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Flotation of Copper Sulfide Ore Using Ultra-Low Dosage of Combined Collectors

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Abstract: Copper sulfide ores frequently co-occur with pyrite, presenting a significant challenge for their selective separation during beneficiation processes. Despite advancements in flotation technology, there remains a critical need for efficient methods to enhance copper recovery while suppressing pyrite interference, particularly without compromising the associated precious metals such as gold and silver. Current practices often struggle with achieving high selectivity and recovery while maintaining environmental sustainability. Here, we investigate the efficacy of a ternary collector mixture consisting of ammonium dibutyl dithiophosphate (ADD), butyl xanthate (BX), and ethyl xanthate (EX) for the selective flotation of copper sulfide from a complex ore containing 0.79% Cu and associated precious metals (0.233 g/t Au and 5.83 g/t Ag). A combination of lime and hydrogen peroxide as inhibitors was employed to suppress pyrite effectively under alkaline conditions (pH = 11.33). The results demonstrate that the optimized ternary collector system (ADD:BX:EX at a ratio of 1:0.5:0.5) significantly improves the copper grade and recovery at an ultra-low dosage of 10 g/t. The optimized flotation method using the combined collectors and inhibitors effectively separated chalcopyrite from pyrite, achieving a copper concentrate with 20.08% Cu content and a recovery of 87.73%. Additionally, the process yielded notable recoveries of gold (9.22%) and silver (26.66%). These findings advance the field by providing a viable and environmentally conscious approach to the beneficiation of sulfide ores, potentially serving as a blueprint for processing similar mineral deposits while minimizing reagent usage and costs.

Keywords: copper sulfide ore; process mineralogy; ultra-low dosage; combined collectors; flotation separation

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1. Introduction

The selective separation of copper sulfide minerals from pyrite has always been a technical challenge that urgently needs to be solved in flotation plants. Flotation is the most widely used technique for separating and enriching metallic minerals [1]. If the pyrite content of a copper sulfide ore is low (<5%), the pH values of the grinding condition and flotation pulp are generally increased, which depresses pyrite flotation [2–6]. A previous study revealed that the addition of depressants could be used to control the oxidation state of the pyrite surface, which is the key to making it hydrophilic, by the formation of secondary iron minerals, such as ferric hydroxide [7]. High pH is conducive to the oxidation of the pyrite surface, releasing ferrous and sulfate ions into solution. These hydrophilic oxidation products react with cations, like with Ca^{2+}, Mg^{2+}, Fe^{3+}, and others, thereby enabling the effective separation of pyrite and chalcopyrite [8–13]. Hu et al. [14] found that the formation of hydrophilic precipitates, such as calcium hydroxide, calcium sulfate, and ferric hydroxide, in a high-alkali lime process is primarily responsible for depressing pyrite floatability. However, chalcopyrite often coexists closely with pyrite (a common gangue mineral) and precious metals such as gold and silver. Under high pH conditions, the surface of chalcopyrite is easily eroded by OH^- ions, resulting in the formation of iron oxides and a decrease in floatability. And it is not conducive to the recovery of associated precious metals such as gold and silver [15,16].

However, in ores with high pyrite contents, the anodic effect of chalcopyrite and pyrite is enhanced, promoting the oxidative dissolution of chalcopyrite and generating copper ions that adsorb onto the pyrite surface, enhancing its floatability [17–20]. Under highly alkaline conditions, oxidants can further promote the formation of hydrophilic components on the pyrite surface to reduce its floatability, thereby achieving the flotation separation of copper sulfide minerals and obtaining a high-grade copper concentrate [21]. Therefore, the floatability of pyrite can be synergistically depressed by the addition of lime and oxidants (H_2O_2, $Ca(ClO)_2$, Na_2SO_3) at high pH ($pH > 8$) [22–25]. In addition, the hydrophobicity of chalcopyrite depends on surface oxidation, which dissolves copper and iron ions and forms a polysulfide layer under alkaline conditions [15,26]. Khoso et al. [27] studied the effect of H_2O_2 oxidation treatment on the flotation separation of chalcopyrite and pyrite collected by xanthate. They found that at pH 9, chalcopyrite treated with hydrogen peroxide had a stronger adsorption capacity for butyl xanthate than pyrite, and the recovery of chalcopyrite was as high as 84%. Therefore, it is necessary to use a combined inhibitor of lime and oxidant to suppress pyrite in the flotation of sulfide copper ore with high sulfur content.

In copper sulfur flotation separation, low-grade and difficult-to-select copper sulfide ores are often accompanied by precious metals such as gold and silver, so the selection of collectors is particularly crucial. Compared with the traditional flotation method of high-dosage xanthate, the combined collector is widely used in the field of mineral flotation due to its advantages of high-efficiency collection and low dosage [28–30]. Dhar [31] conducted a systematic study on Nussir copper ore, using a DBD and mixed collectors (SIBX and DBD) system. The results show that compared with using the DBD collector alone, the xanthate-dithiophosphate mixed collector (ratio of 1:3) improved copper grade and recovery. Subsequently, Dhar [32] conducted a feasibility study on the selective flotation of sulfides using SIBX, BBT, DBD, and their mixtures as collectors. Compared to a single collector, the mixed collector of BBT and SIBX (with a ratio of 3:1) improved the copper grade and recovery of flotation products. At the same time, the order of adding combined collectors will also affect the results of copper flotation. Most flotation experiments use binary combination collectors and new collectors, but there is little research on the combined use of the three traditional collectors of ammonium dibutyl dithiophosphate (ADD), butyl xanthate (BX) and ethyl xanthate (EX).

The purpose of this work was to develop an efficient copper flotation process using an ultra-low dosage of combined collectors for the flotation separation and enrichment of a copper sulfide ore. Ultra-low dosage (<20 g/t) refers to using minimal amounts of flotation reagents while maintaining high flotation efficiency. The process mineralogy of the ore was first assessed to provide a theoretical basis for determining the appropriate flotation process. Flotation separation of the copper sulfide minerals was then carried out and the best reagent system and process flowsheet was explored. A high-quality copper concentrate product was obtained using a closed-circuit test.

2. Materials and Methods

The copper sulfide ore was sourced from Pu'er, Yunnan, China, and was sampled at different supply points by field personnel according to the prevailing production and deposit conditions. Representative ore blocks were subjected to process mineralogy analysis. The remaining ore samples were crushed to below 2.0 mm by a jaw crusher and cone crusher, mixed and prepared for sample preparation, and used for ore sample detection analysis and mineral processing. The crushed ore was ground to an appropriate particle size by a rod mill, and then uniformly sampled for multi-element chemical analysis, phase analysis, and X-ray diffraction (XRD). The XRD results are shown in Figure 1. The gangue minerals in the ore were mainly silicates, carbonates (quartz, calcite, muscovite, dolomite, and clinochlore) and pyrite. The contents of copper sulfide minerals were low, and these are not reflected in the XRD analysis. In the flotation experiments, lime is used as a pH regulator, and combined with hydrogen peroxide and sodium sulfite as inhibitors of pyrite. The collector for copper flotation was a combination of ammonium dibutyl dithiophosphate (ADD), butyl xanthate (BX), and ethyl xanthate (EX) in a ratio of 1:0.5:0.5; terpineol oil was used as a foaming agent. All reagents were chemically pure and purchased from Zhuzhou Flotation Reagent Factory. Before conducting flotation tests, we diluted the reagent in water to a concentration of 0.02%–1%. The types and dosages of reagents ranged in the flotation tests, as shown in Table 1.

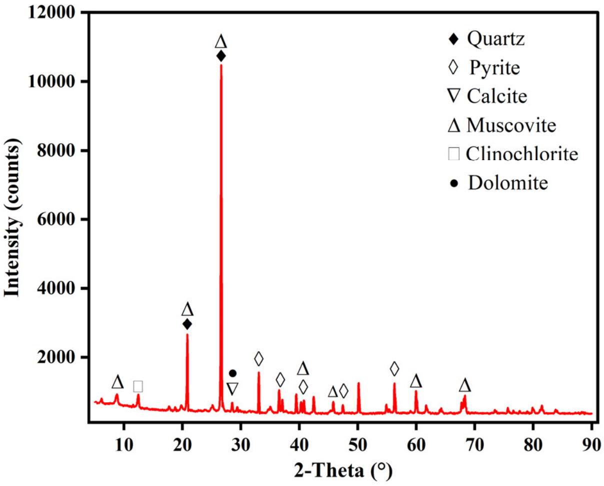

Figure 1. X-ray diffraction pattern of raw ore.

Table 1. Types and dosage ranges of flotation reagents.

Inhibitor	Dosage (g/t)	Collector	Dosage (g/t)
Lime	300–3000	Ammonium dibutyl dithiophosphate	1.5–50
Hydrogen peroxide	0–600	Butyl xanthate	1.5–90
Sodium sulphite	300–700	Ethyl xanthate	1.5–90

XFD single-cell flotation machines (Jilin Exploring Machinery Plant, Changchun, China), the scraper speed is 15 r/min, the spindle speed is 1999 r/min, and the aeration rate is 0.2 m^3/h) were used for the laboratory flotation experiments, at scales of 1.5 L, 0.75 L, 0.5 L, and 0.2 L. Tap water was employed. A sample of 250 g ore was taken each time. It was added to a rod mill and ground for 96 s. The final grinding product had a particle size of –0.074 mm and a content of 70%. Roughing flotation tests were carried out under the condition of a 33% solids content in the pulp. Firstly, the pulp mixing time was 2–3 min, then the inhibitor (the pH of pulp was 11.33) was added and stirred for 5 min; then the collector was added and stirred for 3 min. Finally, 84 g/t of terpineol oil was added and allowed to react for 1 min, followed by 5 min of scraping. The resulting flotation products were filtered, dried, and weighed separately, and the copper grade was analyzed using the AAS (Atomic Absorption Spectroscopy) chemical analysis method. Each experiment was repeated three times, and the average was taken as the final result.

3. Results and Discussion

3.1. Process Mineralogy

3.1.1. Multi-Element Chemical and Phase Analysis

The results of multi-element chemical analysis and copper phase analysis of the raw ore are shown in Tables 2 and 3, respectively. The results in Table 1 show that the main valuable metal in the ore was Cu, at a content of 0.79%. The Pb and Zn contents were low, so these elements were not considered for recovery. The gangue minerals mainly comprised silicates and pyrite, with the SiO_2 content of 61.92%, and Fe was present at 11.64%. In addition, the associated precious metals contents were appreciable, at 0.233 g/t Au and 5.83 g/t Ag, and may have had value for recovery. The results in Table 2 show that copper mainly existed in the form of copper sulfide minerals (88.60%), of which the proportions of primary and secondary copper sulfides were 68.35% and 20.25%, respectively. The remaining copper was present as an oxide (11.39%): the contents of free and combined copper oxides were 6.96% and 4.43%, respectively.

Table 2. Multi-element chemical analyses of copper ore.

Element	**Cu**	**Pb**	**Zn**	**Fe**	**S**	**SiO_2**
Content/%	0.79	0.028	0.25	11.64	11.64	61.92
Element	CaO	MgO	Al_2O_3	As	Au *	Ag *
Content/%	4.91	1.12	8.20	0.025	0.233	5.83

* Unit g/t.

Table 3. Phase analysis of copper ore.

Phase	**Free Copper Oxide**	**Bonded Copper Oxide**	**Secondary Copper Sulfide**	**Primary Copper Sulfide**	**Total Copper**
Content/%	0.055	0.035	0.16	0.54	0.79
Distribution/%	6.96	4.43	20.25	68.35	100

3.1.2. Mineral Composition and Liberation Characteristics of the Ore

Quantitative analysis on the ore was performed using the Maps Mineralogy fully automated mineral analysis system, as shown in Figure 2. Ore samples were examined using optical and scanning electron microscopy (SEM, FEI quanta-650, Portland, OR, USA), as shown in Figures 3 and 4. The ore comprised 31 kinds of minerals in seven categories. The main component was silicates (62.01%), followed by sulfides (34.45%), oxides (1.05%), carbonates (0.64%), phosphates (0.13%), sulfates (0.06%), and halides (0.01%). The metal-containing minerals were mainly pyrite, followed by chalcopyrite, and small amounts of sphalerite and covellite. Pyrite exhibited a high degree of liberation; the liberation of other minerals was poor, and a relatively wide range of liberated particle sizes was apparent. The minerals were not highly enriched. Pyrite was liberated to an extent of 79.10%; the remaining 20.90% occurred in allotriomorphic–semi-automorphic granular form or associated with chalcopyrite and embedded in the gangue minerals, thereby forming pyrite–chalcopyrite and chalcopyrite–pyrite–gangue intergrowths (Figure 3b–d). The liberation of chalcopyrite was poor, at only 21.30%; the remaining 78.70% was mainly in allotriomorphic granular form adjacent to and embedded in the gangue minerals (Figure 4c), or it occurred as network veins embedded in pyrite to form intergrowths. The mineral particles were fine, and the embedded particle size was mainly 0.02–0.05 mm. Most covellite occurred as single grains or in the form of fine particles associated with chalcopyrite: the embedded particle size was mainly 0.005–0.02 mm.

3.1.3. Characteristics of Particle Size Distribution and Liberation Degree

The degree of monomer dissociation of valuable minerals with different particle size ranges varied, as shown in Table 4. For grinding conditions that resulted in 70% of particles passing 0.074 mm, the liberation of the main target minerals (chalcopyrite, cubanite, digenite, covellite, bornite, tetrahedrite, and pyrite) was poor. Chalcopyrite particles within the ore have a size range of 0.0037 to 0.0795 mm, with only 8.37% of particles achieving complete dissociation, and the dissociation degree of the majority of particles was below 80%. For cubanite, 90.41% of particles exhibited a dissociation degree below 80%, with dissociation particle sizes ranging from 0.0026 to 0.1036 mm. Only 6.47% of cubanite particles achieved complete dissociation. The dissociation degree of digenite, covellite, and bornite was less than 60%, with particle sizes of 0.0079–0.0118 mm, 0.0059–0.0950 mm, and 0.0051–0.0408 mm, respectively. Among them, 17.9% of covellite particles achieved complete dissociation. Tetrahedrite demonstrated a relatively good dissociation property, with a particle size range of 0.0053–0.0447 mm. Further, 23.37% of the particles were completely released, while the remaining dissociation degree was less than 80%. In comparison to copper minerals, pyrite exhibited better dissociation, with 42.69% of particles having a dissociation degree greater than 80%. The particle size range for pyrite was broader, ranging from 0.0026 to 0.3015 mm.

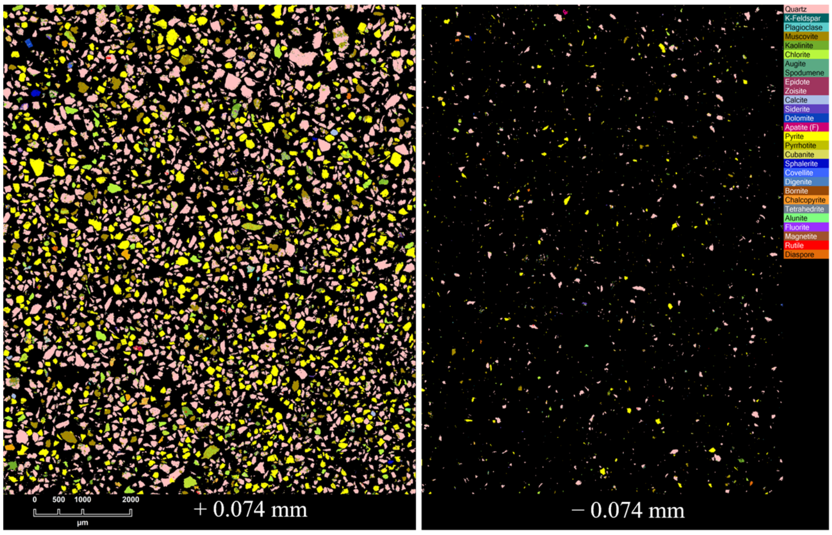

Figure 2. Mineral liberation analysis image of raw ore.

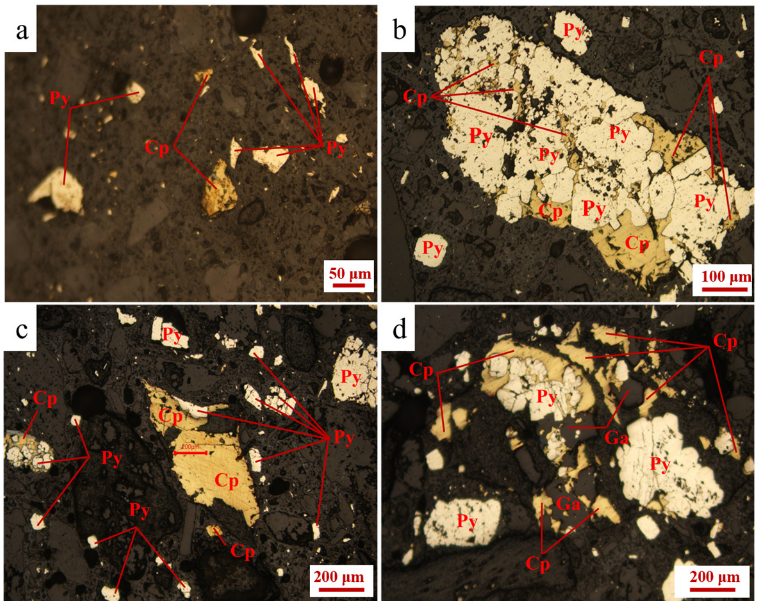

Figure 3. Distribution characteristics of pyrite (Py) and chalcopyrite (Cp). (**a**) Py, Cp monomers; (**b**) Cp–Py intergrowth; (**c**) Py, Cp grains and Py–Cp junction; (**d**) Cp–Py–gangue (Ga) intergrowth.

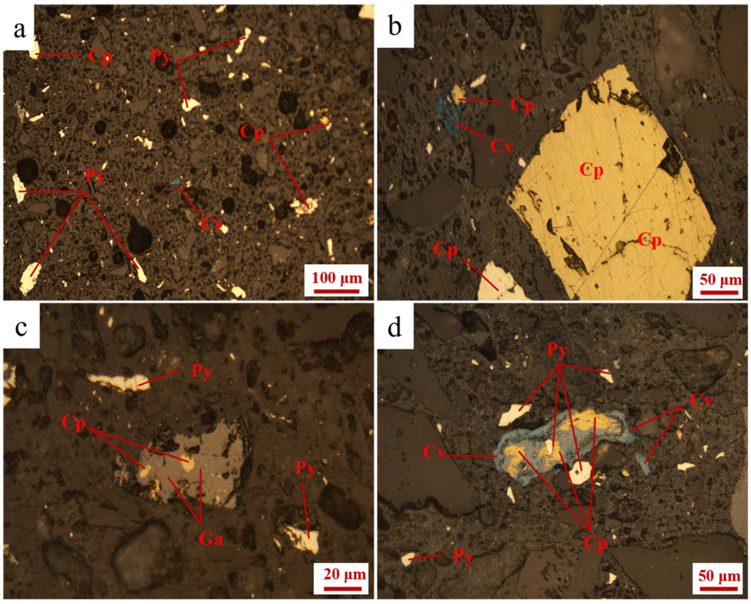

Figure 4. Liberation characteristics of chalcopyrite (Cp) and covellite (Cv). (**a**) Pyrite (Py), Cp, and Cv monomers; (**b**) Cp monomer and Cv–Cp synbiont; (**c**) Cp–gangue (Ga) intergrowth; (**d**) Cv–Cp–Py intergrowth.

Table 4. Relationship between dissociation degree and particle size of valuable minerals.

Target Minerals	Particle Size/mm	Liberation Degree/%					
		[0–20)	[20–40)	[40–60)	[60–80)	[80–100)	100
Chalcopyrite	0.0037–0.0795	44.62	32.57	10.12	3.6	0.72	8.37
Cubanite	0.0026–0.1036	32.9	29.9	12.37	15.24	3.12	6.47
Digenite	0.0079–0.0118	13.62	37.91	48.47	0	0	0
Covellite	0.0059–0.0950	8.83	35.35	37.91	0	0	17.9
Bornite	0.0051–0.0408	82.16	17.84	0	0	0	0
Tetrahedrite	0.0053–0.0447	54.57	5.78	4.82	11.46	0	23.37
Pyrite	0.0026–0.3015	2.19	7.1	17.25	30.77	24.89	17.8

According to the process mineralogy results, the pyrite in the ore had a good degree of single grain liberation, implying that it may have excellent floatability, which increases the difficulty of its flotation separation from copper sulfide minerals. Therefore, it was necessary to focus on the depression of pyrite in the flotation experiments, and consider a depressant to decrease the pyrite floatability or reduce the collector dosage to enhance flotation selectivity.

3.2. Flotation Experiments

3.2.1. Effect of Grinding Fineness

The appropriate fineness of the grind is a prerequisite for ensuring the effective recovery of valuable minerals in a flotation process. The valuable minerals should be liberated to single phases and have an appropriate particle size. If the ore particles are too coarse, they will not float, even if the mineral particles are liberated, because their weight will exceed the floating capacity of the bubbles [33]. The effect of grinding fineness on the flotation index of copper sulfide ore is shown in Figure 5. The tests were carried out by choosing the −0.074 mm particle size content to account for 65%, 70%, 75%, 80%, and 85% of the ore mass. The flow chart is shown in Figure 5a. Lime (1000 g/t) was used as a pH regulator and depressant to adjust the pH value of the pulp and depress pyrite flotation, while butyl xanthate (50 g/t) and ammonium dibutyl dithiophosphate (20 g/t) were used as collectors for the copper sulfide minerals, and terpenic oil (84 g/t) was used as a frother. The results are shown in Figure 5b. As the −0.074 mm particle size content increased from 65% to 85%, the grade of the copper concentrate trended downward; copper recovery showed a trend of rising, falling, and then rising again, but the overall change was not significant. When the −0.074 mm particle size content was 70%, the grade and recovery of the copper concentrate were relatively ideal; for finer particles, the copper grade would be significantly reduced and the grinding cost would increase. Therefore, the optimal grinding fineness was selected to be −0.074 mm particle size content, accounting for 70% of the flotation feed.

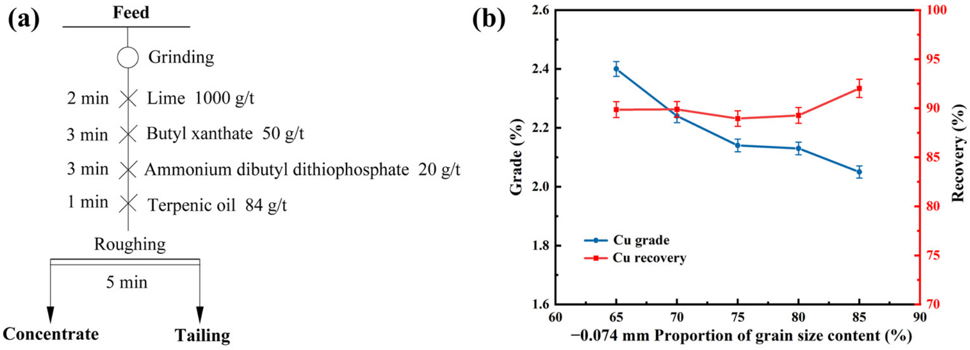

Figure 5. (**a**) Flow chart of grinding fineness tests and (**b**) flotation results.

3.2.2. Effect of Reagent Dosage and Type

The effect of reagent dosage on the flotation index is shown in Figure 6. A lime dosage test was first carried out under conditions of 70% of the feed passing the 0.074 mm particle size, 50 g/t butyl xanthate, 20 g/t ammonium dibutyl dithiophosphate, and 84 g/t terpenic oil. As shown in Figure 6a, when the lime dosage was insufficient, the copper grade in the rougher concentrate was low. With an increase in lime, the grade first increased and then decreased; copper recovery showed the opposite trend. The optimum grade (2.08%) and recovery (90.42%) of the rougher were achieved at a lime dosage of 1500 g/t (pH = 11.33). The lime dosage was fixed at 1500 g/t for subsequent experiments.

The collector performances of ethyl xanthate, butyl xanthate, and ammonium dibutyl dithiophosphate on copper sulfide minerals were investigated using a feed containing 70% passing 0.074 mm, a lime dosage of 1500 g/t, and a terpenic oil dosage of 84 g/t. The effects of different types of collectors on the flotation index are shown in Figure 6b–d. The comparison of Figure 6b,c shows that the copper recovery in the rougher concentrate was significantly higher when using butyl xanthate as the collector than when using ethyl xanthate at the same dosage. Figure 6d shows that with an increase in the dosage of ammonium dibutyl dithiophosphate, the copper grade and recovery in the rougher concentrate first decreased, then increased, and then decreased. At 40 g/t ammonium dibutyl dithiophosphate, the copper grade was relatively high, but recovery was low. Relatively high copper grade and recovery in the rougher concentrate were achieved with 10 g/t ammonium dibutyl dithiophosphate. This reagent is usually used to recover associated precious metals in the flotation of sulfide ore, so was selected as the collector for gold and silver.

The depression effects of lime in combination with hydrogen peroxide or sodium sulfite on the pyrite flotation were investigated (Figure 7). Tests were carried out using a particle size of 70% passing 0.074 mm, 1500 g/t lime, 10 g/t butyl xanthate, and 84 g/t terpenic oil. As shown in Figure 7a, as the hydrogen peroxide dosage increased, the copper grade in the rougher concentrate first increased and then decreased; the opposite trend was observed with respect to copper recovery. Optimum grade and recovery were achieved using 400 g/t hydrogen peroxide—2.48% and 89.68%, respectively. As shown in Figure 7b, as the sodium sulfite dosage increased, the copper grade first increased and then decreased; recoveries were relatively stable. When the dosage of sodium sulfite was 500 g/t, the copper grade and recovery were 2.16% and 89.51%. These results demonstrate that better flotation was achieved using the combination of lime and hydrogen peroxide for the depression of pyrite. This method was therefore selected for subsequent experiments, at the optimal hydrogen peroxide dosage of 400 g/t.

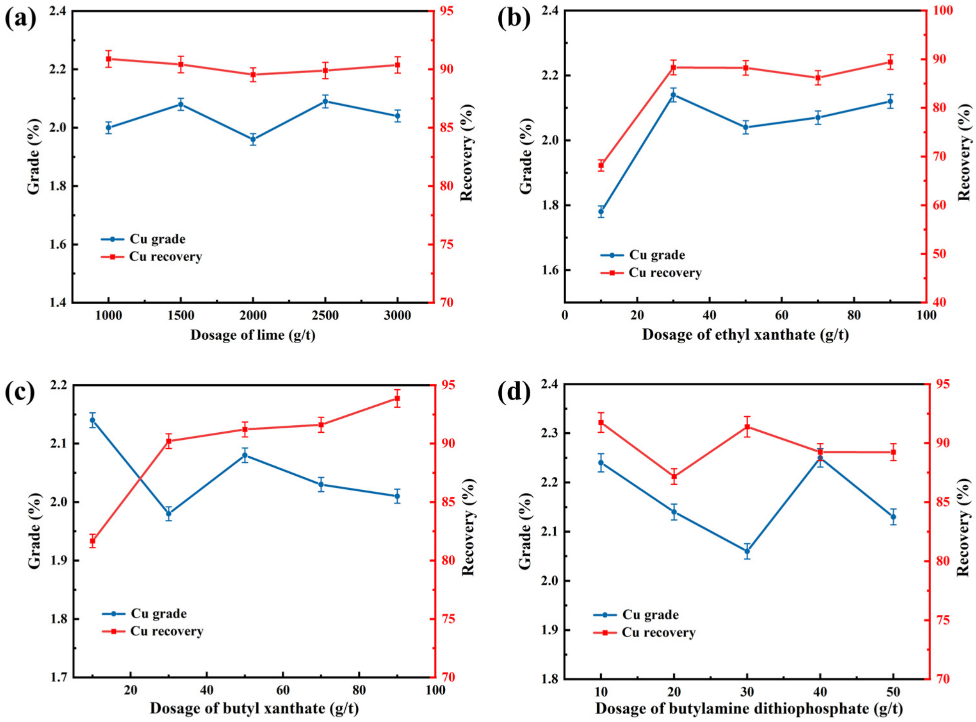

Figure 6. Effects of dosages of different reagents on the flotation index. (**a**) Lime; (**b**) ethyl xanthate; (**c**) butyl xanthate; (**d**) butylamine dithiophosphate.

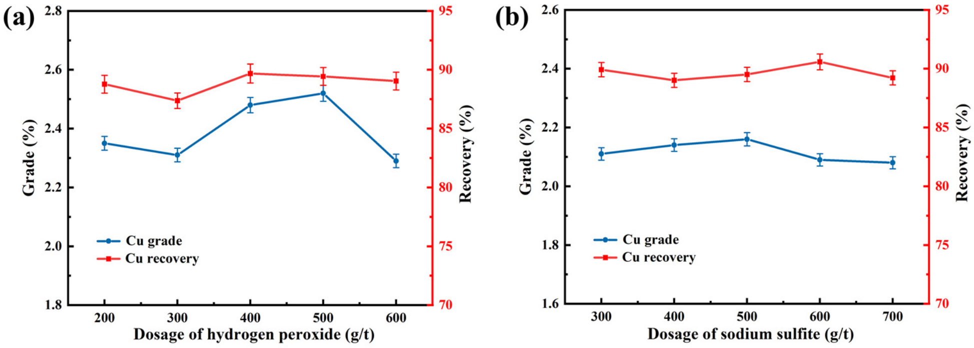

Figure 7. Effects of type and dosage of different depressants on the flotation index. (**a**) Hydrogen peroxide; (**b**) sodium sulfite.

3.2.3. Application of Combined Collectors

The combined collectors co-adsorb on the mineral surface through synergistic effects. In addition, different collectors exhibit different selectivity and collectivity; mixing collectors with strong selectivity and strong collectivity in a certain proportion can establish complementary functions [34,35]. Ammonium dibutyl dithiophosphate (ADD) has good selectivity, and can effectively collect chalcopyrite and precious metals such as gold and silver, but its ability to collect pyrite is relatively weak. However, butyl xanthate (BX) has a strong collection ability but weak selectivity under high alkaline conditions, while ethyl xanthate (EX) is the opposite [36–38]. The application of combined collectors in the flotation of copper sulfide ore was then studied, with the aim of improving the flotation index and reducing reagent dosage. The effects of different collector ratios in the combined collectors on the rougher copper concentrate are shown in Figure 8. The particle size comprised

70% passing 0.074 mm, the dosages of lime and hydrogen peroxide were 1500 g/t and 400 g/t, respectively, and the dosage of terpenic oil was 84 g/t. As shown in Figure 8a, when butyl xanthate, ammonium dibutyl dithiophosphate, and ethyl xanthate were used in a mass ratio of 1:0.5:0.5, the copper grade in the rougher concentrate was relatively low; however, a ratio of 0.5:1:0.5 gave a relatively high grade (Figure 8b). In addition, compared with the results in Figure 7, the use of the combined collectors not only reduced the reagent dosage, but also significantly improved the flotation index, grade, and recovery of the copper concentrate, and achieved the efficient recovery of copper sulfide minerals using ultra-low-dosage conditions. This may be attributed to the combined use of three collectors; the strong collectivities of ADD and BX are synergistically adsorbed on the surface of the target mineral, while EX, with weaker collectability, enhances the synergistic effect among the various components, thus achieving the efficient recovery of copper and associated precious metals such as gold and silver. From these results, ammonium dibutyl dithiophosphate, butyl xanthate, and ethyl xanthate were selected as collectors in the mass combination of 1:0.5:0.5, at a combined optimal dosage of 10 g/t.

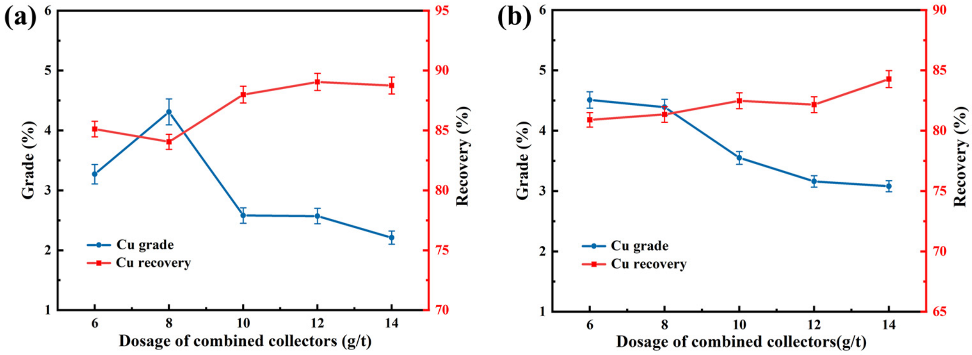

Figure 8. Effects of type and dosage of combined collectors on the flotation index. Butyl xanthate + ammonium dibutyl dithiophosphate + ethyl xanthate at ratios of (**a**) 1:0.5:0.5 and (**b**) 0.5:1:0.5.

3.2.4. Analysis of Depressant Dosage during Cleaning

To determine the effect of depressant dosage during cleaning on the flotation index, the lime and hydrogen peroxide additions were investigated. As shown in Figure 9a, when the dosage of hydrogen peroxide was fixed at 200 g/t, the copper grade in the cleaner concentrate first increased and then decreased as the lime dosage increased; recovery showed the opposite trend. Both the copper grade and recovery of the cleaner concentrate were relatively high when the lime dosage was 700 g/t, so this was selected as the optimal value. Figure 9b shows that when the lime dosage was fixed at 700 g/t, the copper grade in the cleaner concentrate first increased and then decreased as the hydrogen peroxide dosage increased; recovery first increased, then decreased, and then increased. The relatively ideal copper grade of the cleaner concentrate was achieved at 200 g/t hydrogen peroxide. This was selected as the optimum value, owing to the copper grade being assigned higher priority than the recovery.

3.2.5. Open-Circuit Flotation Experiment

To determine the optimal reagent system for an open-circuit test, flotation tests were carried out for different reagent systems (Figure S1–S4). For the rougher stage, the dosages of lime and hydrogen peroxide were fixed at 1500 g/t and 400 g/t, respectively; those of the combined collectors and terpineol oil were fixed at 10 g/t and 84 g/t, respectively. The first cleaner stage used 700 g/t lime and 200 g/t hydrogen peroxide. The results of the four open circuit processes are shown in Figure 10. Compared to the second cleaner stage without lime (Figure S1), the flotation effect of the second cleaner stage with 300 g/t lime was better. During scavenging, adding 4 g/t of combined collector for the first scavenger (Figure S2) and 2 g/t of combined collector for the second scavenger produced better flotation results than not adding the combined collector. However, the flotation effect was poor when adding 4 g/t of the combined collectors in the first cleaner stage (Figure S4). Therefore, the optimal flotation index was obtained by open-circuit process 3 (Figure S3), with a copper grade of 22.65% and recovery of 66.21%.

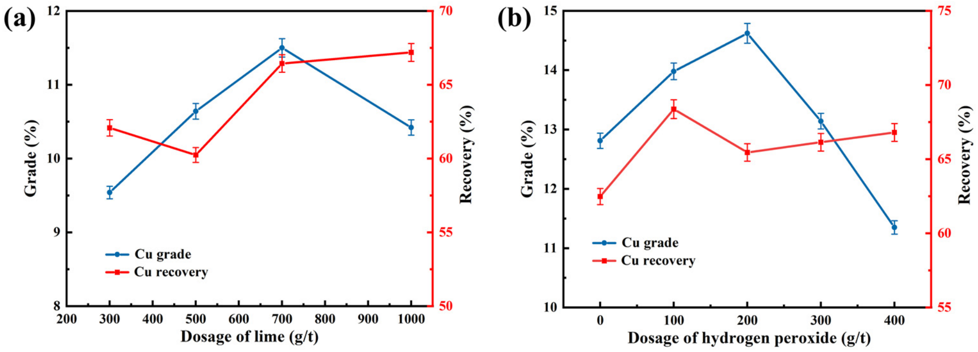

Figure 9. Effect of dosage of (**a**) lime and (**b**) hydrogen peroxide on the flotation index during cleaning.

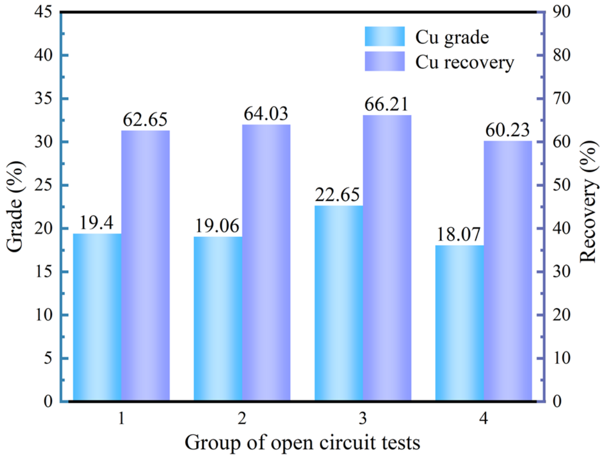

Figure 10. Flotation results of open-circuit tests according to the potential open-circuit flow charts.

3.2.6. Closed-Circuit Flotation Experiment

The experiments using a closed circuit adopted one rougher, two cleaner, and three scavenger stages. The middlings were returned in sequence. The flow chart and reagent system are shown in Figure 11 and the results are shown in Table 5. A flotation index of 20.08% copper grade and 87.73% copper recovery in the concentrate was obtained. The separation efficiency of flotation copper is 85.45%, indicating that this copper sulfide ore can be effectively recovered using this separation process. In addition, the grades of associated precious metals in the concentrate were 0.740 g/t Au and 42.90 g/t Ag, with respective recoveries of 9.22% and 26.66%, indicating that these metals were also recovered to a certain extent. Recoveries of Fe (7.27%) and S (8.86%) in the concentrate were both low, indicating that pyrite was effectively depressed by the combination of lime and hydrogen peroxide. The flotation separation of copper and sulfur minerals was achieved, and the quality of the copper concentrate was effectively improved.

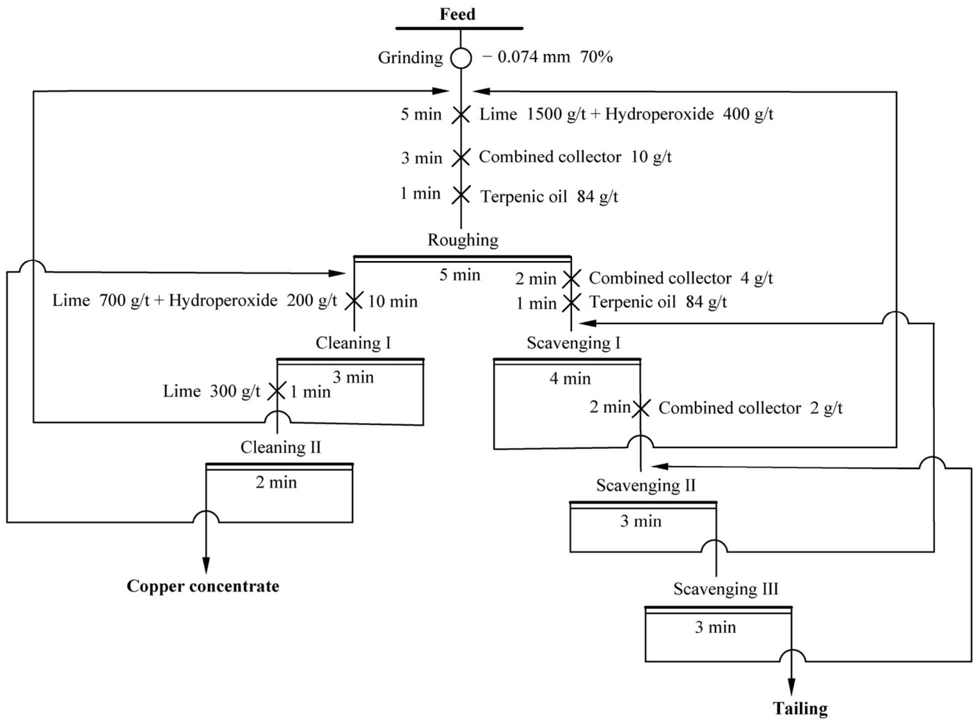

Figure 11. Flow chart of closed-circuit test.

Table 5. Results of closed-circuit flotation experiment.

Product	Yield/%	Grade/%					Recovery/%				
		Cu	Au *	Ag *	Fe	S	Cu	Au *	Ag *	Fe	S
Copper concentrate	2.84	20.08	0.740	42.90	29.50	35.00	87.73	9.22	26.66	7.27	8.86
Tailing	97.16	0.084	0.213	3.45	10.99	10.52	12.27	90.78	73.34	92.73	91.14
Raw ore	100	0.65	0.228	4.57	11.52	11.22	100	100	100	100	100

* Unit g/t.

4. Conclusions

This study conducted process mineralogical research on the copper sulfide ore. The test results reveal the effects of the types and amounts of combination inhibitors and combination collectors on flotation, leading to several specific conclusions, as follows:

1. Process mineralogy research indicates that the ore is a sulfide copper ore with high sulfur content ($\alpha = 11.64\%$). The symbiotic relationship of the target metal minerals is complex, and the degree of dissociation is poor. In the ore, the Cu content is 0.79%, and the associated precious metals' contents Au and Ag are 0.233 g/t and 5.83 g/t;
2. The combined inhibitor of lime and hydrogen peroxide (pH = 11.33) inhibited pyrite better than lime and sodium sulfite. This may be attributed to the Fenton reaction of hydrogen peroxide on the surface of pyrite, which promotes the formation of hydrophilic iron hydroxides and prevents the adsorption of collectors on the surface of pyrite;
3. Using the ADD-BX-EX (1:0.5:0.5) ternary collector resulted in better flotation performance compared to a single collector. This is attributed to the synergistic effects of ADD and BX, while EX, with weaker collectability, intensifies the synergistic effects between each component. Under the condition that the dosage of combined collector was only 10 g/t, the copper grade of the copper concentrate was 20.08% and the copper recovery was 87.73%. The associated metal grades of gold and silver were 0.740 g/t and 42.90 g/t, while the recoveries of gold and silver were 9.22% and 26.66%. Therefore, the present work achieved the recovery of copper sulfide flotation under

the condition of an ultra-low dosage of combined collector, which not only obtained better copper flotation indexes, but also reduced the dosage of reagents, and lowered the production costs.

In this study, certain limitations have been identified regarding the processing of ores containing pyrite, which inhibits the recovery of precious metals associated with it, such as gold and silver. However, the effective and comprehensive recovery of inhibited gold and silver can still be achieved when using sulfur concentrate. Nevertheless, targeting the flotation of gold and silver during copper flotation may lead to a reduction in copper concentrate grade. Therefore, it is crucial to strike a balance between maximizing the recovery of precious metals and maintaining high-grade copper concentrations in mineral processing operations.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min14101026/s1, Figure S1: Potential flow charts of open-circuit tests 1; Figure S2: Potential flow charts of open-circuit tests 2; Figure S3: Potential flow charts of open-circuit tests 3; Figure S4: Potential flow charts of open-circuit tests 4.

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