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Flotation optimization and sulfidation strategies for maximizing copper recovery from a complex mixed oxide-sulfide ore

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ABSTRACT

This study systematically examined the flotation optimization and sulfidation strategies for enhancing copper recovery from a complex mixed oxide-sulfide ore containing approximately 62% copper oxide and 38% copper sulfide. Comprehensive mineralogical characterization using XRD, SEM-EDS, and EPMA identified a silicate-rich gangue and delineated copper-bearing mineral phases. Laboratory flotation experiments investigated the influence of particle size, reagent type and dosage, pulp pH, and reagent addition sequence on copper recovery. Optimal conditions resulted in a copper oxide recovery of 76% at a particle size of 53 µm and pH 10.5, with total copper recovery reaching 81% through staged reagent addition. Sodium sulfide and sodium hydrosulfide proved effective as sulfidizing agents, with potassium amyl xanthate (PAX)—especially in combination with a co-collector—significantly improving performance. Distributing the sulfidizing agent between the grinding mill and flotation cell balanced the activation of oxide and sulfide minerals, maximizing overall recovery. These results highlight the importance of integrated mineralogical analysis and process parameter optimization for efficient beneficiation of complex copper oxide-sulfide ores, providing practical insights for developing robust flotation flowsheets for similar mineral systems.

Keywords: *Copper oxide-sulfide ore; Flotation; Sulfidation; Mineralogical characterization; Reagent optimization.*

1. Introduction

One of the separation methods for the upgradation of copper ores is flotation [1, 2]. In this process, the copper minerals can be separated from the gangue minerals through difference in the surface hydrophobicity [1, 2]. Given that xanthate adsorption occurs well on the surface of copper sulfide minerals (e.g. chalcopyrite, bornite, covellite, and chalcocite), the upgradation of copper sulfide ores is best accomplished through flotation [3-5]. The copper oxide ores tend to have the characteristics of strong surface hydrophilicity of copper oxide minerals, fine particle size, serious mud problems, and complex mineral composition [6-9]. Hence, copper oxide minerals (e.g. malachite, azurite, chrysocolla, brochantite) do not respond well to traditional sulfide copper collectors and require alternative flotation techniques such as sulfidation-flotation process to concentrate the copper oxides ores [6-9]. In the sulfidation-flotation technique initially the activation of copper oxide minerals is performed by a sulfiding agent and then the flotation of surface activated copper oxide minerals is done by xanthate collectors [10, 11].

The other kind of copper ores is mixed copper oxide-sulfide ores in which both of copper oxide minerals and copper sulfide minerals are present. The upgradation this kind of copper ore by sulfidation-flotation process is more difficult since any excess addition of sulfiding agent can act as a strong depressant agent for copper sulfide minerals and any insufficient addition of sulfiding agent will cause poor recoveries of copper oxide minerals.

Recent advancements in the sulfidation-flotation of mixed copper oxide-sulfide ores have focused on improving copper recovery through optimized reagent regimes and mineralogical integration. Cao et al. (2009) studied a mixed oxide-sulfide ore containing 1.19% copper, with 0.84% copper oxide and 0.35% copper sulfide. They obtained a concentrate containing 19.01% copper at a recovery of 35.02% using sodium sulfide and butyl xanthate flotation. Due to the low copper recovery, they suggested that the flotation tailings undergo acidic leaching [12]. Phetla and Muzenda (2010) studied flotation of a copper and cobalt oxide feed with a grade of 4%, recovering 48% of copper in a multi-stage sulfidation process at high temperature and long retention time [13]. Mechanochemical sulfidization via co-grinding with sulfur and additives was shown to improve flotation efficiency, highlighting the role of grind time and additive concentration [14]. Wang et al. (2022) reported that pretreatment with an appropriate concentration of copper ions improved malachite recovery, while excess copper ions reduced malachite surface hydrophobicity; zeta potential tests indicated sodium sulfide and butyl xanthate adsorbed on malachite pretreated with copper ions [15]. Sequential sulfidation strategies addressing slime interference enhanced copper grade and recovery while balancing depressant effects [16].

Oumesaoud et al. (2025) demonstrated enhanced flotation of oxidized copper ores by optimizing flotation parameters to accommodate complex mineral associations [17]. Wang et al. (2025) achieved a significant increase in copper oxide recovery from 40% to 91% by using a novel Pb2+/NH4+ activation method in slag flotation [18]. Sulfidation roasting-flotation processes have further underscored the importance of copper sulfide species stability for flotation

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performance [19]. Collectively, these findings indicate that controlling sulfidation conditions and integrating mineralogical insights are crucial for efficient beneficiation of complex copper oxide-sulfide ores. Recognizing the mineralogical characteristics and determining the optimum operating conditions for the flotation of mixed copper oxide-sulfide ores can significantly improve process efficiency. However, these aspects have not been adequately addressed in previous studies and are the primary focus of this research. Therefore, a representative copper oxide-sulfide ore from northeastern Iran was systematically characterized using X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), and electron probe microanalysis (EPMA). Subsequently, a series of laboratory flotation experiments were conducted to investigate the effects of key process parameters—including particle size, reagent type and dosage, pulp pH, and the sequence and reagent addition point—on the flotation performance of copper oxide and sulfide minerals in an integrated manner. The findings provide new insights into the interplay between mineralogical properties and flotation behavior in complex copper ores, offering practical guidance for designing efficient beneficiation flowsheets for mixed copper systems.

2. Materials and methods

2.1. Sampling and sample preparation

The ore extracted from a copper mine in northeastern Iran, with a particle size of less than 30 cm, is transported via truck to the feed stockpile of the flotation processing plant. Primary crushing is performed using a jaw crusher. The crushed ore is then screened through a double-deck vibrating screen with openings of 25 mm and 10 mm. Particles passing through the finer screen (10 mm opening) are conveyed to the milling circuit via a conveyor belt. Samples weighing 0.5 kg (particle size <10 mm) were collected from this conveyor belt over several consecutive days at one-hour intervals. The collected samples, totaling approximately 400 kg, were mixed, dried, homogenized, and subdivided into 350 g sub-samples using a riffle splitter. Each sub-sample was ground in a laboratory ball mill at 65% solids, with grinding times of 3, 5, 6.5, 10, 15, and 20 minutes.

2.2. Flotation experiment

2.2.1. Material and reagents

Potassium amyl xanthate (PAX) (C6H11KOS2) with trade name of Z6 and sodium isopropyl xanthate (SIPX)(C4H7NaOS2) with trade name of Z11 were used as collectors. Methyl isobutyl carbinol (MIBC) (C6H14O) was used as frother. The pH adjustment was performed by quicklime (CaO). The sodium sulfide (Na2S) and sodium hydrosulfide (NaHS) were used as activator of copper oxide minerals.

2.2.2. Analysis methods

The mineralogical composition of the sample was identified using an X-ray diffraction analyzer (PHILIPS Xpert pro, Netherlands).

X-ray fluorescence (XRF Philips PW1410, Netherlands) analysis was employed for chemical composition determination in this study, recognizing the known limitations of XRF for accurately detecting light elements such as Na, K, Al, and Si. To validate the accuracy of the XRF results, matrix-matched synthetic calibration standards and optimized sample preparation techniques were utilized. Specifically, samples and standards were fused into homogeneous glass beads using a borate flux fusion method, which effectively minimizes matrix effects, particle size variations, and mineralogical interferences. This fusion technique ensures uniform excitation conditions and improves measurement precision and accuracy for both major and minor oxides. The calibration curves were developed using high-purity synthetic standards covering the concentration ranges relevant to the ore samples. Calibration quality was confirmed by excellent linearity (correlation coefficients $r^2>0.999$) and low detection limits. Additionally, precision and accuracy were verified through replicate measurements, with precision parameters meeting recognized validation criteria. These measures establish confidence in the XRF data despite the inherent challenges with light elements, making XRF a reliable tool for mineral chemical characterization in this context.

The total copper content in the samples was measured by leaching with aqua regia, followed by copper concentration analysis in the leachate using a Varian SpectrAA 880Z Atomic Absorption Spectrometer (Australia). To determine the copper oxide grade, the samples were leached with sulfuric acid solution, and the resulting copper concentration in the solution was measured with the same atomic absorption spectrometer.

Scanning electron microscope (SEM) imaging was performed using a LEO 1450 UP (Zeiss, Oberkochen, Germany) in backscattered electron (BSE) mode. BSE images are highly sensitive to differences in atomic number, with materials of higher atomic number appearing brighter in the images.

The SEM system consists of a Leo 1450VP scanning electron microscope equipped with an Oxford Instruments X-Act 10 mm² area Energy Dispersive Spectrometer (EDS), operated using the AZtec Energy software. EDS analysis was conducted on selected points within the SEM images to determine elemental composition from the EDX spectra. In addition to EDS, quantitative chemical analysis of very fine, focused areas (less than 1 μm) on polished sample surfaces was performed using an Electron Probe Micro Analyser (EPMA, SX100, Cameca, France) at the Mineral Processing Research Center. The EPMA was used to obtain accurate compositional measurements for individual mineral grains and inclusion phases, complementing the EDS results and ensuring precise mineral identification.

2.2.3. Flotation test procedure

Flotation experiments were conducted in a 1 liter laboratory flotation cell. A pulp consisting of 350 g of solids at 30% solids content was transferred into the cell. Lime was added to adjust the pulp pH to the target value. After lime addition, one minute was allowed for pH stabilization. The activator was then introduced and conditioned for 5 minutes, followed by the addition of the collector, with stirring continued for another 2 minutes. Finally, 35 g/t of frother was added, and after one minute, the air valve was opened to initiate frothing for 4 minutes. The resulting concentrate (froth phase) and tailings were dried at 85 °C, pulverized, and analyzed for total copper and copper oxide content.

2.2.4. The effect of process parameters on the flotation of copper oxide-sulfide

The influence of collector and activator types, pulp pH, and feed particle size on the flotation performance of copper oxide-sulfide ore was examined. Additionally, the impact of the addition point and distribution of lime and activator-whether introduced into the mill or directly into the flotation cell-was evaluated. The experiments were designed following the One Factor at a Time (OFAT) approach. The test conditions are summarized in Table 1.

3. Result and discussion

3.1. Characterization of the copper oxide-sulfide ore

Table 2 presents the chemical composition of the copper oxide-sulfide ore sample as determined by X-ray fluorescence (XRF) analysis. The copper content of the sample is 0.65%, indicating a low- to medium-grade ore [1]. Silicon dioxide (SiO_2) constitutes 51.75% of the sample, making it the predominant component. Calcium oxide (CaO) is present at 4.15%. The high proportion of SiO_2, together with the presence of other oxides such as CaO, K_2O, and Al_2O_3, suggests that the main gangue minerals in the ore are silicate-based, primarily feldspars, quartz, and clay minerals. This interpretation is supported by the XRD results, which identified sanidine, albite, quartz, smectite, and chlorite as the dominant mineral phases. The prevalence of silicate gangue is characteristic of many copper ores and has important implications for mineral processing, as silicate minerals can affect grinding behavior, reagent consumption, and flotation selectivity [2, 6].

Table 1. Experimental design framework showing the actual parameter levels.

Process parameters	**PAX (Z6) (g/t)**	**SIPX (Z11) (g/t)**	**NaHS (g/t)**	**Na_2S (g/t)**	**pH**	**Lime addition point**	**d_{80} (μ)**	**Time (min.)**
Collector dosage	50	0	1000 (in cell)	0	10.5	In cell	90	10
	100	0	1000 (in cell)	0	10.5	In cell	90	10
	150	0	1000 (in cell)	0	10.5	In cell	90	10
	200	0	1000 (in cell)	0	10.5	In cell	90	10
Co-collector dosage	50	20	1000 (in cell)	0	10.5	In cell	90	10
	50	40	1000 (in cell)	0	10.5	In cell	90	10
	50	60	1000 (in cell)	0	10.5	In cell	90	10
	50	80	1000 (in cell)	0	10.5	In cell	90	10
pH	100	0	1000 (in cell)	0	9	In cell	90	10
	100	0	1000 (in cell)	0	10.5	In cell	90	10
	100	0	1000 (in cell)	0	12	In cell	90	10
Hydrosulfide sodium dosage as activator	100	0	250 (in cell)	0	10.5	In cell	90	10
	100	0	500 (in cell)	0	10.5	In cell	90	10
	100	0	1000 (in cell)	0	10.5	In cell	90	10
	100	0	1500 (in cell)	0	10.5	In cell	90	10
Sodium sulfide dosage as activator	100	0	0	250	10.5	In cell	90	10
	100	0	0	500	10.5	In cell	90	10
	100	0	0	1000	10.5	In cell	90	10
	100	0	0	1500	10.5	In cell	90	10
Multistep flotation 1step	100	0	1000 (in cell)	0	10.5	In cell	90	10
2steps	50	0	0	0	10.5	In cell	90	10
	50	0	1000 (in cell)	0	10.5	In cell	90	10
Feed particle size	100	0	1000 (in cell)	0	10.5	In cell	300	5
	100	0	1000 (in cell)	0	10.5	In cell	150	7.5
	100	0	1000 (in cell)	0	10.5	In cell	90	10
	100	0	1000 (in cell)	0	10.5	In cell	65	20
activator/lime addition point	100	0	1000 (in mill)	0	10.5	In mill	90	10
	100	0	1000 (in cell)	0	10.5	In mill	90	10
	100	0	1000 (in mill)	0	10.5	In cell	90	10
	100	0	1000 (in cell)	0	10.5	In cell	90	10
activator addition point and its dosage scheme	100	0	1000 (in mill)	0	10.5	In mill	90	10
	100	0	750 (in mill) + 250 (in cell)	0	10.5	In mill	90	10
	100	0	500 (in mill) + 500 (in cell)	0	10.5	In mill	90	10
	100	0	250 (in mill) + 750 (in cell)	0	10.5	In mill	90	10
	100	0	1000 (in cell)	0	10.5	In mill	90	10

Table 2. The chemical composition of the copper oxide/sulfide ore by XRF analysis.

Element	**SiO_2**	**BaO**	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**MnO**	**P_2O_5**
Unit	%	%	%	%	%	%	%	%
Content	51.75	<	4.15	6.55	5.28	3.34	0.11	0.72
Element	SO_3	TiO_2	Cr_2O_3	Cu	Pb	Zn	Sr	LOI
Unit	%	%	%	%	%	%	%	%
content	0.79	0.76	<	0.65	0.06	<	<	4.06

Figure 1 presents the mineralogical composition of the copper oxide-sulfide ore as determined by X-ray diffraction (XRD) analysis. The dominant mineral phase identified is sanidine ($(Na,K)(Si_3Al)O_8$), accompanied by minor phases including albite ($(Na,Ca)(Si,Al)_4O_8$), quartz (SiO_2), smectite ($Ca_{0\cdot 2}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}xH_2O$), chlorite ($(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$), hematite (Fe2O3), and vermiculite (Mg, Al)3(Si, Al)4O10(OH)2.4H2O. These results indicate that the primary gangue minerals in the ore are silicates, which is consistent with the typical mineralogy of many copper deposits, where feldspars, quartz, and phyllosilicates constitute the main gangue matrix [9-12].

Copper-bearing minerals were not detected by XRD, likely due to their concentration being below the detection limit of the instrument, which is generally around 1–2 wt%. Copper minerals in such ores often occur as finely disseminated or minor phases, producing diffraction peaks too weak to be distinguished from the dominant gangue mineral signals. This limitation is well recognized in mineralogical studies, where complementary techniques such as scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) or laser-induced breakdown spectroscopy (LIBS) are employed to identify and quantify minor copper phases not visible by XRD.

Figure 2 shows an SEM image of the sample captured in backscattered electron (BSE) mode. In BSE imaging, contrast arises primarily from differences in the average atomic number (Z) of the mineral phases: regions with higher average atomic numbers appear brighter, while those with lower atomic numbers appear darker [2, 20]. In SEM image of Figure2, mineral phases with distinct brightness can be readily distinguished: brighter regions correspond to phases with higher average atomic number and higher specific gravity—most likely metallic minerals, especially copper-bearing sulfides—while darker regions represent gangue minerals with lower atomic number and density. Notably, the SEM image demonstrates that many bright (metallic) mineral grains are intimately locked within or intergrown with the darker (gangue) phases, highlighting the association of valuable copper minerals with non-valuable host rock. This observation underscores the necessity for appropriate comminution to achieve sufficient liberation of the metallic minerals from the gangue, thereby optimizing flotation performance and downstream beneficiation.

To determine the chemical composition of the observed phases with different brightness in the SEM image, energy-dispersive X-ray spectroscopy (EDS) was performed at the marked points. EDS analysis yields both qualitative and semi-quantitative elemental data, enabling accurate phase identification when used in conjunction with BSE imaging. Based on the EDS spectra (Figure 2, EDS 1-4), the mineral phases at spots 1 through 4 were identified as chalcopyrite, ilmenite, sanidine, and albite, respectively.

To accurately identify the mineral phases observed in the SEM images, an Electron Probe Micro Analyzer (EPMA) was employed. EPMA is a powerful microanalytical technique that determines the chemical composition of solid materials at the micrometer scale by directing a focused electron beam onto a polished sample surface [21-23]. Based on the chemical compositions obtained from EPMA analysis, the mineral phases at marked locations in the SEM images (Figure 3) were identified and labeled with standard abbreviations. The primary copper sulfide minerals in the ore were determined to be bornite, chalcocite, and chalcopyrite. Among the copper oxide minerals, malachite was found to be the most abundant, accompanied by azurite and atacamite. Figure 4a presents the grades of copper oxide, copper sulfide, and total copper across 14 representative samples. The copper oxide grade ranges from 0.401% to 0.478%, with an average of 0.442% (variance: 0.000652; standard deviation: 0.025531). Copper sulfide grades vary between 0.234% and 0.316%, averaging 0.275% (variance: 0.000526; standard deviation: 0.022931).

The total copper grade ranges from 0.649% to 0.779%, with an average of 0.716% (variance: 0.001455; standard deviation: 0.03815). Figure 4b illustrates the proportion of copper present as oxide in the samples, which ranges from 58.55% to 64.78%, with a mean value of 61.67% (variance: 4.51; standard deviation: 2.12). These results indicate that the ore is a mixed copper oxide-sulfide type, with approximately 61.67% of the copper content occurring as copper oxide and the remaining 38.33% as copper sulfide.

The classification of this ore as a mixed oxide-sulfide type is supported by the high proportion of copper present as oxides, which typically results from the weathering and supergene enrichment of primary copper sulfide minerals [24, 25]. Mixed copper ores are common in copper deposits, where the upper portions of the deposit are oxidized, producing a significant amount of copper oxide minerals such as malachite, azurite, and chrysocolla, while the lower zones retain primary sulfide minerals like chalcopyrite, bornite, and chalcocite [24, 25].

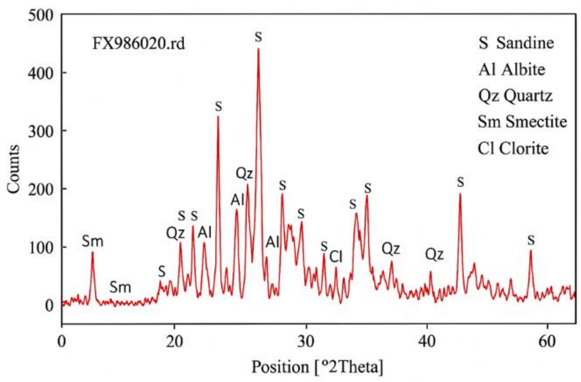

Figure 1. Mineralogical composition of the copper oxide/sulfide ore by the XRD analysis.

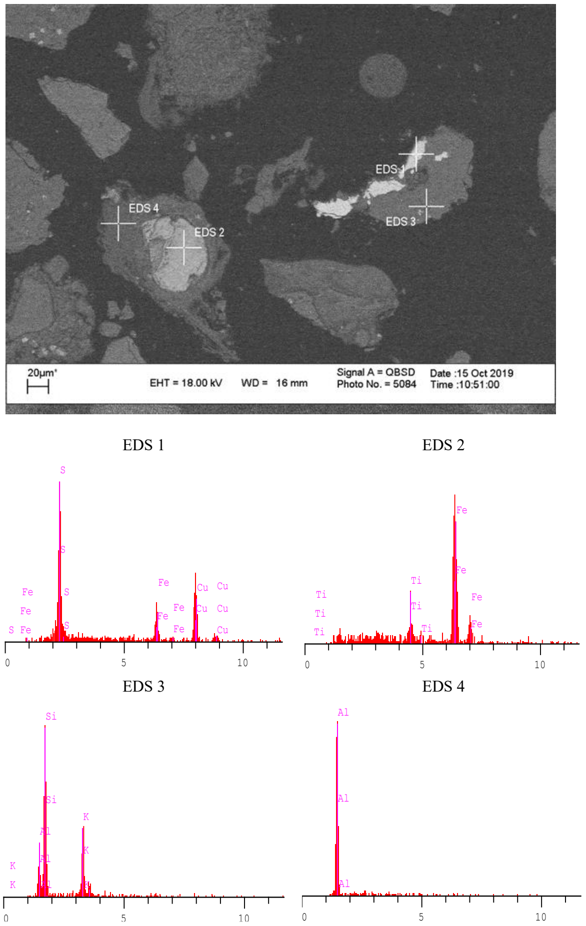

Figure 2. The SEM images of the sample at the BSE imaging mode. The chemical composition of the phases in the SEM images (the marked spots) was determined by energy dispersive X-ray analysis (EDS).

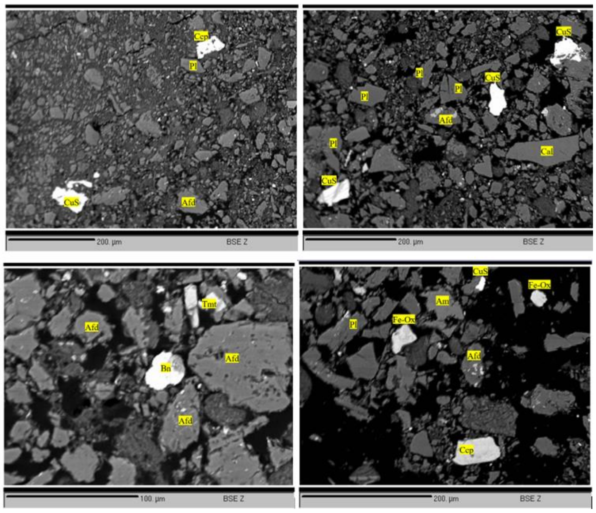

Figure 3. SEM images of the sample captured in backscattered electron (BSE) mode. The chemical composition of the phases observed in the SEM images was determined using an Electron Probe Micro Analyzer (EPMA). The identified mineral phases are indicated in the images by their abbreviations as follows: Ccp – Chalcopyrite; CuS – Copper-bearing minerals such as chalcocite; Bn – Bornite; Tmt – Titanomagnetite; Pl – Plagioclase; Fe-Ox – Iron oxide; Cal – Calcite; Afd – Alkali feldspar.

The mineralogical complexity of such ores has direct implications for processing: copper oxides are typically amenable to hydrometallurgical extraction (acid leaching), while copper sulfides require flotation and pyrometallurgical treatment [25]. Accurate determination of the oxide-to-sulfide ratio is therefore essential for selecting and optimizing the beneficiation route, as well as for predicting metallurgical performance and recovery [24, 25].

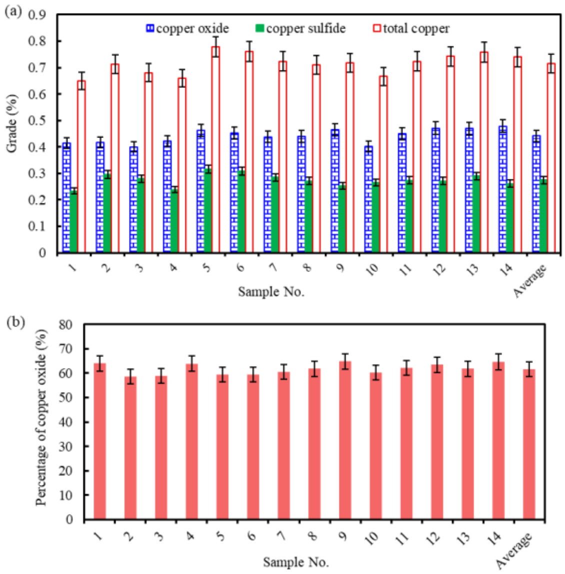

Figure 4. a. The grade of copper oxide, copper sulfide and total copper for 14 samples, b. The percentage of copper oxide in 14 samples.

3.2. *Effect of process parameters on flotation performance*

3.2.1. *Influence of feed particle size on flotation efficiency*

Feed particle size plays a crucial role in flotation performance, with optimal results typically achieved when the liberation of valuable minerals is maximized. To evaluate the impact of feed particle size, 350 g samples were ground for varying durations (3, 5, 6.5, 10, 15, and 20 minutes), after which the particle size distribution was measured. Figure 5 illustrates the particle size distribution curves of the ground samples. The d80 values corresponding to milling times of 3, 5, 6.5, 10, 15, and 20 minutes were found to be 500, 300, 195, 90, 65, and 53 µm, respectively.

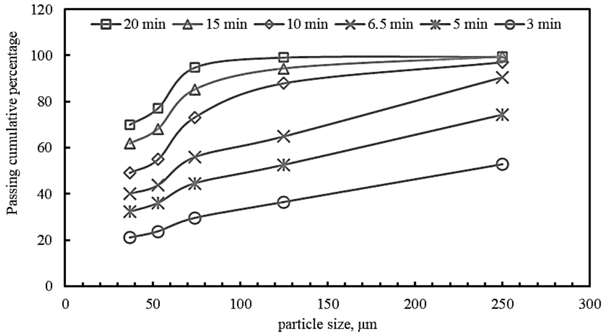

Figure 5. Effect of grinding time on the particle size distribution of the mill product

To assess the impact of feed particle size on copper oxide-sulfide recovery, batch flotation tests were conducted with samples having d80 values of 65, 90, 150, and 300 µm under standardized conditions (PAX collector at 100 g/t, 30% solids concentration, NaHS activator at 1000 g/t, pulp pH 10.5). Figure 6 illustrates the effect of feed particle size (d80) on flotation recovery.

The recovery of copper sulfide increases significantly as particle size decreases, reaching a maximum of 89.83% at an F80 of 90 µm, after which it declines. This initial increase is attributed to enhanced liberation of copper sulfide minerals facilitating better detachment and attachment to bubbles. However, further size reduction to 53 µm leads to diminished recovery due to slime coating—where ultrafine particles create a hydrophilic layer on mineral surfaces, inhibiting bubble-particle adhesion and reducing flotation efficiency. Slime coating, combined with increased surface hydrophilicity, blocks collector adsorption sites, thereby hindering effective mineral separation.

For copper oxide minerals, a slight recovery increase occurs when F80 decreases from 300 to 150 µm, primarily due to improved liberation. Further grinding to 53 µm produces a substantial rise in recovery from 33.4% to 67%, reflecting enhanced liberation that outweighs slime coating effects. However, at very fine sizes, copper oxide recovery may plateau or drop because of poor bubble attachment and altered surface chemistry affecting collector uptake.

The observed divergence in the recovery trends of copper sulfide and copper oxide minerals with decreasing particle size, particularly from 90 µm to 53 µm, can be attributed to differences in their liberation behaviours and the effect of slime coating. Copper oxide minerals tend to achieve adequate liberation at smaller particle sizes compared to copper sulfide minerals. Therefore, the increase in copper oxide recovery below 53 µm is mainly due to enhanced mineral liberation enabling better detachment and flotation. Conversely, copper sulfide recovery reaches an optimum around 90 µm, where adequate liberation and favourable flotation conditions exist. Further reduction in particle size below this threshold increases slime generation and the associated slime coating phenomenon, which predominantly affects sulfide minerals by forming a hydrophilic barrier that hinders bubble-particle attachment, leading to decreased recovery. Hence, copper oxide minerals thus show improved recovery with finer grinding due to their finer liberation size, while copper sulfide minerals suffer from slime interference at ultrafine sizes, explaining the contrasting recovery patterns observed.

Overall, flotation efficiency balances between liberation improvements (increasing surface area and mineral exposure) and adverse effects of slime coating and hydrophilicity at ultrafine sizes. The liberation rate, which determines the availability of discrete mineral particles, alongside surface chemical characteristics, governs these trends. Optimizing particle size within this interplay maximizes flotation recovery for mixed copper oxide-sulfide ores.

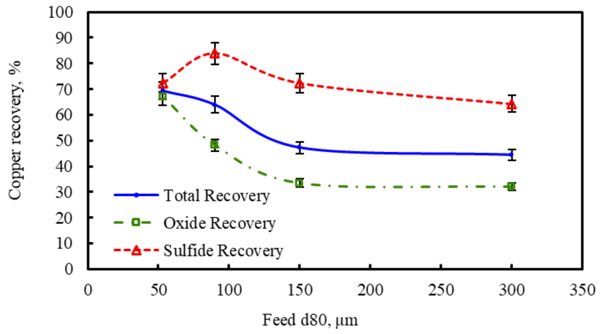

Figure 6. The effect of feed particle size on the recovery of copper oxide, copper sulfide and total copper (PAX as collector at dosage of 100 g/t; solid percent of 30%, NaHS as activator at dosage of 1000 g/t, pH of 10.5).

3.2.2. *Effect of pH on copper recovery in the flotation process*

Figure 7 illustrates the influence of solution pH on flotation recovery. As observed, the recoveries of copper oxide and copper sulfide increase with rising pH, reaching a peak at pH 10.5. This suggests that the flotation conditions become more favourable for the recovery of both mineral types as the environment becomes more alkaline up to this point. This improvement is likely due to enhanced sulfidation of copper oxide minerals and optimal surface chemistry for copper sulfide minerals, which promotes better interaction with the collector [29, 30]. After pH 10.5, the recovery of copper sulfide and total copper begins to decrease. This decline may be attributed to the excessive alkalinity, which can lead to the depression of copper sulfide minerals, possibly due to changes in surface charge or the formation of unwanted surface species that hinder collector adsorption [29-31]. A review on chalcopyrite flotation also notes that at high pH (>9), the formation of iron hydroxides on mineral surfaces renders them hydrophilic, resulting in decreased flotation rates for copper sulfide minerals [29-31].

Interestingly, copper oxide recovery continues to rise even as the recovery of copper sulfide and total copper drops. This suggests that higher pH levels further enhance the sulfidation process for copper oxide minerals, making them more amenable to flotation [29-31]. However, this benefit for copper oxide does not extend to copper sulfide minerals, which become less floatable at higher pH values. Salajegheh et al. (2022), studying the Sarcheshmeh copper flotation circuit, showed that copper recovery increases as pH decreases from 12 to 11.5, with the optimal recovery observed around pH 10–11.7 [29]. Beyond this range, recovery declines, likely due to the formation of hydrophilic metal hydroxides at higher pH, which depress flotation [29-31]. Their data confirm that copper recovery is maximized at a moderately alkaline pH, and excessive alkalinity is detrimental to overall recovery.

3.2.3. Effect of collector dosage on copper recovery in the flotation process

To evaluate the impact of collector dosage on the recovery of copper oxide, copper sulfide, and total copper, four dosages of PAX (50, 100, 150, and 200 g/t) were tested. The results are presented in Figure 8. Increasing the PAX dosage from 50 to 100 g/t led to improved recovery of both copper sulfide and copper oxide. However, further increasing the collector dosage to 150 g/t caused a decline in copper oxide recovery, while copper sulfide recovery continued to increase up to this point but decreased when the dosage exceeded 150 g/t. This behavior is explained by the formation of a hydrophobic layer of xanthate ions on the surface of copper sulfide minerals. Adding collector up to the point where the mineral surface is fully covered enhances flotation recovery. The reduction in copper recovery at higher xanthate collector dosages in flotation, despite the common attribution to micellization, especially for short-chain xanthates (C6 and below) where micellization is typically absent, can be explained by alternative mechanisms. The decrease in recovery at elevated collector concentrations may result from over-adsorption of the collector causing excessive hydrophobic aggregation of mineral particles. This aggregation increases particle mass, leading to inefficient attachment of mineral aggregates to air bubbles and thus their detachment and loss from the flotation stream. Additionally, increased collector concentration can enhance the formation of hydrophobic films and surface roughness that negatively impact bubble-particle detachment dynamics. These factors collectively reduce flotation efficiency beyond an optimal collector dose [32-34].

3.2.4. Effect of Co-collector dosage on the flotation process

Co-collectors are auxiliary reagents used alongside primary collectors to enhance the flotation performance by improving selectivity, flotation kinetics, and recovery rates. Different classes of co-collectors, such as thionocarbamates (e.g. SIPX) and dithiophosphates, exhibit varied adsorption behaviors on mineral surfaces, which influence their efficacy toward copper oxide and sulfide minerals.

SIPX was used as a co-collector at dosages of 0, 20, 40, 60, and 80 g/t alongside PAX as the primary collector at a constant dosage of 50 g/t to evaluate its impact on copper recovery. The results, shown in Figure 9, indicate that increasing the SIPX dosage improves the recovery of both copper oxide and copper sulfide when the PAX dosage remains constant. For example, with 50 g/t PAX (Z6) alone, the recoveries of copper oxide and copper sulfide were 31% and 71%, respectively. When 80 g/t SIPX (Z11) was added as a co-collector with 50 g/t PAX, the recoveries increased to 47% for copper oxide and 78% for copper sulfide. This indicates a synergistic effect between the two collectors, where the presence of SIPX enhances the overall collecting power and effectiveness of the flotation process.

The synergistic effect observed when using a co-collector like SIPX with a primary xanthate collector (PAX) is attributed to enhanced collector adsorption on both oxide and sulfide minerals, providing better surface coverage and improved hydrophobicity.

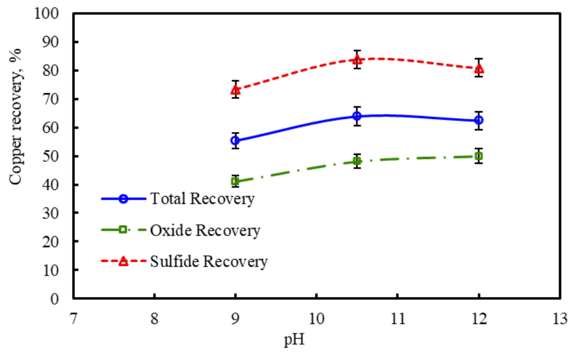

Figure 7. The effect of pulp pH on the recovery of copper oxide, copper sulfide and total copper (PAX as collector at dosage of 100 g/t; solid percent of 30%, NaHS as activator at dosage of 1000 g/t, feed d80 of 90 μm).

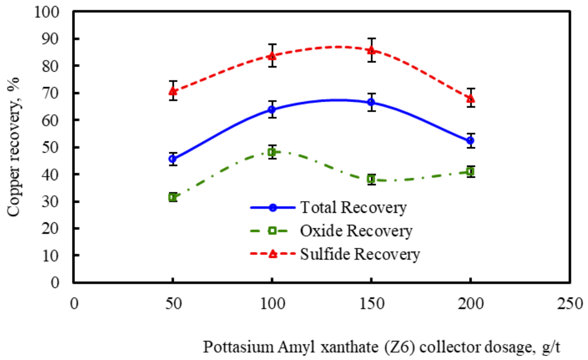

Figure 8. The effect of the dosage of PAX (Z6) as collector on the recovery of copper oxide, copper sulfide and total copper (solid percent of 30%, NaHS as activator at dosage of 1000 g/t, pH of 10.5, feed d80 of 90 μm).

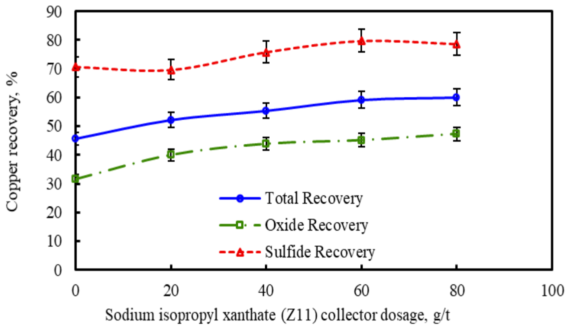

Figure 9. Effect of SIPX dosage as co-Collector on the recovery of copper oxide, copper sulfide, and total copper (Conditions: PAX collector at 50 g/t; solids concentration of 30%; NaHS activator at 1000 g/t; pH 10.5; feed particle size d80 of 90 μm).

This overcomes the limitations typically associated with single-collector systems, where selectivity or collector consumption may pose challenges. The comparative differences in co-collectors regarding their target minerals, adsorption behaviors, and effects on flotation performance are summarized in Table 3. As shown, thionocarbamates like SIPX tend to have stronger adsorption on copper oxides and improve overall flotation recovery, while other co-collectors such as dithiophosphates may act more specifically on sulfide minerals. The optimized use of such reagents not only enhances recovery and selectivity but also reduces collector consumption and improves flotation kinetics, resulting in higher concentrate grades [36-41].

3.2.5. Effect of collector type on the flotation performance

The impact of collector type on copper flotation recovery is clearly demonstrated in Figure 10. The results show that potassium amyl xanthate (PAX, straight-chain C5) consistently achieves higher recovery of copper sulfide minerals than sodium isopropyl xanthate (SIPX, branched C3 chain). This trend is attributed to the longer hydrocarbon chain and straight-chain structure of PAX, which confer greater hydrophobicity, stronger adsorption onto mineral surfaces, and more efficient bubble-particle attachment. According to Ackerman et al. (1987), collector chain length is a key factor in optimizing both recovery and rate for copper sulfide flotation, with PAX (C5) near the ideal range for minimum required dose and maximum flotation performance [42].

SIPX, although used widely in industry, exhibits lower recovery for copper sulfide minerals under the same conditions due to steric hindrance and lower reactivity associated with its shorter iso-alkyl chain. This reduces the effectiveness of hydrophobic film formation and bubble-particle interaction on mineral surfaces, especially compared to PAX [42-44].

For copper oxide minerals, Figure 10 shows a narrower difference between PAX and SIPX in recovery rates after sulfidation. Both collectors can adsorb and facilitate flotation of sulfidized oxide minerals, but PAX still gives maximum oxide recovery (48.12%) in the present experiments. This result is consistent with its higher collecting power and more robust surface adsorption, though after sulfidation, collector structure has a less pronounced effect than for sulfides [42-44].

It is also important to note, as illustrated in Figure 10, that excessive collector dosage can decrease overall copper recovery, regardless of type, due to over-adsorption, aggregation, and loss of efficient bubble-particle attachment at very high collector concentrations [32-34].

Table 3. Comparative characteristics and effects of common co-collectors in copper flotation processes.

Co-collector Type	Target Minerals	Adsorption Behavior	Effect on Recovery	Impact on Selectivity
Thionocarbamates (SIPX)	Copper oxides and sulfides	Strong adsorption on oxides	Increases oxide recovery	Enhances selectivity
Dithiophosphates	Mostly copper sulfides	Preferential sulfide adsorption	Improves sulfide recovery	Moderate selectivity
Xanthates (primary)	Sulfide copper minerals	General collector	Effective sulfide recovery	Standard selectivity

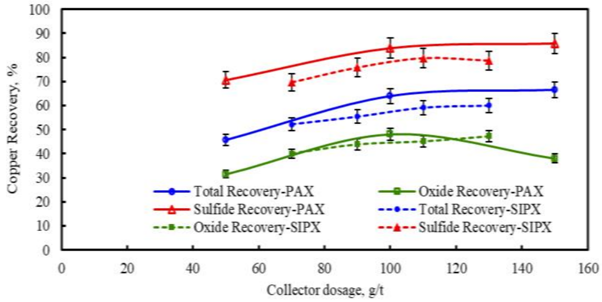

Figure 10. Effect of collector type on the recovery of copper oxide, copper sulfide, and total copper (conditions: solids concentration of 30%; NaHS activator at 1000 g/t; pH 10.5; feed particle size d80 of 90 μm).

3.2.6. One and Two-step flotation of the copper oxide-sulfide ore

A flotation test was conducted in two stages of frothing to separate copper sulfide and copper oxide minerals. In the first stage, 50 g/t of PAX was applied without any sulfiding agent to recover copper sulfide minerals. In the second step, 1000 g/t of sulfiding agent along with 50 g/t of PAX was added to recover copper oxide minerals. The copper recovery results from both stages are shown in Figure 11. In the first step of flotation, only 18% of copper sulfide was recovered, while copper oxide recovery was zero. This indicates that, under these conditions, xanthate (PAX) selectively floats copper sulfide minerals, but cannot recover copper oxide minerals, as xanthates do not adsorb onto their surfaces without prior modification. After adding a sulfidizing agent (1000 g/t) and PAX in the second step of flotation, copper sulfide recovery increased dramatically to 81.26%, and 43% of copper oxide was also recovered. The sharp increase in sulfide recovery suggests that some copper sulfide minerals were partially oxidized and not floatable in the first stage, but became floatable after sulfidation. The recovery of copper oxide minerals in this stage is due to the formation of a copper sulfide layer on their surfaces, enabling xanthate adsorption and flotation.

This staged approach is consistent with established flotation practice for mixed copper oxide-sulfide ores, where direct flotation with xanthate collectors efficiently recovers copper sulfide minerals, but copper oxide minerals require sulfidization prior to flotation [35-37]. Sulfidizing agents such as sodium sulfide or sodium hydrosulfide react with the surface of copper oxide minerals to form a thin layer of copper sulfide, which then allows xanthate collectors to adsorb and promote flotation [1, 35, 37]. Recent studies confirm that sulfidization-flotation is the most effective method for recovering copper from oxide minerals, and that the staged addition of sulfidizing agents and collectors can significantly improve overall copper recovery in complex ores [1, 35, 37]. The effectiveness of this method depends on factors such as reagent dosage, pH, and the degree of oxidation of the ore [1, 36, 37].

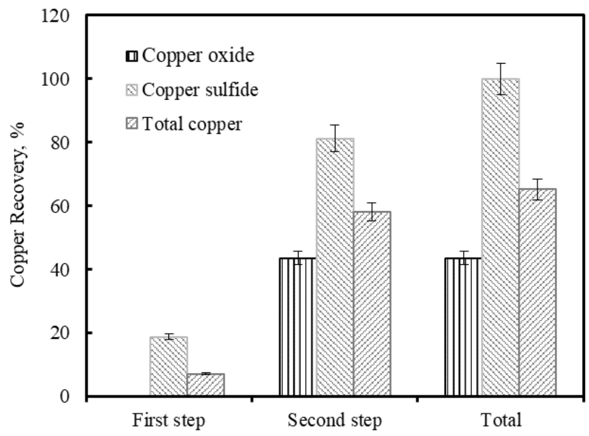

Figure 11. The recovery of copper oxide, copper sulfide and total copper at two consecutive flotation steps (first flotation step: PAX as collector at dosage of 50 g/t, solid percent of 30%, pH of 10.5, feed d80 of 90 μm; second flotation step: PAX as collector 50 g/t, solid percent of 30%, NaHS as activator at dosage of 1000 g/t, pH of 10.5, feed transferred from first flotation step).

In this section, two flotation tests were carried out. In one flotation test, the activator (NaHS) and collector (PAX) were added to the flotation cell and frothing in order to recover both of copper oxide and sulfide was performed in a single step. In the other test, a two-step frothing procedure was used: initially, 50 g/t of PAX was introduced without a sulfidizing agent to recover copper sulfide minerals in the first frothing step. Subsequently, 1000 g/t of sulfidizing agent and 50 g/t PAX were added to recover copper oxide minerals in the second frothing step.

Figure 12 compares the results of one-step and two-step flotation. As shown, the recoveries of copper oxide, copper sulfide, and total copper in the one-step flotation were 48.12%, 83.9%, and 63.91%, respectively. In two-step flotation, the recoveries were 43.61% for copper oxide, 100% for copper sulfide, and 65.16% for total copper. Thus, two-step flotation resulted in higher copper sulfide recovery, while one-step flotation achieved greater copper oxide recovery.

In the two-step flotation, copper sulfide minerals are floated in the first step, and partially oxidized copper sulfide minerals and copper oxide minerals are recovered in the second step after surface sulfidation. This approach allows for the selective recovery of copper sulfide minerals before the introduction of the sulfidizing agent, minimizing potential depression effects on sulfide minerals that can occur when sulfidizing agents are present from the outset [37, 45]. In contrast, in the one-step flotation, simultaneous addition of NaHS and PAX can lead to the depression of copper sulfide minerals due to excessive sulfidation or the formation of hydrophilic surface species, thereby reducing their recovery [35, 45].

The higher copper oxide recovery in one-step flotation is likely because xanthate is present in the pulp before the addition of the sulfidizing agent in the two-step process, which can interfere with the sulfidation reaction and reduce the effectiveness of collector adsorption on newly formed sulfide surfaces [37, 45]. Sequential flotation with stepwise reagent addition has been shown to enhance selectivity and overall recovery in complex copper oxide-sulfide systems by optimizing reagent interactions and surface modifications [1, 45].

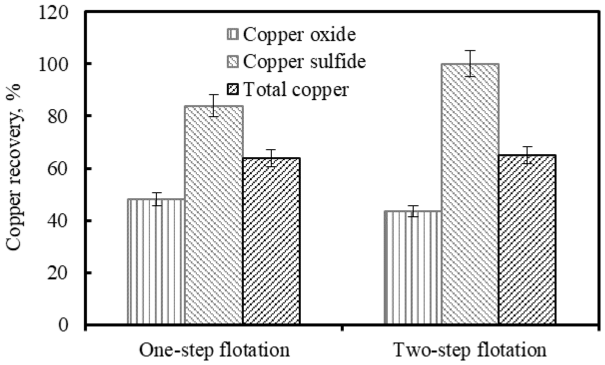

Figure 12. The comparison of one-step flotation with the two-step flotation in terms of recovery of copper oxide, copper sulfide and total copper.

3.2.7. Effect of lime and sulfiding agent addition point on flotation performance

The recovery of copper from copper oxide-sulfide ores via flotation largely depends on the efficiency of the sulfidation process. Therefore, it is crucial to add the sulfiding agent at the proper dosage and at the appropriate stage of the flotation procedure. Moreover, the solution pH plays a significant role in the adsorption of sulfur onto the surfaces of copper oxide minerals, which directly influences their surface hydrophobicity and flotation behavior [35, 45].

Figure 13 compares the flotation performance of copper oxide-sulfide ore based on different addition points for the sulfiding agent and lime. When lime is added to the mill, introducing the sulfiding agent into the mill-rather than the flotation cell-increases copper oxide recovery but decreases copper sulfide recovery. This suggests that adding both lime and the activator to the mill enhances the surface activation of copper oxide minerals through sulfide ions; however, it simultaneously suppresses the flotation of sulfide minerals due to the depressive effect of sulfide ions on copper sulfide minerals [45, 46]. Adding both lime and NaHS during grinding (in the mill) allows for early and thorough sulfidation of copper oxide minerals. The presence of sulfide ions (S^{2-}) in the mill environment promotes the formation of a thin copper sulfide layer (e.g., CuS, Cu_2S) on the surface of copper oxide minerals, which increases their hydrophobicity and affinity for xanthate collectors such as PAX [1, 35].

This mechanism is well-documented in flotation research, where early sulfidation under alkaline conditions (provided by lime) is known to enhance the floatability of oxide minerals by improving collector adsorption [3, 45]. While sulfide ions activate copper oxide minerals, excess sulfide ions in the mill can also have a depressive effect on copper sulfide minerals. Sulfide minerals (such as chalcopyrite or bornite) can be passivated by an overabundance of S^{2-}, leading to the formation of a hydrophilic surface layer (e.g. elemental sulfur or polysulfide species). This passivation reduces collector adsorption and thus decreases the recovery of copper sulfide minerals [35, 45].

If sulfidation occurs in the mill while the pulp pH is still near neutral (lime added later), the sulfidation reaction may be incomplete or less effective, as optimal sulfidation typically requires alkaline conditions. This can result in suboptimal activation of copper oxides and lower overall copper recovery [1, 45]. The efficiency of oxide mineral sulfidation and subsequent collector adsorption is highly pH-dependent, with best results observed under alkaline conditions [35, 45].

When both lime and the activator are added to the flotation cell, the recovery of copper sulfide and oxide is higher compared to when the activator is added to the mill. This implies that if sulfidation occurs in the mill while the pulp pH remains near neutral (because lime is added later in the flotation cell), the flotation performance does not improve, and copper recovery may decrease. When both reagents are added directly to the flotation cell, the timing and local concentration of sulfide ions can be better controlled. This approach minimizes the exposure of copper sulfide minerals to excessive sulfidation in the mill, preserving their natural floatability. Simultaneously, the presence of lime ensures that the pH is optimal for both pyrite depression and effective sulfidation of copper oxides during flotation. This strategy leads to higher recoveries of both copper oxide and copper sulfide minerals compared to adding NaHS in the mill, as it prevents the passivation of sulfide minerals while still activating the oxides [1, 35, 45].

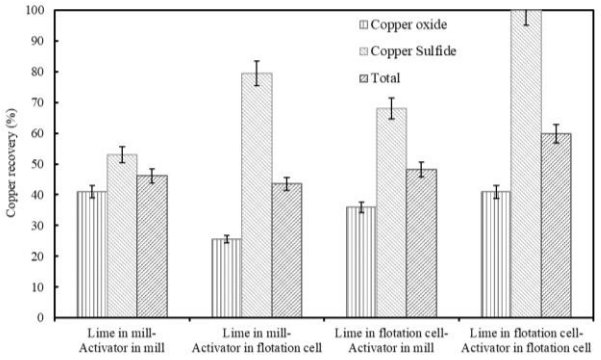

Figure 13. The effect of lime and activator adding point on the recovery of copper oxide, copper sulfide and total copper (PAX as collector at dosage of 100 g/t, solid percent of 30%, NaHS as activator at dosage of 1000 g/t, pH of 10.5, feed d80 of 90 µm).

Figure 14 illustrates the effect of distributing the sulfiding agent between the mill and the flotation cell on flotation performance. The results indicate that adding the entire activator dosage to the mill yields the highest recovery of copper oxide, as sulfidation is more effectively carried out during milling. Conversely, the maximum recovery of copper sulfide is achieved when 25% of the activator is added to the mill and the remaining 75% is introduced into the flotation cell. This is because partial sulfidation of weathered sulfide minerals occurs during milling. When the full activator dosage is added to the mill, copper sulfide recovery significantly decreases, likely due to enhanced sulfidation leading to the depression of sulfide minerals.

Adding the entire sulfiding agent dosage to the mill ensures that copper oxide minerals are thoroughly exposed to sulfide ions (S^{2-}) during grinding. This prolonged interaction facilitates the formation of a uniform and robust copper sulfide layer (e.g. CuS, Cu_2S) on the surface of copper oxide minerals, making them highly hydrophobic and more receptive to xanthate collector adsorption, thereby enhancing flotation recovery [35, 45, 46]. This phenomenon is consistent with flotation studies, which show that effective and early sulfidation under alkaline conditions maximizes the floatability of copper oxides by promoting the formation of a stable sulfide layer [1, 35].

Weathered or partially oxidized copper sulfide minerals can benefit from mild sulfidation during milling, which helps restore their surface hydrophobicity. However, when too much sulfiding agent is present during grinding, even the fresh copper sulfide minerals may undergo excessive sulfidation. This can lead to the formation of a passivating layer (e.g. elemental sulfur or polysulfides), which is hydrophilic and inhibits collector adsorption, thus depressing their flotation [35, 46]. By adding only 25% of the activator in the mill, partial sulfidation of weathered sulfides is achieved without over-sulfidizing the fresh sulfide minerals. The remaining 75% of the activator, added in the flotation cell, ensures that copper oxide minerals are sufficiently activated right before flotation, while minimizing the risk of sulfide mineral depression.

Previous research confirms that excessive sulfidation can depress natural copper sulfide minerals by creating a non-floatable surface layer, while staged or controlled sulfidation optimizes the recovery of both mineral types [3, 35, 45, 46]. Recent advances also highlight the importance of reagent addition sequence and distribution for maximizing the flotation performance of complex copper oxide-sulfide ores [35, 46].

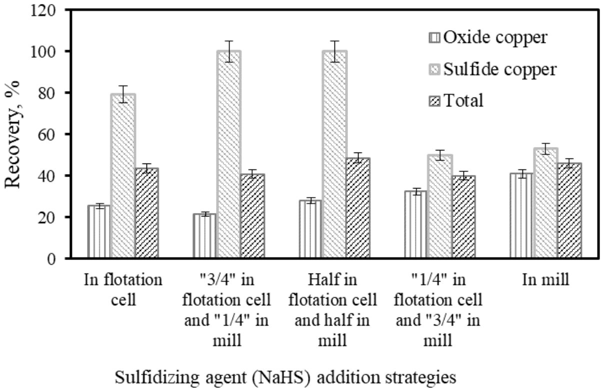

Figure 14. The effect of the distribution of sulfiding agent between the mill and the flotation cell on the recovery of copper oxide, copper sulfide and total copper (PAX as collector at dosage of 100 g/t, solid percent of 30%, NaHS as activator at dosage of 1000 g/t, pH of 10.5, addition of lime into the mill, feed d80 of 90 µm).

3.2.8. Effect of activator type and dosage on flotation performance

The influence of sodium hydrosulfide (NaHS) dosage on flotation performance is presented in Figure 15. As the dosage of sodium hydrosulfide increases from 250 to 500 g/t, copper oxide recovery rises from 46% to 51%, while copper sulfide recovery improves from 79% to 89%. Further increases in NaHS dosage have little impact on copper sulfide recovery; however, copper oxide recovery continues to increase-for example, increasing the dosage from 1000 g/t to 1500 g/t raises copper oxide recovery from 48% to 60%. This suggests that copper sulfide minerals in oxide/sulfide ores often have partially weathered surfaces requiring some sulfidation treatment to enhance flotation. Nevertheless, the amount of sulfidizing agent needed for copper sulfide minerals is lower than that required for copper oxide minerals in such ores.

At lower NaHS dosages, both copper oxide minerals and weathered (partially oxidized) copper sulfide minerals benefit from sulfidation. NaHS provides sulfide ions (S^{2-}) that react with the surface of copper oxide minerals, forming a thin layer of copper sulfide (e.g. CuS, Cu_2S). This layer increases the hydrophobicity of the oxide minerals, making them more receptive to xanthate collector adsorption and thus improving their flotation recovery [35]. Many copper sulfide minerals in mixed ores are partially weathered and may have oxidized surfaces that are less floatable. A moderate dose of NaHS restores their surface hydrophobicity by converting oxidized layers back to a more sulfide-rich, floatable state, resulting in a significant increase in copper sulfide recovery [35, 37]. Once the surface of partially oxidized copper sulfide minerals has been sufficiently sulfidized (typically at moderate NaHS dosages), further increases in NaHS provide little additional benefit. The surface is already optimal for collector adsorption, so copper sulfide recovery levels off. This plateau effect is well-documented, as excessive sulfidation can even risk surface passivation or the formation of hydrophilic sulfur species, but in results, the plateau suggests the optimal dosage is reached without significant depression [35, 37].

Copper oxide minerals generally require a higher dosage of NaHS for effective sulfidation because their surfaces are more refractory and less reactive than those of sulfide minerals. As the NaHS dosage increases beyond the level needed for sulfide minerals, more copper oxide surfaces are converted to a hydrophobic, sulfide-like state, leading to a continued increase in copper oxide recovery. The slow, continued rise in oxide recovery with higher NaHS dosages reflects the greater sulfidation demand of oxides compared to sulfides. This is consistent with the literature, which notes that copper oxides require more extensive sulfidation for optimal flotation [35, 37].

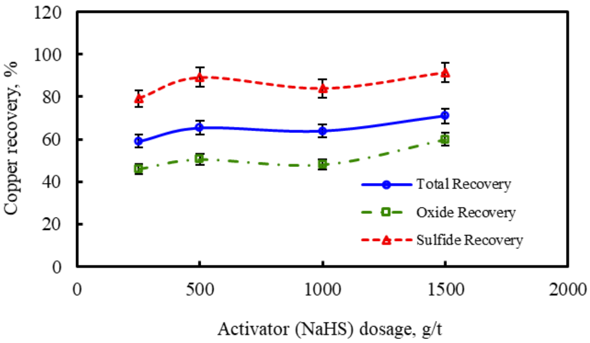

Figure 15. The effect of the dosage of NaHS as activator on the recovery of copper oxide, copper sulfide and total copper (PAX as collector at dosage of 100 g/t, solid percent of 30%, pH of 10.5, feed d80 of 90 µm).

Sodium sulfide is one of the most commonly used industrial activators for copper oxide mineral flotation. Figure 16 illustrates the effect of sodium sulfide dosage on copper oxide and sulfide recovery. Increasing the sodium sulfide dosage from 250 to 1500 g/t improves copper oxide recovery from 49% to 63%, while copper sulfide recovery remains relatively stable at around 80%, showing minimal change. Sodium sulfide (Na_2S) is a widely used sulfidizing agent in the flotation of copper oxide minerals. When added to the pulp, Na_2S dissociates to provide sulfide ions (S^{2-}), which react with the surface of copper oxide minerals (such as malachite, azurite, or chrysocolla). This reaction forms a thin layer of copper sulfide (e.g. CuS or Cu_2S) on the oxide mineral surface, imparting hydrophobicity and making them more amenable to collector (e.g. xanthate) adsorption, thus enhancing their flotation recovery [35, 46, 47]. As the dosage of sodium sulfide increases, more copper oxide mineral surfaces are effectively converted, resulting in a steady increase in copper oxide recovery, consistent with the trend observed in this study and in the literature [35, 46, 47].

Copper sulfide minerals (such as chalcopyrite, bornite, or chalcocite) readily float with xanthate collectors without the need for sulfidation, and their surface chemistry does not require further activation by sulfide ions. As a result, increasing the sodium sulfide dosage does not significantly affect the recovery of copper sulfide minerals, which remains relatively stable around 80% in your experiment [35, 46, 47]. In some cases, excessive sulfidizer can even depress sulfide mineral flotation due to the formation of hydrophilic sulfur species on the surface, but your results indicate that the dosages used did not reach this threshold. This behavior is well-documented in recent flotation research, which confirms that the flotation of natural copper sulfide minerals is largely unaffected by sulfidizer dosage unless it is excessively high [35, 47].

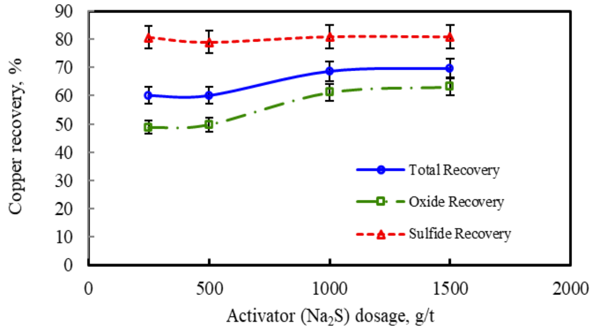

Figure 16. The effect of the dosage of Na_2S as activator on the recovery of copper oxide, copper sulfide and total copper (PAX as collector at dosage of 100 g/t, solid percent of 30%, pH of 10.5, feed d80 of 90 µm).

The comparison of flotation recoveries using sodium sulfide and sodium hydrosulfide as activators (Figure 17) indicates that sodium hydrosulfide consistently demonstrates a stronger ability to activate the surfaces of oxidized copper sulfide minerals across all dosages. Sodium hydrosulfide (NaHS) dissociates in water to produce hydrosulfide ions (HS^-) and, to a lesser extent, sulfide ions (S^{2-}). The HS^- ion acts as a more selective and milder sulfidizing agent compared to S^{2-}. For oxidized copper sulfide minerals (e.g. weathered chalcopyrite, bornite), milder sulfidation is often sufficient to restore surface hydrophobicity without over-sulfidizing or passivating the mineral surface. NaHS, by providing HS^-, can efficiently activate these surfaces, enhancing collector adsorption and flotation recovery. NaHS is less likely to cause the formation of excessive elemental sulfur or polysulfide species that could depress flotation, especially at moderate dosages. This results in consistently higher recovery of oxidized copper sulfide minerals across all dosages. This behaviour is supported by flotation research, which notes that NaHS is particularly effective for activating slightly oxidized sulfide surfaces due to its milder and more controlled sulfidation action [32, 33, 48].

Both reagents exhibit similar effectiveness in activating copper oxide minerals at lower dosages; however, at dosages above 500 g/t, sodium sulfide shows superior performance in recovering copper oxide minerals. At lower dosages ($\leqslant$500 g/t), both NaHS and Na_2S provide sufficient sulfide species (HS^- and S^{2-}) to convert the surface of copper oxide minerals (e.g. malachite, azurite) into a hydrophobic, sulfide-like layer. The amount of available sulfide is adequate for initial activation, so both reagents show similar effectiveness in enhancing copper oxide recovery. Sodium sulfide (Na_2S) dissociates to provide a higher concentration of sulfide ions (S^{2-}) compared to NaHS at equivalent dosages. At higher dosages (>500 g/t), this abundance of S^{2-} ions allow for completer and more robust sulfidation of copper oxide mineral surfaces, which are generally more refractory and require a stronger sulfidizing environment for full activation. The stronger sulfidizing power of Na_2S ensures that even less reactive or more crystalline copper oxide phases are converted to a hydrophobic state, resulting in higher flotation recovery. The need for higher sulfidizer dosages for complete activation of copper oxide minerals, and the greater efficacy of Na_2S in this context, is well-documented in recent studies [32, 33, 48].

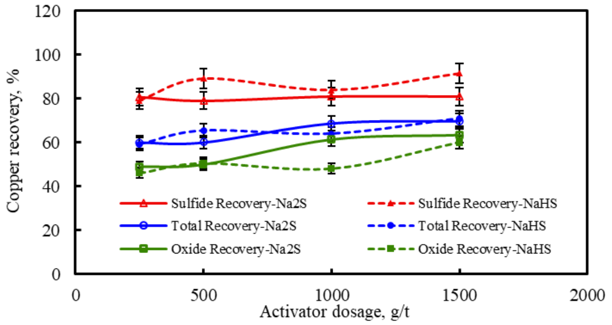

Figure 17. The effect of activator type on the recovery of copper oxide, copper sulfide and total copper at various activator dosages (PAX as collector at dosage of 100 g/t, solid percent of 30%, pH of 10.5, feed d80 of 90 μm).

4. Conclusion

This study systematically evaluated the flotation performance of a mixed copper oxide-sulfide ore containing approximately 62% copper oxide and 38% copper sulfide from northeastern Iran. Through comprehensive mineralogical characterization and process optimization, the sulfidation-flotation approach utilizing xanthate collectors was shown to be effective for upgrading this complex ore type. Under optimized conditions, a copper oxide recovery of 76% and a total copper recovery of 81% were achieved, demonstrating the method's efficacy.

Sodium sulfide was identified as an efficient activator for copper oxide minerals, with recoveries improving as the dosage increased from 250 to 1500 g/t. Sodium hydrosulfide provided superior activation for oxidized copper sulfide minerals due to its milder sulfidation, which minimized surface passivation. Particle size had a significant impact, with copper oxide recovery maximized at 53 μm and copper sulfide recovery at 90 μm. Collector selection and dosage were critical: potassium amyl xanthate (PAX) enhanced copper sulfide flotation, while both PAX and potassium isopropyl xanthate (SIPX) performed similarly for sulfidized copper oxides. Optimal collector dosages maximized recovery, whereas excessive dosing reduced flotation efficiency, particularly for oxides. The use of co-collector systems, such as SIPX with PAX, resulted in synergistic improvements in recovery for both mineral types.

The optimal flotation pH was around 10.5, providing a balance between copper oxide and sulfide recoveries. The strategy for reagent addition was also crucial: adding lime and activator to the mill favored copper oxide recovery but could depress copper sulfides, while addition in the flotation cell improved sulfide recovery. Distributing the activator between the mill (25%) and flotation cell (75%) optimized overall copper recovery by partially sulfidizing weathered sulfides without over-sulfidizing fresh sulfides.

Tailoring sulfidizer dosage to ore mineralogy was essential: moderate NaHS dosages (250–500 g/t) were sufficient for weathered sulfides, whereas higher dosages (500–1000 g/t) were needed for copper oxides. Sodium sulfide effectively enhanced copper oxide flotation by forming hydrophobic sulfide layers, while copper sulfide recovery remained stable due to their inherent hydrophobicity. Sodium hydrosulfide's milder sulfidation was advantageous for oxidized sulfides, whereas sodium sulfide's stronger action was necessary for robust oxide activation.

Finally, a two-stage flotation process with inter-stage sulfidation effectively separated and recovered copper sulfide and oxide minerals, maximizing overall copper recovery. These findings emphasize the importance of integrated reagent selection, dosage optimization, pH control, and staged reagent addition in the efficient flotation of complex copper oxide-sulfide ores, providing practical guidance for the development of beneficiation flowsheets for similar ore types.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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