachite, azurite, and chrysocolla sulfidation primarily yields Cu(1) species, 41,42 with identified sulfide phases (CuS, CuS₂, and CuS_n) demonstrating enhanced efficacy at higher CuS_n proportions. External parameter adjustments can modulate these copper sulfide distributions.43,44 Unlike these minerals, cuprite likely resists complete oxidation under hypoxic conditions, forming predominantly Cu₂O.

The collector dosage significantly governs both concentrate grade and recovery; experiments evaluating collector types revealed these effects (Fig. 7(b)). KM3, KM6, and F5B are all xanthate-type collectors developed by a certain domestic research institute. Under the same dosage of collectors, using these five collectors, the grade of Cu in the concentrate is approximately within the range of 16.5-19.5%. Using F5B as the collector, the copper grade was 16.61% and the recovery rate was 75.00%. Using butyl-xanthate (BX) as the collector, the copper grade was 19.25% and the recovery rate was 49.10%. Therefore, considering both grade and recovery rate comprehensively, these two types of collectors cannot be considered simultaneously. With Z200 as the collector, the copper grade was 18.25% and the recovery rate was 53.92%. By using the KM series of collectors, both the grade and the recovery rate can be well balanced. When the collector is KM3, the copper

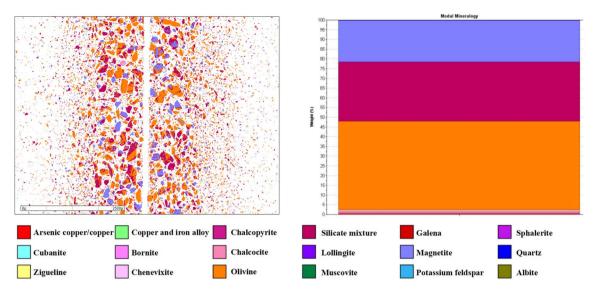


Fig. 5 General analytical drawing of MLA micro-analysis of CS.

concentrate grade and recovery are 17.35% and 78.43%, respectively. When the collector is KM6, the copper concentrate grade and recovery are 17.47% and 78.09%, respectively. Since the initial experiments mainly focused on the recovery rate, KM3 was adopted for the subsequent experimental studies.

3.2.2 Grinding time and step on copper recovery

3.2.2.1 One-stage grinding process. According to the MLA detection result as shown in Fig. 8, the distribution size is between 0.004–0.4 mm. Grinding liberates valuable minerals by reducing particle size, concurrently altering particle distribution, morphology, and surface roughness. These changes—modulated by milling conditions—directly impact mineral wettability and flotation response. Coarse particles exhibit poor floatability due to incomplete liberation and insufficient bubble buoyancy. Flotation relies on three core stages: particle-bubble collision, attachment, and detachment. Mineral surface

morphology critically governs this process: angular particles penetrate hydration layers, enabling stable reagent/bubble adhesion, whereas rounded particles readily detach, reducing recovery.45 Moreover, expanded specific surface area and hydraulic entrainment reduce fine particle floatability in flotation systems.46 Grinding liberates target minerals from gangue via particle size reduction, delivering optimally sized feed for subsequent beneficiation. Ore granulometry directly governs the required grinding fineness and process selection. Since the copper content in the tailings after grinding and flotation is relatively high, it is advisable to adopt one-stage grinding and prioritize the flotation of easily selectable sulfide copper ore and oxidized copper ore (shown in Fig. 8(a)). As Fig. 8(b) shows, in this range of grinding time, with the increase of grinding time from 5 to 11 min, the recovery of copper minerals increases from 52.34% to 91.19%. However, the copper concentrate grade

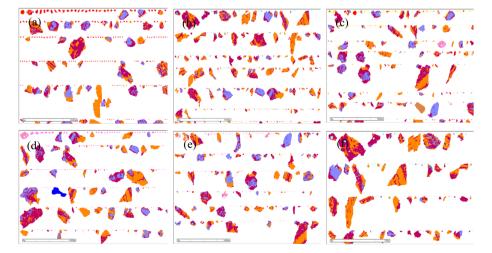


Fig. 6 MLA micro-analysis of CS in the mineral particle analysis diagram: (a) arsenite copper/copper; (b) chalcocite; (c) cuprite; (d) bornite; (e) ferrocopper; and (f) cubanite.

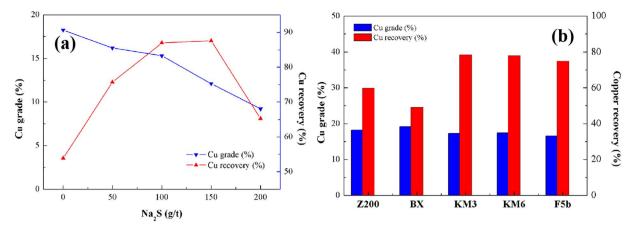


Fig. 7 Effects of reagents on the copper grade and recovery: (a) Na₂S additive amount and (b) collector types

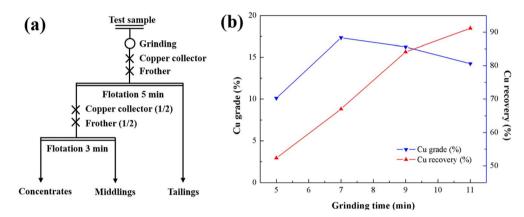


Fig. 8 One-stage grinding process: (a) flow chart of the grinding principles and (b) effects of grinding time on the copper grade and recovery.

increased sharply with the increased grinding time from 5 to 7 minutes, and it slowly decreased when the grinding time exceeded 7 minutes. When the grinding time is 7 min, the tailing copper grade and recovery are 0.63% and 24.42%, respectively, indicating that copper-bearing minerals are still present in the tailing.

3.2.2.2 Two-stage grinding process. Based on the results of the one-stage grinding process, the second stage grinding was carried out, and the grinding time was fixed at 7 minutes. Extended grinding operations risk producing undersized particles through over-grinding phenomena. The $-10 \mu m$ content is usually defined as "overgrinding".47 The resultant slime particles (<10 µm) preferentially adsorb collector molecules through enhanced surface area effects, significantly deteriorating flotation discrimination between valuable and gangue minerals. An appropriate particle size distribution enhances the collision probability between target minerals and bubbles, thereby improving flotation kinetics and concentrate grade. To achieve this, a two-stage grinding process was investigated, as outlined in Fig. 9(a). Concurrently, refractory copper oxide was sulfidized using sodium sulfide. Fig. 9(b) demonstrates that extending the grinding time from 3 to 5 minutes progressively elevates copper recovery. At 9 minutes, recovery

peaked at 94.77%, albeit with a concentrate grade of 12.77%. While the copper grade rose steadily from 10.11% to 17.35% with increasing grinding duration up to 5 minutes, further extension beyond this point led to a decline in grade. These findings confirm that precise particle size control, achieved through classification and staged grinding, optimizes both energy efficiency and mineral recovery, aligning with previous grinding experiment results.^{48,49}

3.2.3 Closed-circuit flotation test and product analysis. Upon the completion of open-circuit flotation experiments, a closed-circuit flotation process was meticulously examined to ascertain its efficacy in copper recovery from CS. The associated flowchart is depicted in Fig. 10, with the outcomes detailed in Table 3. The copper concentrate attained a grade of 21.24% Cu with 36.31% recovery, while the middlings product yielded 7.79% Cu at 32.94% recovery. Moreover, the copper grade in the flotation tailings was cut down to 0.20%, markedly below the usual range of 0.3–0.5% often seen in flotation tailings.^{50,51}

As shown in Fig. 5, the independent minerals of copper include arsenic copper/copper, chalcocite, cuprite, bornite, chenevixite, copper and iron alloy, chalcopyrite, with the contents of 0.56%, 1.29%, 0.25%, 0.24%, 0.19%, 0.03%, 0.01%, 0.004%, respectively. Thus, copper minerals in copper slag, such as

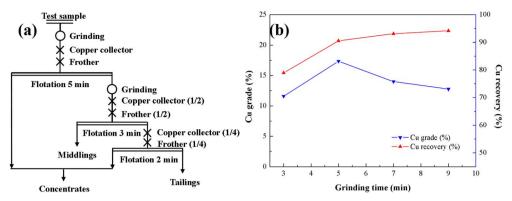


Fig. 9 : Two-stage grinding process: (a) flow chart of the grinding principles; (b) effects of grinding time on the copper grade and recovery.

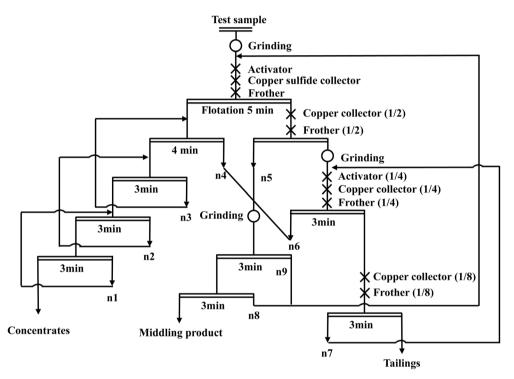


Fig. 10 Flow chart of closed-circuit flotation for the copper slag.

chalcocite, bornite, chalcopyrite, *etc.*, often form a coexisting structure of encapsulation or intercalation with the olivine matrix or magnetite. The floatation properties of arsenic copper are like those of glacial copper chalcocite, and arsenic minerals are often encapsulated in glacial copper in the form of fine particles, increasing the arsenic content in the copper concentrate and polluting the quality of the concentrate. In addition, the floatability of copper oxide minerals, including chalcocite and cuprite, and copper sulfide minerals varies significantly, making floation more difficult. The difficulty in beneficiation of this copper slag mainly stems from its complex mineral composition, fine particle size distribution, risk of arsenic contamination, and the coexistence of multiphase copper minerals, which lead to higher requirements for the floatation

 Table 3
 Results of the product analysis of closed-circuit flotation

Product	Yield (%)	Grade (%)	Recovery (%)
Concentrates	4.23	21.24	36.31
Middling product	10.45	7.79	32.94
n1	3.25	3.94	5.18
n2	5.09	2.67	5.50
<i>n</i> 3	7.37	1.98	5.91
<i>n</i> 7	3.94	0.37	0.59
<i>n</i> 8	7.32	0.67	1.99
<i>n</i> 9	13.59	1.45	7.97
Tailings	44.76	0.20	3.62

process. The results of this research show that the novel integrated process devised here successfully cuts down copper losses in the tailings, thus promoting effective copper retrieval from CS.

4. Conclusion

CS has led to significant resource waste and environmental pollution. This study has combined mineralogical characteristics and flotation investigations to identify the key factors influencing the synchronous flotation enrichment of copper in CS. It was found that copper slag has a high oxidation rate, and Na₂S can enhance copper recovery from CS; KM3 as a collector also aids in this process. The grinding comparison experiment revealed that segmented grinding is more effective for precise particle size control and copper recovery. Employing a closedcircuit flotation process yielded a copper concentrate grade of 21.24% and a recovery of 36.31%, while reducing the tailings copper content to 0.20%. This study successfully addresses the challenge of enriching copper from CS via flotation, providing valuable insights for mitigating hazardous copper waste. Collectively, the findings offer critical guidance for future CS resource utilization and the sustainable development of the copper industry.

Author contribution

Yumeng Chen: investigation, data curation, writing-original draft, funding acquisition; Wenjie Zhang: writing-review & editing, investigation, data curation.

Conflicts of interest

There are no known competing financial interests or personal relationships that could influence the publishing of this manuscript.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

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References

 A. Potysz, E. D. V. Hullebusch, J. Kierczak, et al., Copper Metallurgical Slags – Current Knowledge and Fate: A Review, Crit. Rev. Environ. Sci. Technol., 2015, 1046769.

- 2 R. Liu, Q. Zhai, C. Wang, X. Li and W. Sun, Optimizing the Crystalline State of Cu Slag by Na2CO3 to Improve Cu Recovery by Flotation, *Minerals*, 2020, (9), 820.
- 3 Z. L. Qin, J. H. Xiao, T. Y. Du and J. H. Zhang, Eco-friendly iron extraction from fe-containing copper smelting slag *via* reduction roasting with coal and magnetic separation: Experimental and mechanism insights, *J. Environ. Chem. Eng.*, 2024, **12**(5), 114117.
- 4 V. Ettler, P. Piantone and J. C. Touray, Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long-term assessment, *Mineral. Mag.*, 2003, 67(6), 1269–1283.
- 5 M. Vítková, V. Ettler, Z. Johan, B. K?íbek, O. ?ebek and M. Mihaljevi?, Primary and secondary phases in coppercobalt smelting slags from the Copperbelt Province, Zambia, *Mineral. Mag.*, 2010, 74(4), 581–600.
- 6 R. G. Reddy, V. L. Prabhu and D. Mantha, Recovery of copper from copper blast furnace slag, *Min., Metall., Explor.*, 2006, 23(2), 97–103.
- 7 K. Gargul, Ammonia leaching of slag from direct-to-blister copper smelting technology, *AIMS Mater. Sci.*, 2020, 7(5), 565–580.
- 8 A. Sarrafi, B. Rahmati, H. R. Hassani and H. H. A. Shirazi, Recovery of copper from reverberatory furnace slag by flotation, *Miner. Eng.*, 2004, 17(3), 457–459.
- 9 K. Tungpalan, E. Wightman and E. Manlapig, Relating mineralogical and textural characteristics to flotation behaviour, *Miner. Eng.*, 2015, **82**, 136–140.
- 10 Q. Feng, Y. Zhang, G. Zhang, G. Han and W. Zhao, Innovative scheme for hemimorphite flotation: Synergistic activation performance and mechanism, *Int. J. Miner., Metall. Mater.*, 2025, 32(6), 1297–1308.
- 11 E. Bidari and V. Aghazadeh, Investigation of Copper Ammonia Leaching from Smelter Slags: Characterization, Leaching and Kinetics, *Metall. Mater. Trans. B*, 2015, **46**(5), 1–10.
- 12 M. K. Khalid, J. Hamuyuni, V. Agarwal, J. Pihlasalo, M. Haapalainen and M. Lundström, Sulfuric acid leaching for capturing value from copper rich converter slag, *J. Cleaner Prod.*, 2019, 215, 1005–1013.
- 13 E. Bidari and V. Aghazadeh, Investigation of Copper Ammonia Leaching from Smelter Slags: Characterization, Leaching and Kinetics, *Metall. Mater. Trans. B*, 2015, 46(5), 2305–2314.
- 14 B. Das, B. K. Mishra, S. Angadi, S. K. Pradhan, S. Prakash and J. Mohanty, Characterization and recovery of copper values from discarded slag, Waste Manag. Res. J. Int. Solid Wastes Public Cleansing Assoc. ISWA, 2010, 28(6), 561–567.
- 15 Q. Feng, Y. Zhang, G. Zhang, G. Han and W. Zhao, A novel sulfidization system for enhancing hemimorphite flotation through Cu/Pb binary metal ions, *Int. J. Min. Sci. Technol.*, 2024, 34(12), 1741–1752.
- 16 W. Yang, Y. Tang, B. Huang, G. Han and Q. Feng, Experimental and molecular dynamics simulation insights into enhanced flotation of sulfidized smithsonite in a Cu-Pb dual activation system, *Green Smart Min. Eng.*, 2025, 2(1), 8–17.

- 17 C. Arslan and F. Arslan, Recovery of copper, cobalt, and zinc from copper smelter and converter slags, *Hydrometallurgy*, 2002, **67**(1), 1–7.
- 18 H. Boostan and A. Sam, Reprocessing of copper and molybdenum by flotation method from final fresh low-grade sulfide tailings (case study: Sarcheshmeh copper complex), *J. Environ. Chem. Eng.*, 2025, **13**(2), 115496.
- 19 Z. Xian-Lin, Z. De-Qing, P. Jian and W. Teng-Jiao, Utilization of Waste Copper Slag to Produce Directly Reduced Iron for Weathering Resistant Steel, *ISIJ Int.*, 2015, 55(7), 1347–1352.
- 20 B. Xia, X. Zeng and Z. Mao, Research on One Borehole Hydraulic Coal Mining System, *Earth Sci. Front.*, 2008, 15(4), 222–226.
- 21 J. J. Sun, T. F. Zhang, L. Y. Dong, H. Zhu, P. L. Shen and D. W. Liu, Eco-friendly recovery of copper from copper slag *via* magnetic separation followed by flotation: Experimental and mechanistic insights, *J. Environ. Chem. Eng.*, 2025, 13(2), 115746.
- 22 Z. Q. Guo, D. Q. Zhu, J. Pan, F. Zhang and C. C. Yang, Industrial Tests to Modify Molten Copper Slag for Improvement of Copper Recovery, *Jon*, 2018, 70(4), 533–538.
- 23 X. C. Yu, B. Yu, H. Wang, P. L. Shen and D. W. Liu, Evolution of sulfur species on malachite surfaces in the presence of calcium and magnesium ions and implications for xanthate flotation, *Adv. Powder Technol.*, 2024, 35(7), 104538.
- 24 X. C. Yu, Z. D. Yin, Y. Chen, P. L. Shen, H. Wang, Y. Q. Mao and D. W. Liu, Experimental and DFT study of modified malachite with 2,5-dimercap-to-1,3,4-thiadiazole and its response to sulfidization-xanthate behavior, *Colloids Surf.*, *A*, 2024, **693**, 134057.
- 25 S. W. Li, Z. Q. Guo, J. Pan, D. Q. Zhu, T. Dong and S. H. Lu, Stepwise Utilization Process to Recover Valuable Components from Copper Slag, *Minerals*, 2021, 11(2), 1–14.
- 26 X. Chi, Z. Ye, H. Wang, W. Weng and S. Zhong, A novel trithiocarbonate collector featuring high-temperature resistance for copper slag flotation, *Miner. Eng.*, 2023, 202, 108275.
- 27 H. H. Zhou, G. J. Liu, L. Q. Zhang and C. C. Zhou, Mineralogical and morphological factors affecting the separation of copper and arsenic in flash copper smelting slag flotation beneficiation process, *J. Hazard. Mater.*, 2021, 401.
- 28 T. Kundu, S. Senapati, S. K. Das, S. I. Angadi and S. S. Rath, A comprehensive review on the recovery of copper values from copper slag, *Powder Technol.*, 2023, 426.
- 29 H. Han, A. Liu, C. L. Wang, R. Q. Yang, S. Li and H. F. Wang, Flotation kinetics performance of different coal size fractions with nanobubbles, *Int. J. Miner.*, *Metall. Mater.*, 2022, 29(8), 1502–1510.
- 30 H. J. Zhang, J. T. Liu, Y. J. Cao and Y. T. Wang, Effects of particle size on lignite reverse flotation kinetics in the presence of sodium chloride, *Powder Technol.*, 2013, **246**, 658–663.
- 31 J. Sun, L. Dong, T. Zhang, P. Shen and D. Liu, Efficient recovery of copper from copper smelting slag by gravity separation combined with flotation, *Chem. Eng. J.*, 2024, **494**, 153159.

- 32 A. R. Batchelor, D. A. Jones, S. Plint and S. W. Kingman, Increasing the grind size for effective liberation and flotation of a porphyry copper ore by microwave treatment, *Miner. Eng.*, 2016, **94**, 61–75.
- 33 Y. Jin, W. Sun, J. Peng, Z. Geng, Q. Wu, F. Jiang and F. Fan, Recovering the coarse particles associated with copper tailings by a new fluidized flotation column, *Miner. Eng.*, 2025, 227, 109305.
- 34 B. Wei, Z. Li, X. Yu, H. Wang and D. Liu, Surface modification mechanism of copper oxide in copper smelting slag by lead ions and its influence on sulfidization flotation, *Sep. Purif. Technol.*, 2025, **366**, 132684.
- 35 X. Yu, H. Wang, L. Wang, Y. Mao and D. Liu, Enhance recovery mechanism of difficult to enrich copper oxide component in copper smelting slag: Sulfidization-xanthate flotation, *Chem. Eng. J.*, 2024, **502**, 157857.
- 36 T. Moimane, C. Plackowski and Y. Peng, The critical degree of mineral surface oxidation in copper sulphide flotation, *Miner. Eng.*, 2020, 145, 106075.
- 37 K. Lee, D. Archibald, J. McLean and M. A. Reuter, Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors, *Miner. Eng.*, 2009, **22**(4), 395–401.
- 38 L. T. Tijsseling, Q. Dehaine, G. K. Rollinson and H. J. Glass, Flotation of mixed oxide sulphide copper-cobalt minerals using xanthate, dithiophosphate, thiocarbamate and blended collectors, *Miner. Eng.*, 2019, **138**, 246–256.
- 39 A. J. H. Newell, W. M. Skinner and D. J. Bradshaw, Restoring the floatability of oxidised sulfides using sulfidisation, *Int. J. Miner. Process.*, 2007, **84**(1), 108–117.
- 40 D. W. Clark, A. J. H. Newell, G. F. Chilman and P. G. Capps, Improving flotation recovery of copper sulphides by nitrogen gas and sulphidisation conditioning, *Miner. Eng.*, 2000, 13(12), 1197–1206.
- 41 R. Peng, Z. Xie, Q. Wei, H. He, H. Wang, J. Cai and D. Liu, Comodification of chrysocolla with ammonia and 1,2-diaminopropane and its response to flotation, *Colloids Surf.*, *A*, 2024, **698**, 134566.
- 42 P. Shen, D. Liu, X. Xu, X. Jia, X. Zhang, K. Song and J. Cai, Effects of ammonium phosphate on the formation of crystal copper sulfide on chrysocolla surfaces and its response to flotation, *Miner. Eng.*, 2020, **155**, 106300.
- 43 Q. Feng, W. Zhao and S. Wen, Ammonia modification for enhancing adsorption of sulfide species onto malachite surfaces and implications for flotation, *J. Alloys Compd.*, 2018, 744, 301–309.
- 44 Q. Feng, W. Zhao and S. Wen, Surface modification of malachite with ethanediamine and its effect on sulfidization flotation, *Appl. Surf. Sci.*, 2018, **436**, 823–831.
- 45 C. Dai, P. Chen, Y. Yang and W. Sun, Effect of grinding media on surface property and flotation performance of ilmenite, *Powder Technol.*, 2024, 447, 120232.
- 46 W. Li, F. Jiao, X. Wang, W. F. Che, Z. Q. Zhang, B. J. Xin and W. Q. Qin, Improve flotation efficiency of refractory tungsten ore and reduce carbon emission in flotation process: A case

study of Sandaozhuang deposit in Henan, China, *Miner. Eng.*, 2024, 216, 108917.

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- 47 X. Fang, C. B. Wu, N. N. Liao, C. F. Yuan, B. Xie and J. Q. Tong, The first attempt of applying ceramic balls in industrial tumbling mill: A case study, *Miner. Eng.*, 2022, 180.
- 48 E. M. Pérez-García, J. Bouchard and É. Poulin, Integrating online mineral liberation data into process control and optimisation systems for grinding-separation plants, *J. Process Control*, 2021, **105**, 169–178.
- 49 S. K. Sriramoju, D. Kumar, S. Majumdar, P. S. Dash, D. Shee and R. Banerjee, Sustainability of coal mines: Separation of clean coal from the fine-coal rejects by ultra-fine grinding

- and density-gradient-centrifugation, *Powder Technol.*, 2021, **383**, 356-370.
- 50 J. Sun, T. Zhang, L. Dong, H. Zhu, P. Shen and D. Liu, Ecofriendly recovery of copper from copper slag *via* magnetic separation followed by flotation: Experimental and mechanistic insights, *J. Environ. Chem. Eng.*, 2025, **13**(2), 115746.
- 51 L. S. Wang, Z. Y. Gao, H. H. Tang, L. Wang, H. S. Han, W. Sun and Y. Yang, Copper recovery from copper slags through flotation enhanced by sodium carbonate synergistic mechanical activation, *J. Environ. Chem. Eng.*, 2022, **10**(3), 107671.