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Study on Enrichment of Copper Oxide-Sulphide Ore Samples by Flotation Method

Hossein Hamedani, Arash Sobouti, Mohammad Baqaeifar, Bahram Rezai*, Fatemeh Sadat Hoseinian

Department of Mining Engineering, Amirkabir University of Technology, Tehran, Iran

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Abstract

In this work, a representative sample was initially prepared from exploratory drilling cores, followed by identification and characterization studies based on XRD analysis; the sample consists primarily of quartz, kaolinite, muscovite-illite, calcite, potassium, feldspar, albite, dolomite, siderite, and chalcopyrite. Optical and scanning electron microscopy studies revealed that the sulfide minerals in the sample include chalcopyrite, chalcocite, and pyrite, with the most significant copper minerals primarily comprising chalcopyrite, chalcocite, and malachite. No free gold was observed, and gold mainly exists as a substitute within the structure of sulfide minerals. AAS analysis results indicated that the copper grade in the sample is 0.99%. To investigate the flotation of copper minerals, influential parameters such as pH, collector concentration, frother concentration, sodium sulfide concentration, and the effect of particle size were examined. The results demonstrated that under optimal conditions (pH = 11, collector concentration of 100 g/t Potassium Amyl Xanthate (PAX), 100 g/t Sodium Isopropyl Xanthate (SIPAX), 60 g/t frother methyl isobutyl carbinol (MIBC), 1000 g/t Na_2S at a particle size of d80= 75µ), the total copper grade and recovery following two stages cleaner flotation were achieved at 21.2% and 60.2%, respectively.

1. Introduction

Copper is a strategic metal used in many industries, including electronics, construction, energy, and automotive. Given the growing demand for this metal, the extraction and processing of its mineral resources are of paramount importance. Copper occurs naturally in two forms: oxide ore and sulphide ore, each presenting unique characteristics and challenges. Sulphide ores, including minerals such as chalcocite and chalcopyrite, are more commonly processed using flotation methods, whereas oxide ores like malachite and azurite typically require hydrometallurgical processes. Due to the depletion of high-grade sulphide deposits and the increased extraction from oxide-sulphide sources, the development and optimization of concentration methods for these ores are essential [1-4].

The flotation process, which extensively concentrates sulphide minerals, is one of the most important methods for concentrating copper ores [5,6]. This process operates based on the differences in the surface properties of valuable minerals and gangue, incorporating the use of chemicals like collectors, frothers, and other reagents to enhance mineral separation. Various factors such as the chemical composition of the ore, type and concentration of collector, pH levels, and operational conditions have a direct impact on the efficiency of this method. For example, thiol-based collectors such as xanthates are effective for the flotation of sulphide minerals, while oxide minerals require pre-activation with sodium sulphide to become suitable for collector adsorption [5,7].

Lee et al. (2009) investigated the effect of n-octyl hydroxamate as a collector for the simultaneous recovery of copper sulphide and oxide minerals. Their results indicated that this collector enhanced the recovery of malachite and azurite [8]. Additionally, Bulatović et al. (2010)

✉ *Corresponding author: Rezai@aut.ac.ir (Bahram Rezai)*

demonstrated that the use of depressants such as sodium silicate and sodium carbonate significantly improved flotation selectivity, and reduced the impact of gangue impurities [9].

Further studies have shown that combining thiol and amine collectors can lead to higher copper recovery from oxide-sulphide ores. Fuerstenau et al. (2007) assessed how the oxidized or sulphide nature of copper ores affects flotation performance. They found that sulphide ores are typically well-flotated using xanthate collectors, whereas oxide ores require a pre-activation stage [10]. Koleini et al. (2013) optimized the selective flotation process of chalcopyrite, sphalerite, and pyrite from the copper-zinc ore of the Taknar mine. The results indicated that the most effective parameter for copper and zinc recoveries in the copper concentrate was the type of collector mixture. The optimization results demonstrated that by maximizing copper recovery, the respective recoveries of copper, zinc, and pyrite were 89.04%, 25.3%, and 2.02%, achieved using a mixture of sodium isopropyl xanthate and sodium di-butyl dithiophosphate as collectors, dextrin as a pyrite depressant, 500 g/t of zinc sulfate, and a pH of 11.35 [11]. Ghodrati et al. (2013) optimized the concentration of chemical reagents used in the copper flotation process of the Shahre Babak complex through statistical design. The optimal conditions for achieving a maximum copper recovery of 91.31% were identified as follows: sodium isopropyl xanthate collector at 8.99 g/t, thionocarbamate collector at 22.8 g/t, dithiophosphate collector at 5.05 g/t, frother A65 at 12.52 g/t, and frother A70 at 7.68 g/t [12]. Additionally, Wills and Finch (2015) studied the optimization of flotation process through precise control of operational parameters is crucial for improving efficiency and reducing processing costs [13].

Marion et al. (2017) conducted a study investigating the effect of the structure of seven hydroxamic acid collectors on the flotation of malachite, finding that certain collectors, such as benzohydroxamic acid and C8 alkyl hydroxamate, demonstrated superior performance in flotation [14]. Additionally, Zarei Varzeqan (2017) showed in a work that the use of potassium octyl hydroxamate at a dosage of 10 g/t could increase the recovery of oxide copper by up to 74.46%. Furthermore, the simultaneous use of ammonium sulphide and hydroxamates improved oxide copper recovery to 77.31% [15].

Barfeyi and Paraspoor (2022) examined the effect of pH and chemical reagents on froth stability, using a sample obtained from the copper processing plant in Mohammadabad Delijan, employing the Taguchi method. The results showed that the best froth stability happened at a pH of 11.2, using 20 g/t of sodium isopropyl xanthate collector, 15 g/t of di-thiophosphate collector, 20 g/t of the frother MIBC, and 15 g/t of the frother Dowfroth 250 [16].

Canpolat and Ziyadanoğullari (2023) investigated the extraction of copper from complex copper oxide ore, using flotation enrichment experiments. For the sulphidation of the surface of oxide minerals, Na_2S and H_2S were used. The use of H_2S led to an increase in recovery [17]. Yu et al. (2024) investigated the recovery of copper from copper smelting slag, using the flotation-sulphidization-xanthate method. The results indicated Na_2S-modified CuO surface apparently adsorbed more xanthate collection, resulting in an improved hydrophobicity. The results demonstrate good recovery efficiency under the conditions of pH = 8.5, pulp density = 45.6 % and Na_2S concentration = 80 g/t [18].

Recent studies indicate that the direct flotation method for recovering copper from Copper Smelting Slag (CSS) faces limitations, due to the high malleability of metallic copper and difficulties in grinding, often resulting in recovery rates of less than 90%. A work conducted by Jianjun et al. (2024) showed that combining gravity separation and flotation can more effectively recover copper from CSS, and improve the overall process efficiency by reducing the copper grade in the tailings. These findings may also be beneficial in optimizing the concentration of oxide-sulphide copper ores [19].

Conventional collectors such as xanthates cannot directly flotate oxide minerals, which constitute a portion of copper deposits. In the recent years, the sulphide-coating method for copper oxide minerals followed by flotation with xanthate collectors has gained attention, especially in areas like the Bouji region, which contains both sulphide and oxide copper minerals. The primary challenge in the processing and concentration of copper ores from this region lies in the presence of copper oxide minerals that typically cannot be floated with conventional collectors like xanthates. As such, the processes for concentration and optimized methods for recovering copper from these minerals remain incompletely identified. Additionally, there isn't enough information about the exact details of the minerals, the characterization of waste minerals, and gold-containing minerals, especially using modern methods like scanning electron microscopy (SEM). The aim of this research is to first perform detailed identification and characterization from the perspective of mineral processing for samples from the Bouji region. In this study, SEM equipped with WDX was used, along with element distribution mapping, to accurately identify copper minerals, accompanying gangue minerals, and gold-bearing minerals. Subsequently, to achieve appropriate grade and recovery, flotation methods were applied, examining optimal levels of effective parameters such as pH, collector concentration, frother concentration, and Na_2S concentration.

2. Material and Methods

2.1. Material

Approximately 120 kg of representative samples were obtained from the core drillings of the Bouji ore deposit, located 65 km east of Zanjan. The samples were crushed, using jaw and roll crushers to a size of less than 2 mm. After homogenization, the samples were further ground in a ball mill according to liberation studies to a size of 80% passing 75 µm (d_{80}) for flotation tests.

To identify the chemical composition of the sample, X-Ray Fluorescence (XRF) analysis was conducted, using the X unique II model from Philips. For identifying the present minerals, X-Ray Diffraction (XRD) analysis was performed, using the X'Pert MPD model from Philips. The quantitative determination of the elements in the sample was carried out using Atomic Absorption Spectroscopy (AAS). Additionally, for more precise identification of minerals and calculating the degree of liberation of copper-bearing minerals, petrographic and mineralographic studies were conducted using optical and electron microscopy, utilizing polished and thin sections.

After preparing the polished sections, studies were continued with the XL 30 model scanning electron microscope from Philips, equipped with WDX, along with the preparation of element distribution maps. When using the BackScattered Electron (BSE) detector for imaging, heavier minerals stand out clearly, and the image gets dimmer as the average atomic number of the mineral decreases.

2.2. Chemicals used

Various chemicals were utilized for the flotation experiments (Table 1).

Table 1. Specifications of the chemicals used in flotation experiments.

Chemical reagent	Chemical formula	Role and application
Potassium Amyl Xanthate (PAX)	$C_5H_{11}OCS_2K$	Collector
Sodium IsoPropyl Xanthate (SIPAX)	$C_3H_5S_2Na$	Collector
Sodium sulfide	Na_2S	Activator
Methyl Isobutyl Carbinol (MIBC)	$C_6H_{13}OH$	Frother
Calcium carbonate	$CaCO_3$	pH Regulator
Sulfuric acid	H_2SO_4	pH Regulator

2.3. Flotation experiments

In all flotation experiments, 1 kg of sample were mixed with water to prepare a pulp with 30% solids, which was then transferred to a flotation cell in the Denver laboratory. Figure 1 shows a view of the flotation cell used in the Denver laboratory. Subsequently, chemicals including pH regulator, activator, collector, and frother were added to the pulp. After a set preparation time, the aeration process was conducted. Finally, the froth collection was performed. The collected concentrate and the remaining tailings in the cell were weighed after filtration and drying. After each experiment, we determined the grades of the concentrate and tailings by sampling each using an atomic absorption device. With the grade and weight available, the recovery for each test was calculated using Equation (1). Additionally, all data were mass balanced, and tests with high mass balance errors were repeated [20].

$$R = \frac{C.c}{F.f} \times 100 \tag{1}$$

Where:

C: Weight of the concentrate (g)

c: Copper grade in the concentrate (%)

F: Weight of the feed (g)

f: Copper grade in the feed (%)

Following crushing by jaw, cone, and cylindrical crushers; the ore underwent size analysis and grinding in a ball mill based on liberation studies. According to Table (2) and Figure (2), 80% of the particles are less than 75 microns (d_{80} = 75 µm).

Table 2. Particle size analysis.

Sieve Size (µm)	Weight percent retained (%)	Cumulative percent retained (%)	Cumulative percent passing (%)
+177	0.5	0.5	99.5
+149 –177	0.75	1.25	98.75
+105 –149	2.25	3.5	96.5
+74 –105	7.0	10.5	89.5
+53 –74	20.5	31.0	69.0
+44 –53	28.5	59.5	40.5
-44	40.5	100.0	0.0
Total	100	---	---

Figure 1. Denver laboratory flotation cell used

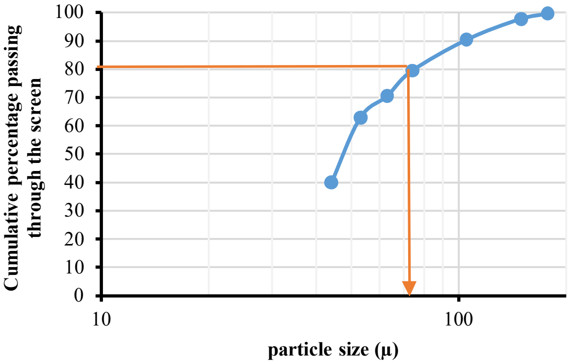


Figure 2. Particle size analysis curve.

3. Results and Discussion

3.1. Results of optical microscope studies

According to Figure 3, the optical microscope studies showed that the copper minerals in the sample are mostly chalcopyrite and malachite. Some of the chalcopyrites are changing due to iron hydroxide, which is replacing them with malachite, chalcocite, and quartz. Some chalcopyrites are being replaced by malachite, chalcocite, and quartz due to iron hydroxide. Chalcopyrite alteration products have more iron hydroxide and malachite than the others, but chalcocite and quartz are much less. Bornite is also present in minimal amounts, mainly as minor intergrowths with chalcopyrite. Magnetite is primarily observed in semi-mafic volcanic rocks, where its occurrences are quite limited. Hematite is also present in low amounts, occurring as aggregates of platy-shaped crystals in a few samples.

The most common pairing of chalcopyrite grains, especially in the larger pieces, is with non-metallic gangue minerals. Due to the nature of the deposit, some chalcopyrite particles are being substituted by iron hydroxide; the most significant association of chalcopyrite occurs with gangue minerals and iron hydroxides, specifically limonite and goethite. In finer fractions (250–150 microns) and smaller fractions, the association of chalcopyrite is mainly with iron hydroxides. For malachite, it is mixed with non-metallic minerals, and in smaller sizes, it is found together with iron hydroxide. Overall, the abundance of chalcopyrite is approximately 2 to 2.5%, while the abundance of malachite is around 1%.

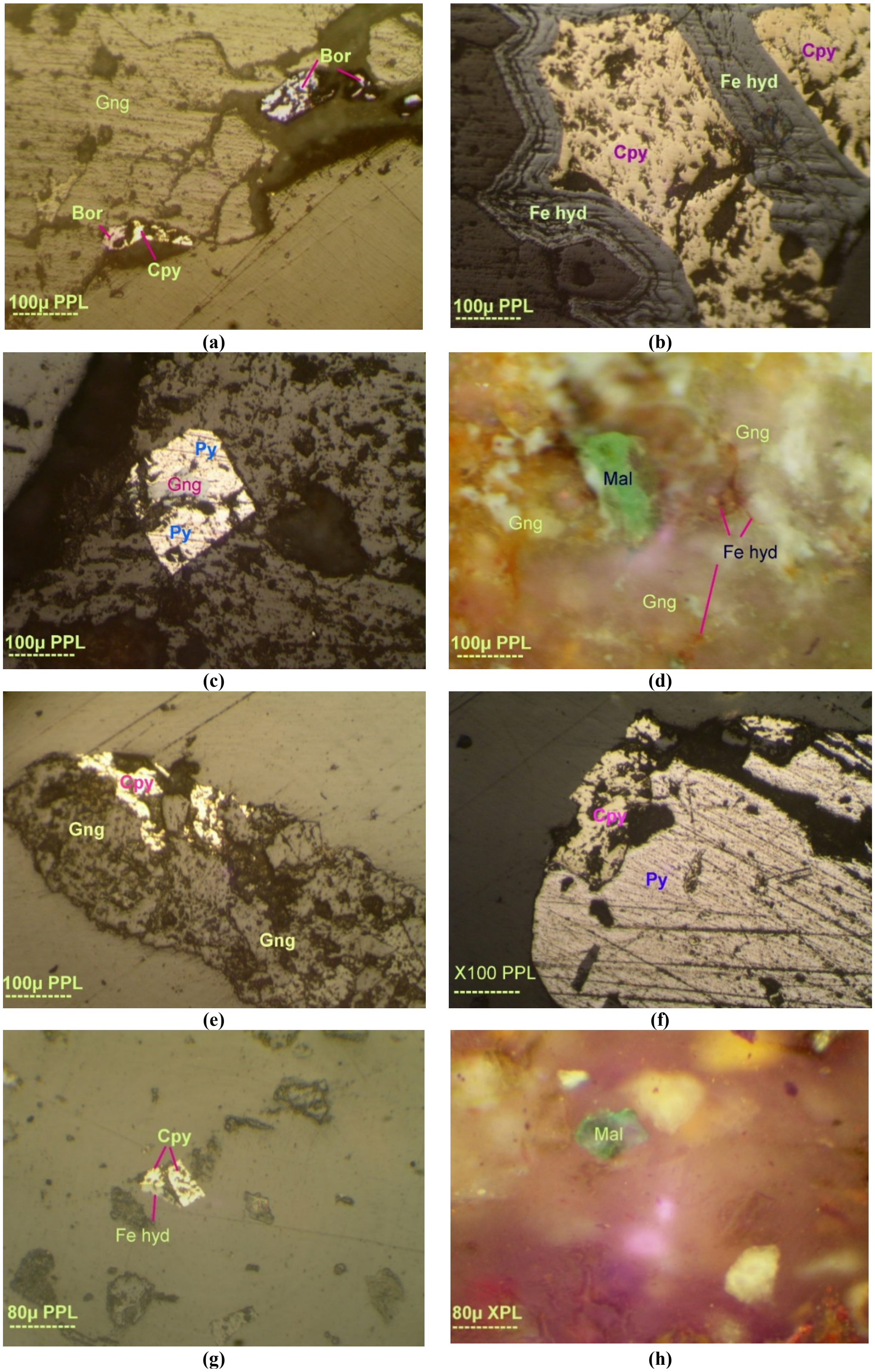


Figure 3. Illustrates various associations within the studied fractions: (a) the association of chalcopyrite (Cpy) with bornite (Bor) and gangue, as well as the association of bornite with gangue (Gng) in the 2830+ micron fraction; (b) chalcopyrite (Cpy) undergoing substitution by iron hydroxide (Fe hyd) in the 2830+ micron fraction; (c) The association of pyrite (Py) crystals with gangue in the 2830+ micron fraction; (d) The association of malachite (Mal) with gangue in the 2830+ micron fraction; (e) The association of chalcopyrite particles with gangue in the -500+350 micron fraction; (f) the association of chalcopyrite with pyrite in the -500 + 350 micron fraction; (g) The association of chalcopyrite and iron hydroxide in the -75 + 62 micron fraction; and (h) a free malachite particle in the -75 + 62 micron fraction.

3.2. XRD, XRF, and AAS analysis

The results of the XRD analysis confirmed the findings from the microscopic studies. Figure 4 and Table 4 show that the main minerals in the sample are mostly lbite, quartz, kaolinite, muscovite-illite, calcite, potassium feldspar, adolomite, siderite, and chalcopyrite. Additionally, the results of the XRF analysis are presented in Table 5, indicating a loss on ignition (L.O.I) of approximately 7.32%, which includes carbonates, sulphates, and water in the sample. The AAS analysis revealed that the copper and gold grades in the sample were 0.99% and 1616 ppb, respectively. The amount of oxidized copper in the sample was 0.43%. Due to the low gold content, identifying associated minerals through XRD analysis and optical microscopy was not feasible. Therefore, to identify gold-bearing minerals, SEM equipped with WDX was utilized.

Table 4. X-ray diffraction analysis.

Mineral name	Chemical formula
Quartz	SiO_2
Albite	$NaAlSi_3O_8$
Muscovite	$KAl_2[(OHF)_2\text{–}AlSi_3O_{10}]$
Dolomite	$CaMg(CO_3)_2$
Siderite	$FeCO_3$
Calcite	$CaCO_3$
Kaolinite	$Al_2Si2O_5(OH)_4$
Orthoclase feldspar	$KAlSi_3O_8$
Chalcopyrite	$CuFeS_2$

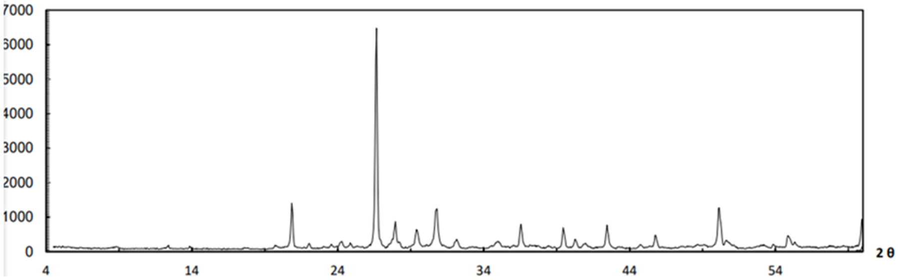


Figure 4. XRD of ore sample

Table 5. Chemical composition of sample determined by XRF.

SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SO_3	TiO_2	Cu	LOI
62.74	8.95	4.66	7.44	1.8	1.58	0.45	1.38	0.13	2.15	0.46	0.99	7.32

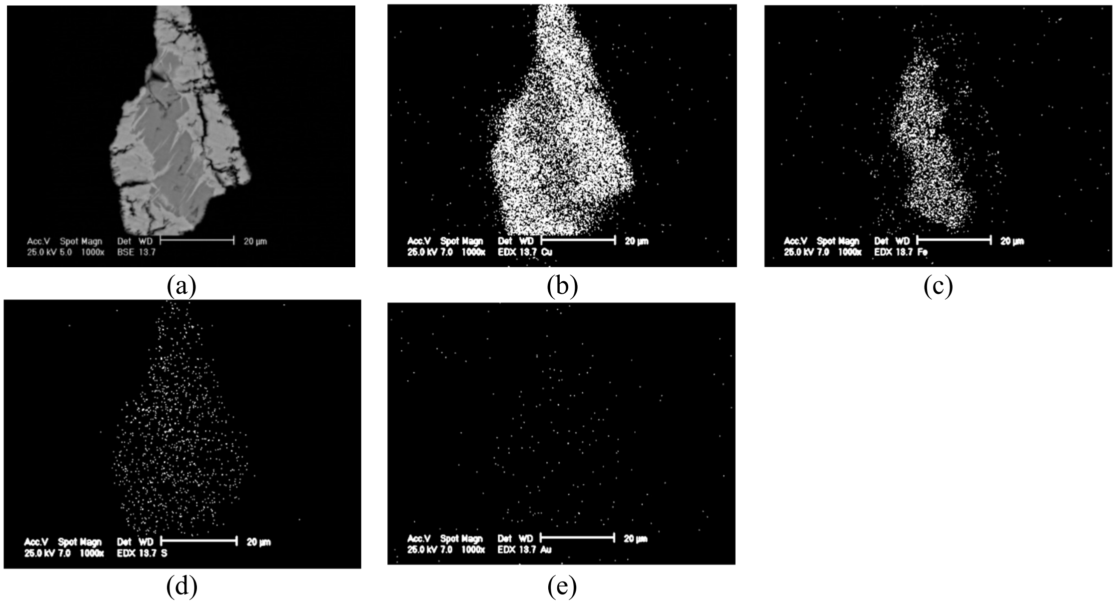
3.3. SEM studies

The findings from the scanning electron microscope studies of the sample are shown in element distribution maps in Figures 5, 6, and 7. Figure 5 shows the association of chalcocite and pyrite particles in the 150-105 micron size fraction. Analysis of these particles and the X-ray mapping of copper, iron, sulfur, and gold indicates that the light-colored mineral is chalcocite, due to the simultaneous presence of copper and sulfur, while the dark portion is pyrite due to the simultaneous presence of iron and sulfur. It is evident that both minerals contain some gold in their structure. Figure 6 depicts the free and associated particles of valuable minerals and gangue in the 150-105 micron size fraction. The light-colored, free mineral in this image is chalcopyrite, which has copper and some gold in its structure. Figure 7 displays several free and associated heavy mineral particles and gangue together in the 75-62 micron size fraction. An analysis of some of the light-colored particles suggests the presence of two chalcopyrite particles along with one iron oxide particle. The brighter particles are identified as chalcopyrite containing copper, iron, and sulfur along with some gold in their structure, while the darker particle is due to the presence of iron without other elements, indicating iron oxide.

3.4. Effective parameters

3.4.1. pH

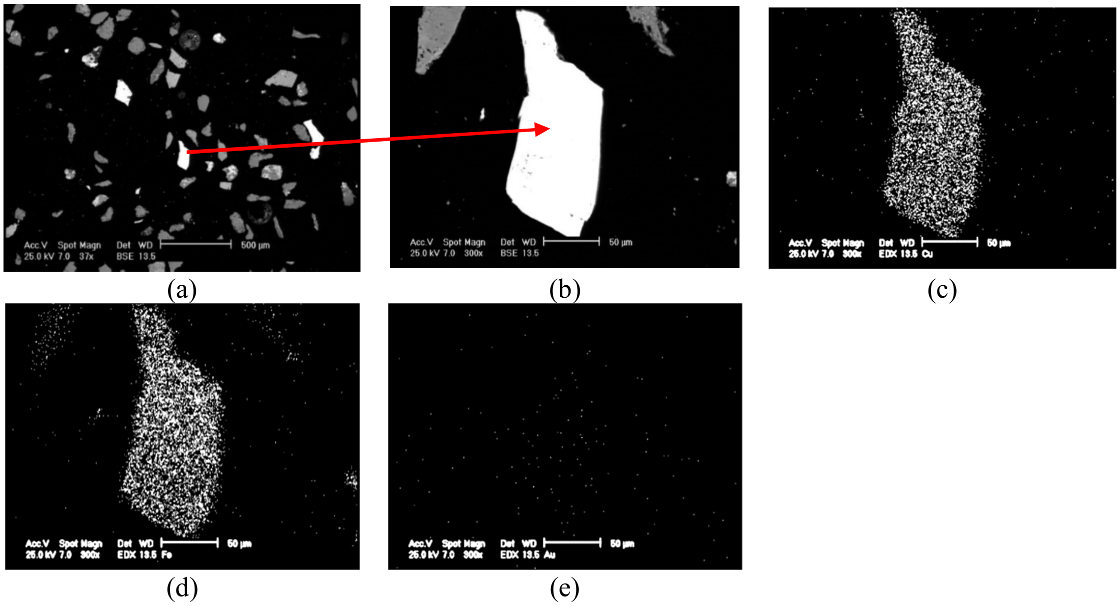
pH is a key parameter in the flotation of sulphide and oxide minerals. In this work, the effect of pH was investigated by conducting flotation tests under similar conditions at three different pH levels, with the results presented in Figure 8. Figure 8(a) illustrates the copper recovery at three pH levels. Based on the results, increasing pH positively effects the recovery of both oxidized and total copper, but it has little effect on recovering sulphide copper. As pH increases from 9 to 10, the recovery of both oxidized and sulphide copper increases. As the pH increases from 10 to 11, the recovery of sulphide copper decreases. The reason for this is that raising the pH to higher levels requires a significant amount of lime. This quantity of lime leads to an increased precipitation of magnesium and calcium ions on the surface of valuable minerals, negatively impacting the flotation process. Additionally, the adsorption of $Mg(OH)_2$ and $CaCO_3$ precipitates on the surface of copper sulphide minerals alters their surface characteristics, resulting in decreased recovery. Overall, these changes in surface properties lead to a reduction in the efficiency of the recovery and flotation process of sulphide copper [21], whereas a further increase in pH from 10 to 11 results in a decrease in sulphide copper recovery, although oxidized copper recovery continues to rise at a slower rate. The increase in oxidized copper recovery with higher pH is attributed to improved sulfidization of oxide minerals. Additionally, the decrease in the recovery of sulphide minerals at pH 11 results from the depression of sulphide minerals such as pyrite and galena.



(a) (b) (c)

(d) (e)

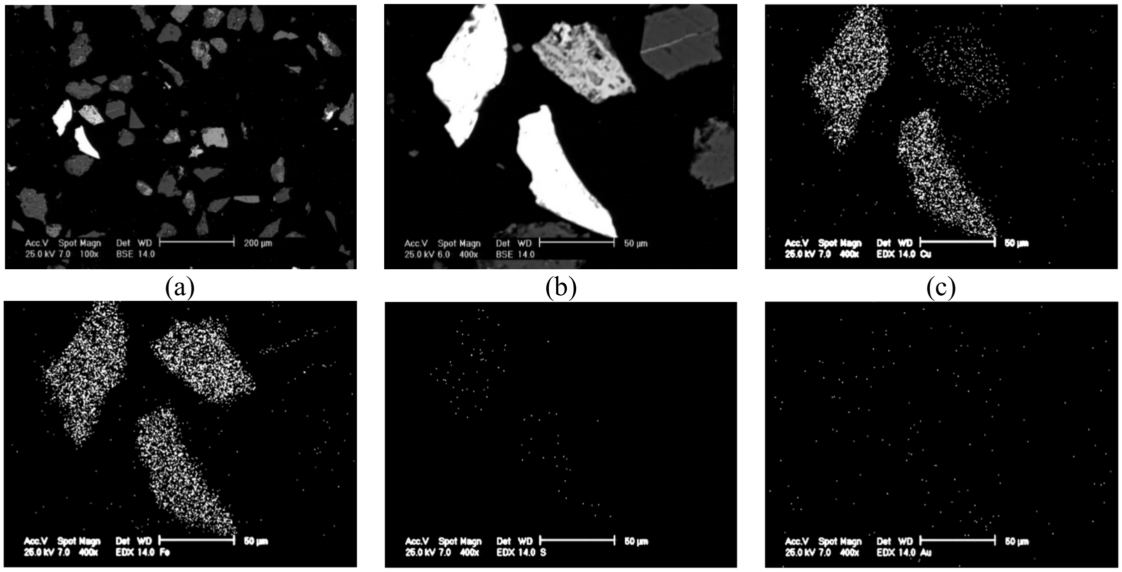
Figure 5. a) The interaction of chalcocite and pyrite within the particle size fraction of 105-150 microns. b) Distribution map of Cu in image a. c) Distribution map of Fe in image a. d) Distribution map of S in image a. e) Distribution map of Au in image a.



(a) (b) (c)

(d) (e)

Figure 6. a) Free and locked particles of valuable minerals and gangue in the particle size fraction of 105-150 microns. b) An almost free particle of chalcopyrite. c) Distribution map of Cu in image b. d) Distribution map of Fe in image b. e) Distribution map of au in image b.

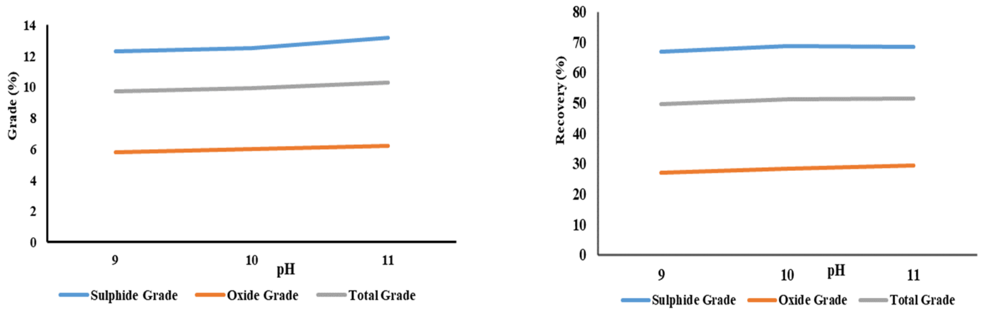


(a) (b) (c)

(d) (e) (g)

Figure 7. a) Free and locked particles of valuable minerals and gangue in the particle size fraction of 62-75 microns. b) Free particles of heavy minerals in image a with increased magnification. c) Distribution map of Cu in image b. d) Distribution map of Fe in image b. e) Distribution map of S in image b. f) Distribution map of Au in image b.

Figure 8(b) shows the grade versus pH chart. As depicted in Figure 8(b), with pH increasing from 9 to 11, the sulphide copper grade rises from 12.3% to 13.2%, indicating enhanced flotation performance. This grade increase is due to the depression of pyrite and galena in pH =11 and improved separation of chalcopyrite from the tailings [22]. Moreover, the oxidized copper grade increases from 5.8% at pH 9 to 6.2% at pH 11, indicating that a portion of oxidized copper is also entering the concentrate in alkaline environments. Ultimately, the total copper grade rises from 9.72% to 10.3%, reflecting improved concentrate quality, which may be attributed to optimized flotation conditions and increased selective separation of copper particles. At higher pH levels, the formation of hydroxide complexes for certain impurities, such as iron and silica, increases, leading to a reduced presence of these impurities in the concentrate and consequently enhancing the copper grade. The increase in oxidized copper recovery with rising pH is a result of improved sulfidization of oxide minerals. Since the goal during the rougher and scavenger stages is to achieve maximum recovery, pH=11 is considered the optimal value for determining other process parameters.



(a) **(b)**

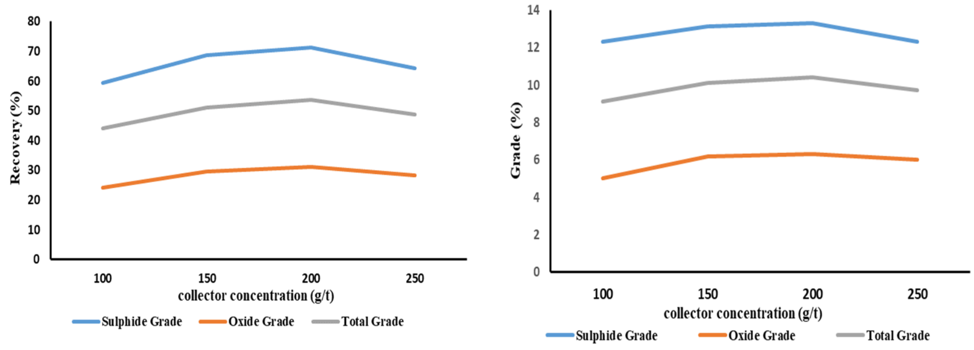
Figure 8. Effect of pH on copper a: recovery b: grade (collector concentration: 150 g/t, MIBC concentration: 45 g/t, and sodium sulphide concentration: 500 g/t).

3.4.2. Collector concentration

In this work, two collectors—sodium isopropyl xanthate and potassium amyl xanthate—were used in equal weight ratios of 50%. The potassium amyl xanthate collector, because of its longer hydrocarbon chain, exhibits a powerful flotation compared to sodium isopropyl xanthate. To investigate the effect of collector concentration, flotation tests were conducted under similar conditions at four different levels of collector concentration, with the results illustrated in Figure 9. Figure 9(a) displays the impact of collector concentration on copper grades As shown in Figure 9(a), increasing the concentration of both sodium isopropyl xanthate and potassium amyl xanthate, in an equal weight ratio of 50%, from 100 to 200 g/t results in an increase in the sulphide copper grade from 12.3% to 13.3%, representing the maximum value within this range. However, further increasing the concentration to 250 g/t leads to a decrease back to 12.3%, indicating that the optimal collector amount for sulphide copper flotation is 200 g/t. The subsequent reduction in grade is attributed to surface saturation of the particles and decreased flotation recovery [21]. On the other hand, the grade of oxide copper, which is 5% at 100 g/t, shows a slight increase at concentrations of 150 and 200 g/t, reaching 6.3%. However, at 250 g/t, the grade drops to 6%, suggesting that the collector has a minimal effect on oxide copper. The overall copper grade, starting at 9.12% at 100 g/t, rises to 10.12% at 150 g/t, but subsequently declines to 10.4% and 9.72% at 200 and 250 g/t, respectively. This data indicates that excessive collector addition can lead to a decrease in grade. Given that the objective in rougher and scavenger stages is to achieve maximum recovery, the best performance of the collector is noted at a concentration of 200 g/t, which is regarded as the optimal amount for determining other process parameters.

Figure 9(b) illustrates the effect of collector concentration on copper recovery. The recovery of sulphide copper exhibits an increasing trend with the rise in concentration of two collectors—sodium isopropyl xanthate and potassium amyl xanthate—in an equal weight ratio of 50%, ranging from 100 to 200 g/t, resulting in an increase from 59.3% to 71.25%. The increase in collector concentration enhances the surface coverage of the sulphide minerals present in the sample. This phenomenon increases the hydrophobicity of the surface, thereby improving their flotation. In this context, the collector is sufficiently available to cover the active sites of sulphide particles and facilitates bubble attachment by reducing interfacial energy. However, at a collector concentration of 250 g/t, it was observed that the recovery of sulphide copper decreased to 64.35% with increasing collector concentration. This is because the excess amount of collector can lead to increased foam stability due to micelle formation. In this situation, micelles cause a mix of minerals instead of separating the desired ones effectively, which lowers the recovery rate. Furthermore, the saturation of particle surfaces with the collector can lead to detrimental effects such as particle repulsion, increased froth buoyancy, and the mixing of valuable minerals with gangue [23].

Conversely, the recovery of oxide copper initially increases with the concentration from 100 to 200 g/t, rising from 24.18% to 31.06%. However, it decreases at 250 g/t, reaching 28.18%, indicating that the optimal point for oxide copper recovery is also at 200 g/t. Finally, the overall copper recovery, which stands at 44.05% at 100 g/t, increases at 150 and 200 g/t to 51.04% and 53.79%, respectively. However, it drops to 48.64% at 250 g/t, showing that 200 g/t is the best amount for overall copper recovery; using too much of the collector reduces recovery.



(a) (b)

Figure 9. Effect of collector concentration on copper a: recovery b: grade (pH = 11, MIBC concentration = 45 g/t, and sodium sulphide concentration = 500 g/t).

3.4.3. Frother concentration

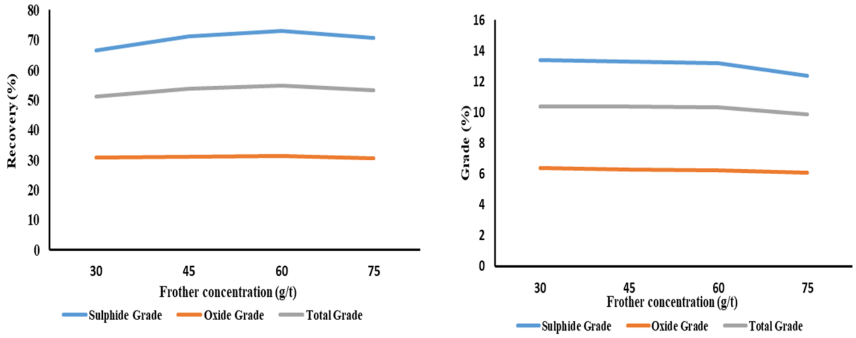
To determine the optimal concentration of frother, experiments were conducted at four levels: 30, 45, 60, and 75 g/t of MIBC frother under identical conditions. MIBC frother produces low-density bubbles, which can lead to lower recovery and increased transfer of water and slimes to the froth zone. Figure 10(a) demonstrates the effect of frother concentration on copper grade. According to Figure 10(a)**,** the sulphide copper grade at a concentration of 30 g/t is 13.4%, and as the concentration of MIBC frother increases to 45 and 60 g/t; the sulphide copper grade slightly decreases from 13.3% to 13.2%, ultimately reaching 12.4% at 75 g/t. This indicates that excessive frother concentration negatively impacts the sulphide copper grade; an excessive amount of frother like MIBC can lead to the production of unstable froths or excessive froth stability. This results in the recovery of slimes or non-floatable particles, thereby reducing the selectivity of the flotation process and ultimately lowering the grade of the final concentrate (including the sulphide copper concentrate). Furthermore, highly stable froths can impede the effective separation of valuable particles from waste materials. On the other hand, the grade of oxide copper decreases from 6.4% to 6.1% when the concentration of MIBC frother increases from 30 to 75 g/t. Flotation of oxide copper is more challenging due to its more hydrophilic surface compared to sulphide copper. The increased concentration of frother can hinder the effective attachment of oxide copper particles to air bubbles by thickening the froth layer and reducing the concentration of materials in the liquid phase, thus decreasing flotation recovery [24,25]. As a result, the frother has a lesser impact on the flotation of oxide copper, and increasing its amount does not lead to improved recovery. The overall copper grade at 30 g/t is 10.4%, and remains relatively constant at 45 and 60 g/t, measuring 10.4% and 10.35%, respectively; however, it decreases at 75 g/t to 9.86%. This reduction indicates that an increase in frother concentration beyond the optimal amount leads to decreased flotation efficiency, thus showing that the best performance of the frother in this range occurs at 30 g/t, after which the increase in concentration results in a decline in recovery.

Based on Figure 10(b)**,** the recovery of sulphide copper at a concentration of 30 g/t is 66.52%. With the increase in frother concentration from 45 to 60 g/t, the recovery of sulphide copper rose from 71.25% to 73.07%. However, at a concentration of 75 g/t, the recovery decreased to 70.85%, indicating that an increase in frother concentration up to 60 g/t improves sulphide copper recovery, while higher concentrations have a diminishing effect. At elevated concentrations, frothers can lead to excessively stable froths, which hinder the proper separation of valuable minerals from waste, resulting in a higher retention of gangue particles in the froth. Additionally, high frother concentrations increase the viscosity of the froth, and the bubbles can't move as easily, consequently decreasing flotation performance and leading to lower recovery rates. Conversely, the recovery of oxide copper, which is 30.95% at 30 g/t, increases to 31.06% and 31.25% at 45 and 60 g/t, respectively, but decreases to 30.5% at 75 g/t. This indicates that the effect of frother on oxide copper recovery is not significant and shows only slight variations. At higher frother concentrations, bubble size decreases, reducing the likelihood of oxide particles adhering to the bubbles [26]. Furthermore, excessive frother concentration may preferentially adsorb onto the surfaces of gangue particles, disrupting the selectivity of the process. Finally, the overall copper recovery at 30 g/t is 51.07%, and it increases to 53.79% and 54.9% at 45 and 60 g/t, respectively, but drops to 53.32% at 75 g/t. This trend indicates that optimal performance occurs at 60 g/t, after which flotation recovery declines.

3.4.4. Sodium sulfide concentration

To investigate the effect of sodium sulphide (Na_2S) concentration, experiments were conducted at four levels: 500, 750, 1000, and 1250 g/t of Na_2S under identical conditions. According to Figure 11(a), increasing the concentration of Na_2S from 500 to 1250 g/t had no effect on the sulphide copper grade, which remained constant at 13.2%. In contrast, the oxide copper grade increased from 6.25% at 500 g/t to 8.1% at 750 g/t. Sulphide ions activated the oxide copper surface, making it more hydrophobic and improving its flotation, which may account for this increase. As the Na_2S concentration further increased to 1000 g/t, the oxide copper grade increased to 9.9%, indicating optimal activation conditions. However, when the Na_2S concentration reached 1250 g/t; the oxide copper grade decreased to 9.5%. This reduction could be due to excessive coverage of the particle surfaces by sulphide ions, leading to a reversion to a more hydrophilic nature. The overall copper grade also initially increased with rising Na_2S concentration, from 10.35% at 500 g/t to 11.02% and 11.68% at 750 and 1000 g/t, respectively, but decreased at a concentration of 1250 g/t to 11.54%. These changes suggest that the optimal Na_2S concentration for achieving maximum overall copper grade is around 1000 g/t, and exceeding this amount reduces process efficiency due to its negative effect on oxide copper flotation.

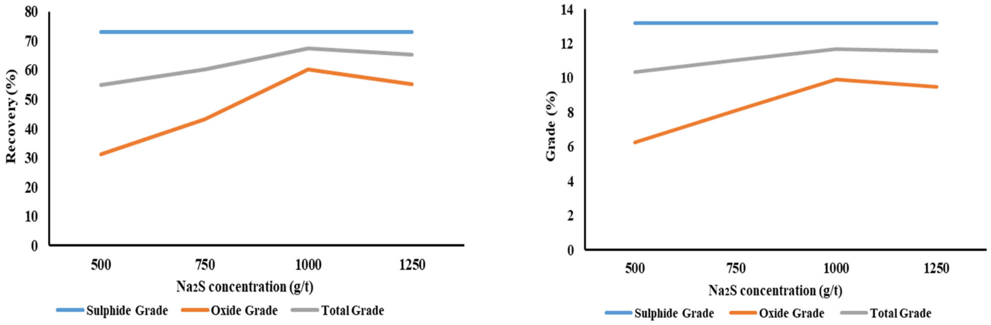
The optimal flotation performance observed at a dosage of 1000 g/t can be attributed to the effective activation of non-sulfide copper minerals, whereby their surfaces are sufficiently transformed into a sulfide-like state. This surface modification enhances their interaction with flotation collectors, thereby improving both copper recovery and concentrate grade. At this concentration, sodium sulfide appears adequate to induce the necessary surface changes that facilitate the selective flotation of valuable copper-bearing minerals.



(a) **(b)**

Figure 10. Effect of frother concentration on copper a: recovery b: grade. (pH = 11, collector concentration = 200 g/t, and sodium sulphide concentration = 500 g/t).

According to Figure 11(b), the recovery of sulphide copper at a concentration of 500 g/t is 73.07%, and as the Na_2S concentration increases; the recovery of sulphide copper remains constant. This is because sulphide minerals inherently possess hydrophobic properties, and float easily with common collectors such as xanthates. When Na_2S reacts with water, it creates sulphate compounds and elemental sulphur, which helps to improve the recovery of oxide copper. This increase in recovery is due to the formation of sulfur layers on the surface of oxide minerals. With the increase in Na_2S concentration, the recovery of oxide copper rises from 31.25% at 500 g/t to 43.02% at 750 g/t, indicating a positive effect on oxide copper recovery within this range. The coating of oxide mineral surfaces with sulphide ions from Na_2S results in the formation of a layer of copper sulphides, which enhances the adsorption capacity for the collector xanthate. This process increases the hydrophobicity of the mineral surface and improves recovery in flotation. As Na_2S concentration increases to 1000 and 1250 g/t, oxide copper recovery reaches 60.32% and 55.23%, respectively, indicating that optimal performance occurs at 1000 g/t, after which recovery declines. At concentrations above 1000 g/t of Na_2S, oxide copper recovery decreases to 55.23%, indicating a negative effect of high Na_2S concentration on flotation process efficiency. At lower concentrations, Na_2S aids in increasing the hydrophobicity of mineral particle surfaces, facilitating their adhesion to air bubbles. However, as concentration increases, the likelihood of particle coverage by sulphide ions rises. This coverage can ultimately lead to a reversion to a hydrophilic nature in mineral particles, competing with the existing collectors and causing these ions to act as depressants. Therefore, increasing Na_2S concentration may reduce the ability of collectors to adsorb onto copper particle surfaces, resulting in lower recovery of oxide copper and potentially leading to the stability of weaker froths and decreased recovery [22,27]. Ultimately, the optimal amount of Na_2S for achieving maximum overall copper recovery is around 1000 g/t, and any further increase results in a decline in recovery.



(a) (b)

Figure 11. Effect of Na_2S concentration on copper a: recovery b: grade. (pH = 11, collector concentration= 200 g/t, and MIBC concentration = 60 g/t).

3.5. Optimal conditions

Based on the results of flotation experiments at various parameter levels, the optimal values for the parameters were determined. Under the optimal conditions of pH = 11, a concentration of 100 g/t of potassium amyl xanthate and 100 g/t of sodium isopropyl xanthate, a concentration of 60 g/t of MIBC frother, and a concentration of 1000 g/t of Na_2S, with a particle size of $d_{80} = 75\mu$, the copper grade and recovery were obtained as 21.2% and 60.2%, respectively, after two stages of cleaner flotation.

4. Conclusions

This work investigated the flotation behavior of a complex copper ore from the Bouji region containing both sulphide (primarily chalcopyrite) and oxide (notably malachite) minerals, using a combination of mineralogical characterization and flotation parameter optimization. The mineralogical studies, including XRD, XRF, AAS, and SEM-WDX, confirmed the presence of copper-bearing minerals and their associations with gangue, revealing critical information about mineral liberation and intergrowths, which significantly influence flotation performance. Flotation experiments highlighted the importance of key operational parameters such as pH, collector concentration, frother concentration, and Na_2S concentration to achieving optimal recovery and grade. The results demonstrated that optimal flotation performance was achieved at pH 11, with a collector concentration of 200 g/t (equal parts potassium amyl xanthate and sodium isopropyl xanthate), 60 g/t MIBC frother, and 1000 g/t Na_2S. Under these optimized conditions, the final concentrate achieved a copper grade of 21.2% and a recovery of 60.2% after two stages of cleaner flotation. These results underscore the necessity of process customization based on ore mineralogy and confirm the potential for improving the recovery of mixed oxide-sulphide copper ores through integrated mineralogical analysis and flotation optimization. This approach not only enhances resource utilization but also provides a methodological framework for similar deposits facing processing challenges due to mineralogical complexity.

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دانشگاه صنعتی شاهرود

بررسی پرعیارسازی نمونه کانسنگ اکسیدی-سولفیدی مس به روش فلوتاسیون

حسین همدانی، آرش ثبوتی، محمد بقایی فر، بهرام رضایی*، فاطمه سادات حسینیان

دانشکده مهندسی معدن، دانشگاه صنعتی امیرکبیر، تهران، ایران.

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کلمات کلیدی

کالکوپیریت

pH

فلوتاسیون

غلظت کلکتور

غلظت Na_2S

چکیده

در این مطالعه، ابتدا نمونه معرف از مغزه‌های حفاری اکتشافی تهیه شد، سپس مطالعات شناسایی و خواص سنجی صورت گرفت، بر اساس آنالیز XRD نمونه عمدتاً از کامی‌های کوارتز، کائولینیت، موسکویت-ایلیت، کلسیت، پتاسیم فلدسپات، آلبیت، دولومیت، سیدریت و کالکوپیریت تشکیل شده است. بر اساس مطالعات میکروسکوپی نوری و میکروسکوپ الکترونی روبشی، کانی‌های سولفیدی موجود در نمونه شامل کالکوپیریت، کالکوسیت و پیریت هستند که مهم‌ترین کانی‌های مس در نمونه عمدتاً شامل کالکوپیریت، کالکوسیت و مالاکیت می‌باشند و هیچ‌گونه طلای آزاد مشاهده نشد و طلا عمدتاً به‌عنوان جایگزین در شبکه کانی‌های سولفیدی است. نتایج آنالیز AAS نشان داد که عیار مس در نمونه ۰/۹۹ درصد است. به منظور بررسی فلوتاسیون کانی‌های مس، پارامترهای موثر مانند pH، غلظت کلکتور، غلظت کفساز، غلظت سدیم سولفید و تأثیر اندازه ذرات بررسی شد. نتایج نشان داد که در شرایط بهینه pH=۱۱، غلظت ۱۰۰ گرم بر تن پتاسیم آمیل گزنتات (PAX) و ۱۰۰ گرم بر تن سدیم ایزوپروپیل گزنتات (SIPAX)، غلظت ۶۰ گرم بر تن کفساز متیل ایزوبوتیل کربینول (MIBC) و غلظت ۱۰۰۰ گرم بر تن سولفید سدیم در دانه بندی 80d =75 µ، عیار و بازیابی مس با دو مرحله فلوتاسیون به ترتیب ۲۱/۲ و ۶۰/۲ درصد بدست آمد.

✉ **نویسنده مسئول مکاتبات**: *Rezai@aut.ac.ir* (ب. رضایی)