Journal of Mining and Environment (JME) Published online

Shahrood University of Technology

Journal of Mining and Environment (JME)

Journal homepage: www.jme.shahroodut.ac.ir

Iranian Society of Mining Engineering (IRSME)

Surface Enrichment in Malachite Sulfurization Flotation: Adsorption Mechanisms and Performance Optimization

Ayman M. Ibrahim[1,2,3], Han Wang[1]*, Nazar Mekawi[3], Jaber A. Yousif[4], Emadeldin Adam[5], Alfarouq Alnoor[5], Mohammed Kabashi[5], and Dianwen Liu[1]*

1. State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Yunnan Key Laboratory of Green Separation and Enrichment of Strategic Metal Resources, Faculty of Land Resources Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, PR China
2. Department of Mining Engineering, Faculty of Engineering Science, University of Nyala, Nyala 63311, PR Sudan
3. Department of Mining Engineering, Faculty of Engineering, University of Khartoum, Khartoum 11115, PR Sudan
4. Department of Mining Engineering, Faculty of Engineering, Eldaein University, Eldaein 63312, PR Sudan
5. Department of Mining Engineering, Faculty of Engineering Science, Omdurman Islamic University, 14411, Khartoum, PR Sudan

Article Info

Received 29 April 2025
Received in Revised form 6 June 2025
Accepted 19 June 2025
Published online 19 June 2025

DOI:10.22044/jme.2025.16134.3115

Keywords

Malachite
Hydrolysis reaction
Copper–ammonium complex
Surface enrichment
Adsorption

Abstract

This work investigates the surface enrichment of malachite during sulfurization flotation to enhance copper recovery. The goal is to improve flotation efficiency by modifying malachite's surface properties through sulfurization, using sodium sulfide as the sulfurizing agent. The effects of pre-treatment reagents on flotation recovery were evaluated, focusing on their impact on the surface chemistry of malachite. The findings indicated that malachite treated with ammonium sulfate ($(NH_4)_2SO_4$) exhibited superior flotation recovery compared to ammonium phosphate ($(NH_4)_3PO_4$), achieving an optimal recovery rate of 87.5%. FESEM-EDS and ToF-SIMS analyses revealed a significant increase in sulfur species on the surface, promoting the formation of copper sulfide (CuS) films and enhancing the mineral's reactivity during flotation. Theoretical solution chemistry calculations corroborated these findings, showing that ammonium salt treatments facilitate the formation of copper-ammonium complexes, stabilizing copper ions in solution and preventing their precipitation as copper hydroxides or carbonates. By maintaining copper in a stable reactive form, these complexes improve flotation efficiency. Both theoretical calculations and experimental observations confirm that stabilizing copper ions is crucial for enhancing flotation, ensuring copper remains available for interaction with flotation reagents and ultimately, improving copper recovery. The integration of theoretical and experimental approaches enhances the understanding of the sulfurization process and provides an optimized method for improving flotation performance and copper recovery.

1. Introduction

Copper minerals such as malachite ($Cu_2(CO_3)(OH)_2$) are commonly found in large copper deposits worldwide among oxide copper ores [1, 2, 3, 4]. The demand for copper is expected to rise steadily, driven by technological advancements, rapid urbanization, the global shift toward renewable energy, and the increasing adoption of electric vehicles. However, balancing this growing demand with sustainable production and supply practices presents a complex challenge [5]. Despite the rising demand for copper, its supply faces significant challenges. Copper mining and production are resource-intensive processes that require large amounts of water, energy, and labour. Additionally, many of the world's richest copper deposits are located in remote or environmentally sensitive areas, which complicates logistics and raises concerns about sustainability. Furthermore, the declining quality of ore deposits increases both the difficulty of

---

Corresponding author: wanghankmust@126.com (H. Wang)

extraction and costs, further straining supply chains. Malachite is often associated with other copper minerals, including azurite, chrysocolla, and cuprite, which may help mitigate the resource gap caused by the depletion of copper-sulfide ores [6–11]. Flotation is widely used to process copper oxide minerals, employing chemical reagents to selectively separate valuable minerals from gangue materials [12, 13, 14]. Specifically, copper oxide flotation exploits the different surface properties of these minerals. During flotation, collectors, frothers, and modifiers help copper minerals attach to air bubbles, which then rise to the surface, carrying the valuable minerals with them [15, 16, 17]. Xanthates are commonly used as flotation collectors in mineral processing, particularly, for extracting sulfide minerals. Due to their strong interaction with sulfur atoms in these minerals, xanthates are primarily employed in the flotation of sulfide ores such as copper, lead, zinc, and nickel.

Malachite, with the formula [$CuCO_3 \cdot Cu(OH)_2$] has a strong hydrophilic surface, which complicates direct flotation with sulfur-terminated collectors [18, 19, 20]. It is usually concentrated through sulfide flotation [21], where a sulfidizing agent makes it hydrophobic, further enhancing mineral recovery with xanthate collectors. Consequently, the addition of activators can improve the stability and efficiency of the process, making flotation more cost-effective and reliable, especially in complex ore systems or challenging processing conditions [22]. Enrichment without pre-treatment can be difficult due to impurities; therefore, pre-treatment steps are typically employed to remove these impurities and enhance the effectiveness of the enrichment process. During sulfurization, additional reagents such as ammonium sulfate ($(NH_4)_2SO_4$) or ammonium phosphate ($(NH_4)_3PO_4$) are often used to enhance the flotation process. The presence of ammonium sulfate and phosphate is known to optimize interactions between mineral particles and flotation agents. Shen et al. demonstrated that the flotation behavior of malachite improves due to the formation of a dense copper sulfide film on its surface [23]. These reagents have a significant impact on the mineral surface, enhancing flotation performance and improving overall copper recovery. Sulfurization-assisted flotation is an advanced technique designed to enhance the flotation efficiency of non-sulfide minerals such as malachite. This method involves modifying the surface properties of malachite by introducing sulfur or sulfur-containing compounds, thereby increasing its compatibility with flotation processes. The effectiveness of sulfurization is critical for optimizing the flotation of copper oxide minerals [24, 25]. In the sulfurization mechanism for malachite, reagents such as sodium sulfide (Na_2S), ammonium sulfide ($(NH_4)_2S$), and sodium hydrogen sulfide (NaHS) are used to convert copper oxide into copper sulfide [26, 27, 28, 29, 30].

Hence, this paper focuses on the adsorption properties of malachite surfaces and the optimization of their enrichment using various ammonium salts. The research aims to evaluate the impact of pre-treatment on sulfurization processes and to implement necessary adjustments. To achieve this, we analyzed morphological changes using micro-flotation tests, FESEM-EDS, EPMA, Zeta potential measurements, and ToF-SIMS, along with the elemental composition and surface characteristics of malachite after the addition of $(NH_4)_3PO_4$ or $(NH_4)_2SO_4$ during the sulfurization process. Furthermore, the study investigates how ammonium salts can mitigate the inhibitory effects of excessive sodium sulfide.

2. Materials and Methods

2.1. Sample preparation

Malachite samples from Yunnan, China, were first crushed using a double-roll laboratory crusher and then ground in an agate mortar to a fine powder. The ground ore was dry-sieved to select the appropriate particle size for micro-flotation experiments. Fresh solutions of the required reagents such as ammonium sulfate ($(NH_4)_2SO_4$), ammonium phosphate ($(NH_4)_3PO_4$), sodium isobutyl xanthate (NaBX), methyl isobutyl carbinol (MIBC), and sodium sulfide (Na_2S) were prepared at optimal concentrations for the sulfurization process. These reagents were subsequently added to the flotation solution to facilitate the modification of the malachite surface and improve flotation efficiency.

2.2. Flotation experiments

Flotation experiments were conducted using an XFGC II flotation apparatus with a 40 mL cell volume. The impeller speed was maintained at 1200 rpm to ensure consistent agitation during the process, while the flotation duration was kept at 5 minutes for each test, to allow sufficient time for the mineral to separate. In each test, 0.5 g of malachite was carefully washed with deionized water (DI) to remove any impurities or fine particles that could hinder the flotation process. After flotation was completed, the foam and sink were manually collected, dried, and weighed, and the flotation recovery was calculated to determine the flotation efficiency. Each experiment was repeated three times under varying conditions to ensure reproducibility and reliability of the results. The experimental flowchart is presented in Figure 1, which illustrates the procedure and sequence of operations.

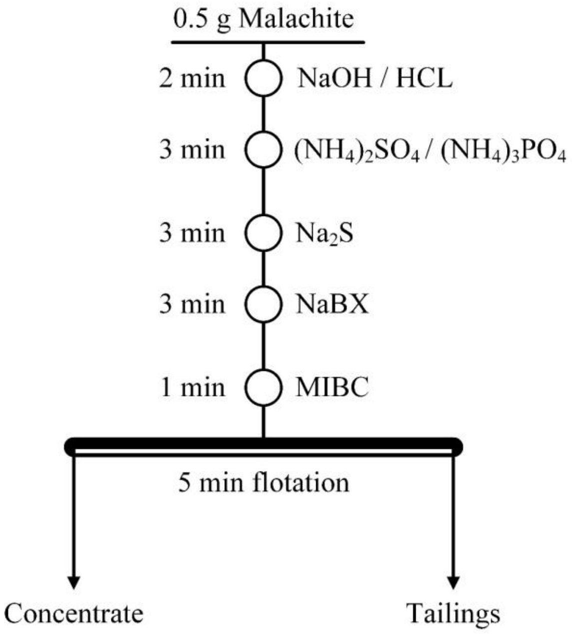

Figure 1. Flow chart of malachite flotation experiments.

2.3. ToF-SIMS analysis

ToF−SIMS IV (ION−TOF, Münster, Germany) was employed to analyze the malachite surface composition. For this analysis, malachite samples were placed directly into 40 cm^3 of reagent solution at varying concentrations and submerged for 2 hours at 25 °C. The malachite sample was affixed to a double-conducting adhesive and then moved to the device's sample loading room. The analysis region was set to 50 µm × 50 µm, with three pulse widths for each point. The samples were analyzed in negative ion mode at a 500 µm × 500 µm resolution. After testing, the malachite samples were washed with distilled water, dried using pure N_2, and analyzed via ToF−SIMS.

2.4. EPMA studies

The variation in the malachite surface before and after enhancement with ammonium salts was thoroughly examined using an EPMA−1720 Series (Shimadzu Corporation, Japan). To obtain accurate and detailed elemental information, a 15 kV accelerating voltage and a 20 nA probe current were applied during the analysis. The beam diameter was 50 µm to ensure sufficient resolution for surface imaging and elemental detection, with counting durations of 15 s for the peak and 10 s for the background. The key elements analyzed in the study included carbon (C), oxygen (O), copper (Cu), and sulfur (S), which are critical in understanding the surface modifications and the effects of ammonium salt treatment on malachite.

2.5. Zeta potential measurements

The zeta potential of malachite samples was measured at varying pH values, using a Zeta Plus analyzer (Brookhaven Instruments, USA). The sample liberation size was approximately 5 µm, and the samples were suspended in a laboratory beaker containing an electrolyte solution of 1×10^{-5} mol/L KNO_3. Fresh solutions of $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, $Na_2S{\cdot}9H_2O$ (at 2×10^{-3} mol/L), and NaBX (at 1×10^{-4} mol/L) were prepared for the experiments. 0.5 g of malachite was combined with the appropriate reagent solutions in each test. The zeta potential suspensions were agitated and measured five times at five-minute intervals. The average of these measurements was used to determine the zeta potential.

3. Results and Discussion

3.1. Influence of ammonium salts on the malachite flotation behaviour

The micro-flotation recoveries of malachite as a function of Na_2S concentration at pH 9 ± 0.05 are shown in Figure 2(a). Malachite floatability is influenced by sodium sulfide concentrations; as the concentration increases (from 0 to 2×10^{-3} mol/L), floatability improves, but it decreases beyond a certain threshold. Excessive sodium sulfide leads to an overabundance of sulfur ions in the solution, which consumes the added collector and destabilizes the sulfur layer, resulting in poor sulfurization. In contrast, ammonium sulfate more effectively enhances the surface properties of malachite compared to ammonium phosphate. The maximum flotation recovery with ammonium phosphate was approximately 79.6%, while ammonium sulfate with sodium sulfide achieved around 85.8%. This result indicates that ammonium sulfate is more effective at enhancing malachite's surface properties than ammonium phosphate. The sulfate ions in ammonium sulfate likely promote the attachment of flotation reagents, modifying the surface to increase hydrophobicity. As a result, malachite becomes more hydrophobic and is more likely to float, leading to higher flotation recoveries.

Figure 2(b) illustrates the effect of ammonium salts on malachite flotation during sulfurization, influenced by the NaBX collector. When ammonium salts were added before sulfurization, the recovery of malachite gradually increased throughout the flotation process, compared to direct sulfurization. Malachite recovery improved significantly in the ammonium sulfate pre-treatment system, rising from 48.21% to 82.69%. The highest recovery rate, 86.31%, was observed at a NaBX concentration of 8×10^{-3} mol/L, which was higher than that seen in the ammonium phosphate pre-treatment system. These results suggest that ammonium sulfate pre-treatment significantly improves the sulfurization process. Furthermore, NaBX adsorbs onto the malachite surface, forming a hydrophobic layer. However, when NaBX concentration exceeded a certain point, the increase in mineral floatability became marginal, and the recovery rate stabilized. Overall, the addition of NaBX positively impacted malachite recovery, demonstrating that both ammonium phosphate and ammonium sulfate act as effective activators, significantly enhancing floatability [31].

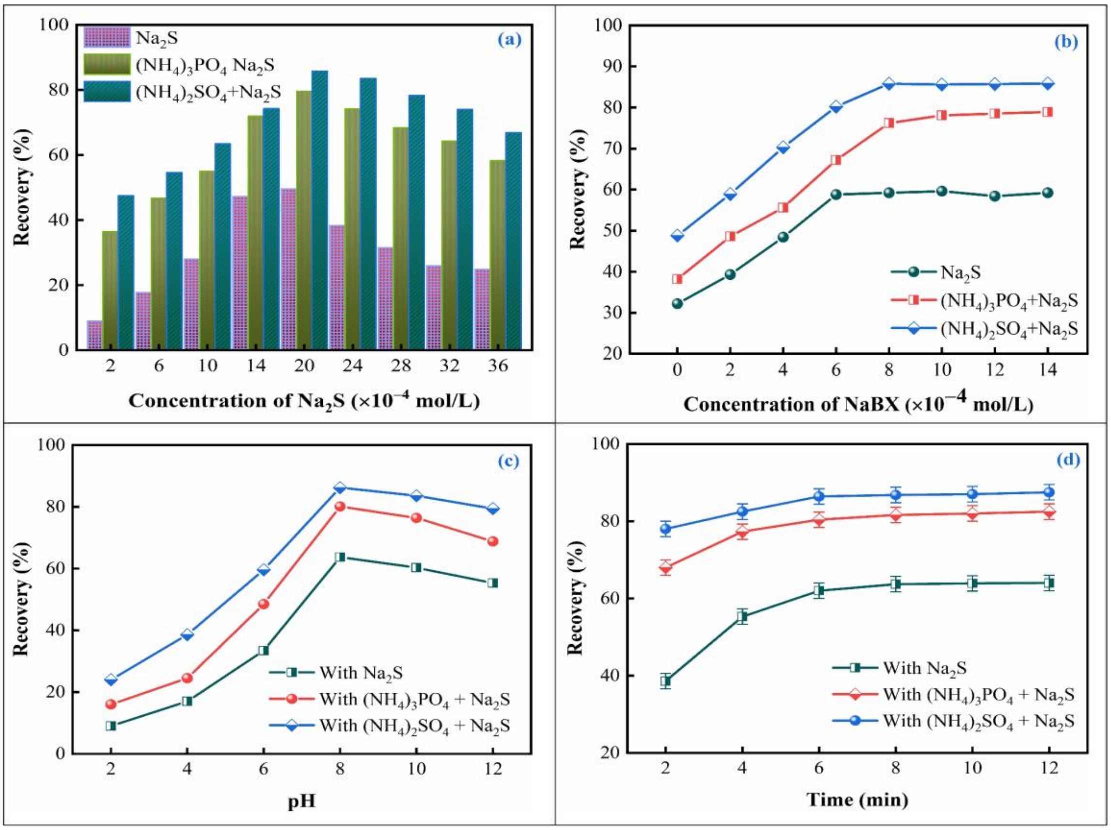

Figure 2. Micro-flotation recovery of malachite as a function of (a) Na_2S, (b) NaBX concentrations, (c) pH, and (d) time conditions.

The performance of malachite sulfurization flotation was further studied, using different ammonium salts at varying pH levels, as shown in Figure 2(c). After treatment with sodium sulfide, flotation recovery was below 20% at pH 2, indicating poor flotation under acidic conditions. However, the highest recovery, at 63.7%, occurred at pH 8.0. This variation is due to the chemical reactions between sodium sulfide and malachite, which affect the mineral's hydrophobicity and, consequently, its floatability. As pH increased, recovery slightly decreased, likely due to changes in the surface characteristics of malachite that made it less favorable for flotation at higher pH values [32]. When malachite was pretreated with ammonium salts, such as ammonium phosphate ($(NH_4)_3PO_4$) or ammonium sulfate ($(NH_4)_2SO_4$), flotation recovery improved significantly. At pH 8.0, flotation recovery reached 80.1% with ammonium phosphate and 86.2% with ammonium sulfate. These results demonstrate that ammonium salts effectively enhance malachite surface enrichment across a range of pH levels, leading to improved flotation performance compared to direct sulfurization. The data suggest that ammonium salts can activate and optimize malachite flotation, making them promising reagents for enhancing recovery in flotation processes.

Several experiments were conducted to evaluate flotation recovery over time. Figure 2(d) summarizes three tests performed from 2 to 12 minutes. In the malachite-sodium sulfide treatment, flotation recovery was initially low but gradually increased after 2 minutes, reaching a maximum of 64% at 12 minutes. The gradual increase suggests that sulfide ions initially interacted slowly with the malachite surface; however, over time, more effective sulfurization and hydrophobicity were achieved, thereby improving flotation recovery. In contrast, when ammonium phosphate and sodium sulfide were used, flotation recovery reached 82.5% at 12 minutes. Compared to direct sulfurization, ammonium phosphate modification of the malachite surface enhanced its reactivity with sodium sulfide, further supporting the beneficial effect of $(NH_4)_3PO_4$. This preconditioning step promotes sulfur adsorption, thereby facilitating the formation of a hydrophobic sulfide layer, which is essential for flotation. In the ammonium sulfate treatment system, recovery was approximately 78% at 2 minutes, increasing to 87.5% after more than 10 minutes. This suggests that ammonium sulfate performs better in sulfurization flotation due to its greater sulfurizing capacity and faster reaction kinetics. This results in more favorable surface chemistry for malachite than ammonium phosphate. The copper grade and recovery relationship improved significantly when the flotation time of all tests exceeded 6 minutes. These results indicate that the overall concentrate grade increased from 18.5% to 22.5%.

3.2. FESEM-EDS analysis

FESEM−EDS analysis was conducted to examine variations in malachite morphology. In this study, malachite was sulfurized and treated with $(NH_4)_2SO_4$ or $(NH_4)_3PO_4$ throughout the flotation process, with natural malachite used as a comparison. This analysis confirmed the presence of Cu, C, O, and S elemental compositions and the spatial distribution of these elements on the malachite surface. The surface microtopography of pure malachite, examined via elemental scanning, is shown in Figure 3, revealing only three elements, Cu, O, and C, which are inherent to malachite, with mass concentrations of 55.70%, 30.12%, and 14.18%, respectively. No sulfur (S) was detected on the surface, confirming that the malachite purity meets the required standards for analysis [Figure 3(a)].

After treatment with sodium sulfide, a new peak corresponding to sulfur was detected in the EDS spectrum, showing a mass concentration of 0.9%. This low sulfur content suggests that only a small portion of the malachite reacted with sodium sulfide, leading to partial sulfurization rather than complete surface modification. Additionally, the mass concentrations of Cu, O, and C on the treated malachite surface were 52.6%, 28.1%, and 18.4%, respectively, as shown in Figure 3(b) [32, 33]. These results indicate that the treatment reduced the copper and oxygen components on the malachite surface, likely due to oxidation and other surface interactions. The increase in carbon concentration suggests the formation of new carbon-based species. Following treatment with $(NH_4)_3PO_4$ and Na_2S, elemental mapping results revealed higher mass concentrations of Cu and S, about 53.21% and 2.85%, respectively, compared to direct sulfurization. This suggests that $(NH_4)_3PO_4$ modifies the surface chemistry, possibly by promoting a more efficient reaction or enhancing sulfur incorporation, with an increase of more than 1.95% in sulfur relative to direct sulfurization [34], as shown in Figure 4(a). Concurrently, the concentrations of C and O decreased to 17.90% and 25.04%, respectively, likely due to chemical reactions in which oxygen atoms are replaced by sulfur in the malachite structure, resulting in the loss of carbon and oxygen from the surface. In contrast, when malachite was treated with $(NH_4)_2SO_4$ and Na_2S [Figure 4(b)], ammonium sulfate introduced sulfate ions (SO_4^{2-}), which likely interacted with copper ions (Cu^{2+}), altering the surface properties and enhancing reactivity upon the addition of sodium sulfide. The results revealed a more uniform spatial distribution, with higher mass concentrations of Cu and S of 54.68% and 3.11%, respectively, suggesting a more complete surface modification. This demonstrates that ammonium sulfate significantly enhances the reactivity of malachite's surface, compared to ammonium phosphate pre-treatment. Meanwhile, the concentrations of C and O decreased to 17.48% and 24.73%, respectively, indicating the removal or transformation of carbon- and oxygen-containing species.

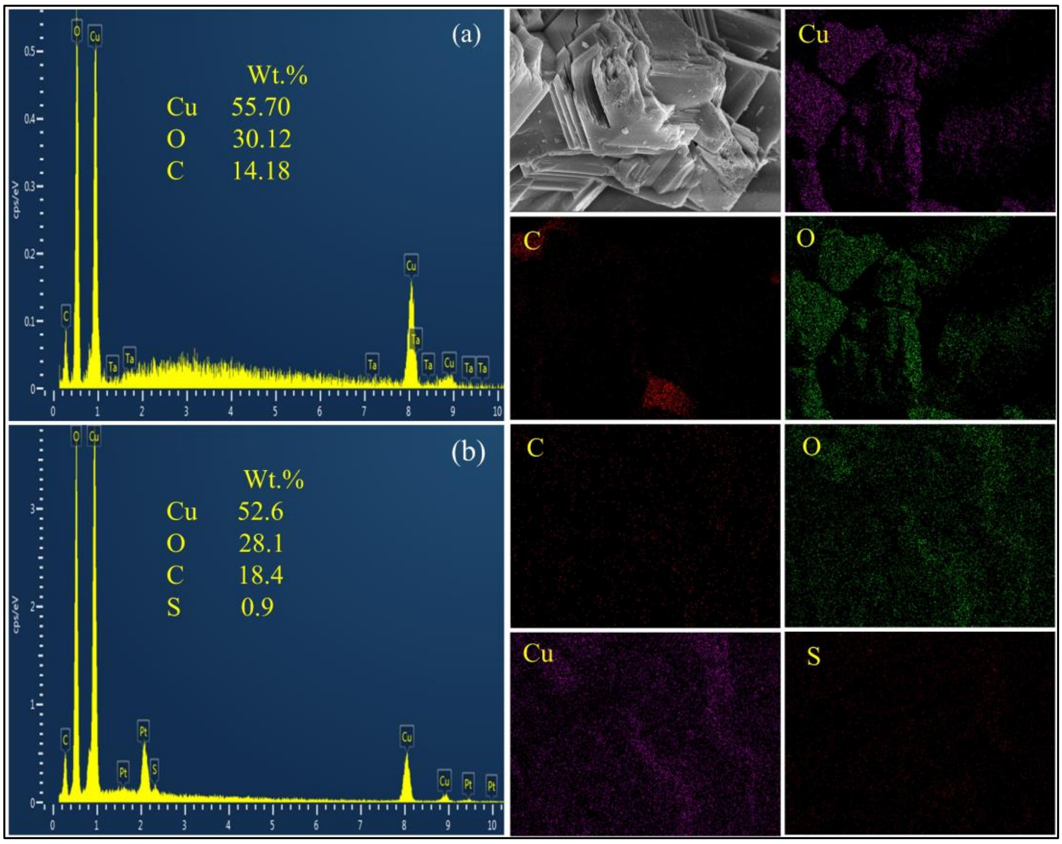

Figure 3. EDS surface scan and elements mapping of (a) pure malachite, and (b) treated with Na_2S.

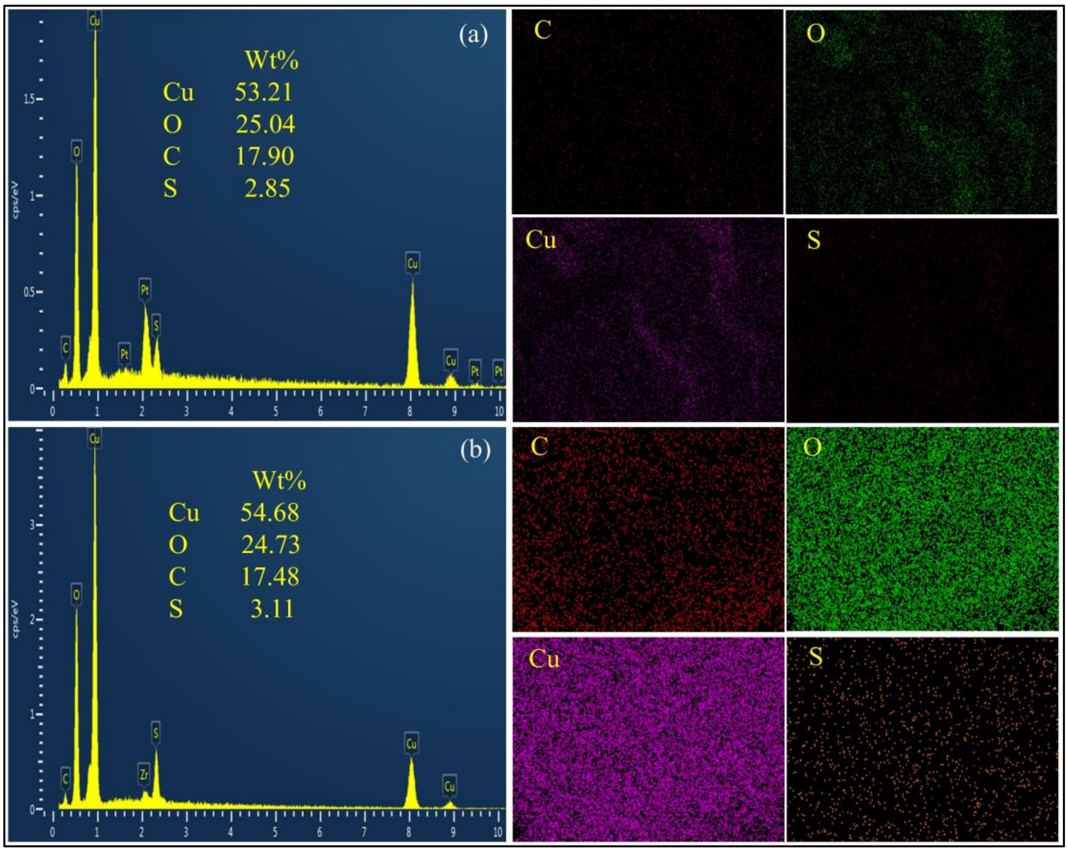

Figure 4. EDS spectra and elements mapping of malachite treated with (a) $(NH_4)_3PO_4$ + Na_2S, and (b) $(NH_4)_2SO_4$ + Na_2S.

3.3. ToF−SIMS analysis

To investigate the surface enrichment caused by the addition of appropriate concentrations of ammonium salts to the surface layer of sulfurized malachite, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was conducted. Figure 5 displays two-dimensional distributions of the fragment peaks for S^{-}, S_2^{-}, CO_3^{-}, and Cu^{+} ions on the malachite surface, comparing test conditions with and without the addition of typical ammonium salts. When malachite is treated with sodium sulfide, distinct S^{-}, S_2^{-}, CO_3^{-}, and Cu^{+} fragment ions are observed, partially covering the mineral surface. The signal intensities for these ions are relatively low, with values of (1.841e + 005), (1.087e + 005), (2.205e + 005), and (1.636e + 005), respectively, as shown in Figure 5(a). These results suggest the formation of a surface layer containing these species. However, the low intensities indicate limited surface coverage or incomplete interaction under the experimental conditions. After treatment with $(NH_4)_3PO_4$ + Na_2S [Figure 5(b)], the signal intensities for the S^{-}, S_2^{-}, CO_3^{-}, and Cu^{+} fragments were significantly higher compared to direct sulfurization. The measured intensities were ((2.140e + 005), (2.432e + 005), (4.615e + 005), and (2.179e + 005), respectively. This increase in intensity suggests that the addition of $(NH_4)_3PO_4$ enhanced the formation of these ionic species on the malachite surface. Furthermore, a larger proportion of copper oxide was converted into copper sulfide, improving the floatability of the malachite [35]. In contrast, malachite treated with $(NH_4)_2SO_4$ + Na_2S [Figure 5(c)] exhibited even higher signal intensities for the S^{-}, S_2^{-}, CO_3^{-}, and Cu^{+} fragments than those observed with $(NH_4)_3PO_4$ + Na_2S. The corresponding signal intensities were ((2.602e + 005), (7.543e + 005), (5.940e + 005), and (2.440e + 005), respectively. These values were significantly higher on the malachite surface treated with both $(NH_4)_2SO_4$ and Na_2S compared to sodium sulfide treatment alone, suggesting enhanced collector adsorption onto the surface. These results provide further evidence that $(NH_4)_2SO_4$ can prevent the formation of copper sulfide colloids during malachite sulfurization, thus promoting more optimal conditions for xanthate adsorption [36]. Moreover, ammonium ions (NH_4^{+}) likely interact with the malachite surface, promoting the reduction of Cu^{2+} to Cu^{+}, while sulfate ions (SO_4^{2-}) help stabilize Cu^{+} by modifying the local environment. Consequently, this leads to markedly increased Cu^{+} signal intensity in the ToF-SIMS analysis, indicating that $(NH_4)_2SO_4$ treatment alters the copper sulfurization state and enhances the surface reactivity of malachite.

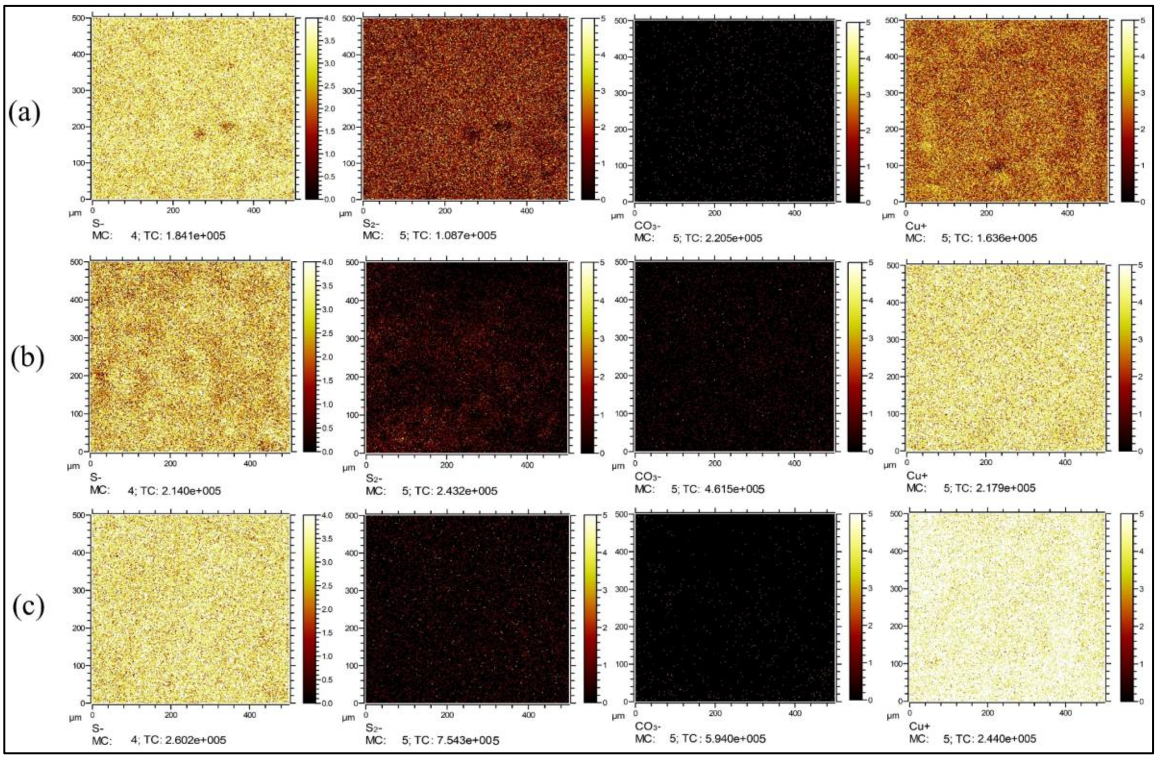

Figure 5. 2D distribution of ion on the malachite treated with (a) Na_2S, (b) $(NH_4)_3PO_4$ + Na_2S, and (c) $(NH_4)_2SO_4$ + Na_2S.

Figure 6 shows the normalized intensity of positive and negative ion fragments on the surface of malachite before and after pre-treatment with different ammonium salts. After treatment with Na_2S, the signal intensity of S^-, S_2^-, CO_3^-, and Cu^+ ionic fragments was notably high [37]. However, when treated with $(NH_4)_3PO_4$ + Na_2S, the signal intensity of S^-, S_2^-, and Cu^+ significantly increased, while the amount of CO_3^- fragments decreased, indicating a change in the surface composition. This change can be attributed to the degree of sulfurization on the mineral surface. In contrast, after treatment with $(NH_4)_2SO_4$ and Na_2S, the signal intensity of S^-, S_2^-, and Cu^+ ions gradually increased. This enhancement can be explained by the facilitated formation of sulfide-related species, with a greater proportion of copper oxide species being converted into copper sulfide species, thereby improving the floatability of malachite. Meanwhile, the CO_3^- signal intensity decreased, suggesting that sulfur species from $(NH_4)_2SO_4$ and Na_2S treatments displaced or neutralized the carbonate species on the malachite surface.

Therefore, $(NH_4)_2SO_4$ is more effective than $(NH_4)_3PO_4$ at chemisorbing onto the malachite surface due to the strong chemical affinity between sulfate ions (SO_4^{2-}) and copper ions (Cu^{2+}). As a result, sulfate ions react with copper ions on the malachite surface, forming copper sulfide species, such as CuS or Cu_2S. This reaction effectively transforms the copper component of malachite into a sulfur-rich phase, enhancing the sulfurization process and improving flotation. Additionally, the ToF-SIMS results confirmed that the normalized intensities of copper-sulfide species on the malachite surface increased after pre-treatment. This finding is consistent with the FESEM-EDS results and supports the optimized surface enrichment.

3.4. EPMA analysis

EPMA mapping was performed on pure malachite, with and without sodium sulfide treatment, to assess its effects on flotation performance, as shown in Figure 7. No sulfur was detected in the pure malachite sample; however, a distribution of Cu and O was observed on the surface, with approximately 55.47 wt.% Cu and 29.51 wt.% O [Figures 7(a1, a2, a3)], along with other elements. After treatment with sodium sulfide [Figures 7(b1, b2, b3)], the results indicate that sodium sulfide promotes the formation of copper sulfide species, slightly enhancing the flotation response [38, 39]. The elemental composition of Cu, O, and S on the surface was 57.15%, 34.78%, and 0.27 wt.%, respectively. These findings confirm the formation of copper sulfides (such as CuS or Cu_2S), indicating successful sulfurization [40].

Figure 8 presents an EPMA mapping analysis of malachite treated with different ammonium salts and sodium sulfide, exploring the role of the activation mechanism. After treatment with $(NH_4)_3PO_4$ + Na_2S (Figure 8(a1, a2, a3)), the elemental composition of Cu and S increased to 67.18 wt.% and 1.49 wt.%, respectively, while the O content decreased to 25.06 wt.%, compared to the direct sodium sulfide treatment.

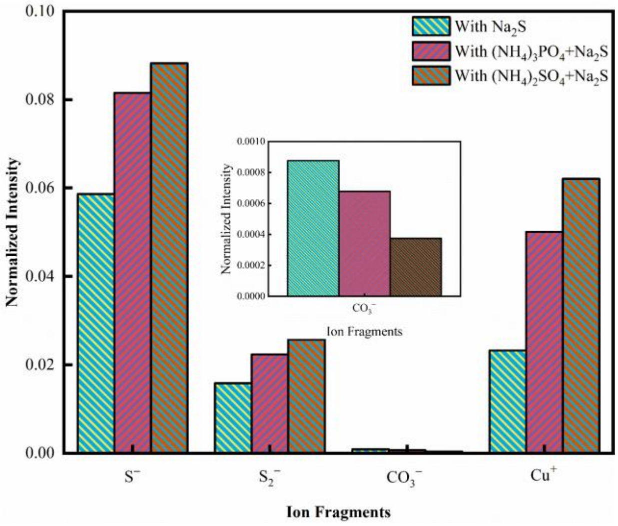

Figure 6. Normalized intensity of positive and negative ion fragments on the malachite surface.

This suggests that $(NH_4)_3PO_4$ enhances the sulfurization process by further modifying the surface chemistry and increasing sulfur incorporation [41]. The decrease in oxygen content likely indicates a sulfur replacement, which increases surface hydrophobicity and improves its suitability for flotation. Following treatment with $(NH_4)_2SO_4$ + Na_2S, the elemental composition of Cu and S rose significantly to 73.41 wt.% and 2.30 wt.%, respectively, while the O content gradually decreased to 19.86 wt.%, as shown in Figure 8(b1, b2, b3). These results confirm the positive effect of ammonium sulfate on malachite sulfurization, promoting the replacement of oxygen-based groups with sulfur and facilitating the formation of additional copper sulfide species. This enhancement improves flotation efficiency. Therefore, these findings are consistent with our previous ToF-SIMS results.

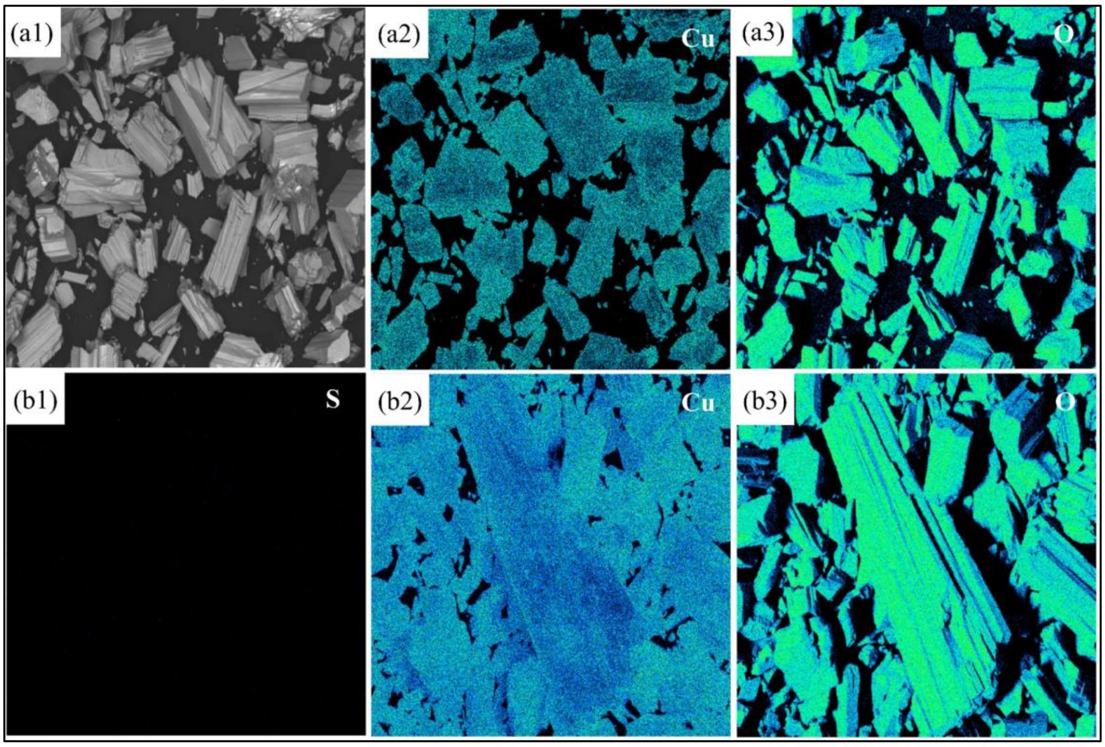

Figure 7. EPMA mappings of pure malachite (a) and (b) malachite treated with sodium sulfide.

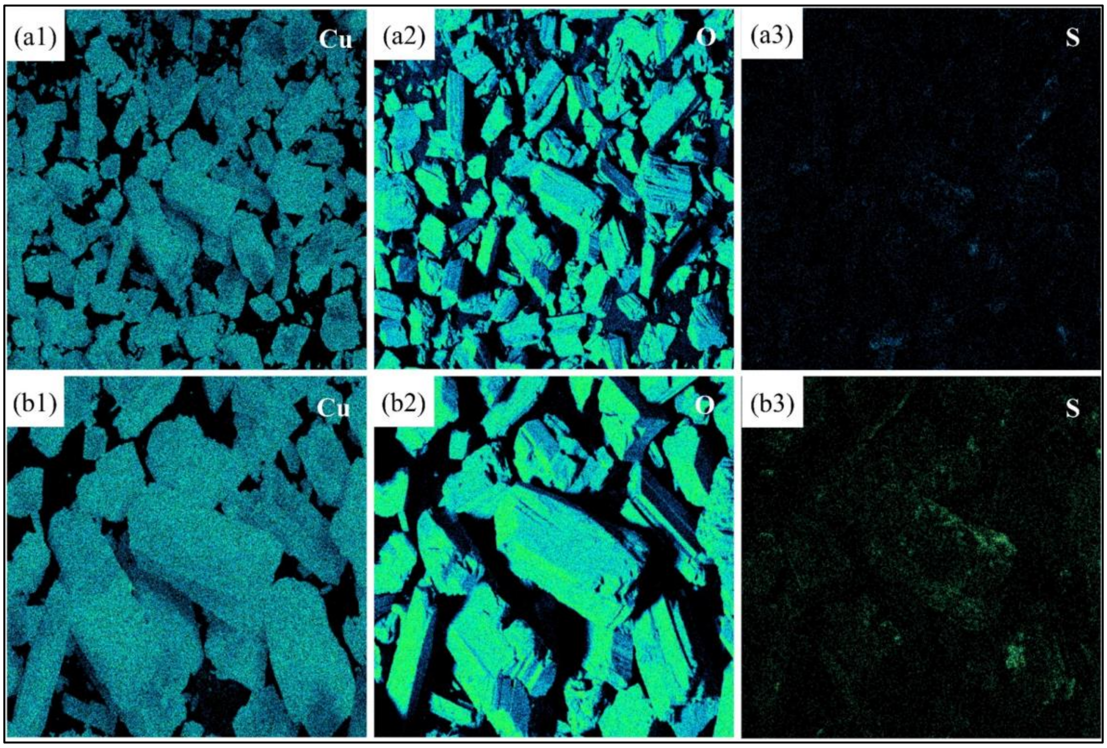

Figure 8. EPMA mappings of pure malachite treated with (a) $(NH_4)_3PO_4 + Na_2S$, and (b) $(NH_4)_2SO_4 + Na_2S$.

3.5. Zeta potential analysis

Surface zeta potentials were measured to assess the influence of ammonium phosphate ($(NH_4)_3PO_4$), ammonium sulfate ($(NH_4)_2SO_4$), and sodium sulfide (Na_2S) on the sulfurized malachite surface without the addition of a xanthate collector, as shown in Figure 9. After treatment with $(NH_4)_3PO_4$ and Na_2S, the potential difference during sulfurization was significantly reduced. At lower pH, the concentration of hydrogen ions (H^+) is higher, leading to the protonation of hydroxyl groups on the malachite surface, converting them into positively charged species, represented as ($-OH_2^+$). As the pH increases, the deprotonation of hydroxyl groups occurs, forming ($-OH^-$) species, which results in a more negative surface charge on the malachite particles. These results indicate that phosphate ions can alter the zeta potential, shifting it toward a more neutral or negative value as pH increases. Treatment of malachite with (($(NH_4)_2SO_4$) and (Na_2S) results in a more negative zeta potential. Copper ions on the malachite surface bond with sulfide ions, forming a copper sulfide (CuS) or copper-hydrosulfide layer, which exhibits a more negative charge compared to the layer formed by (($(NH_4)_3PO_4$). This indicates that sulfide ions significantly alter the surface chemistry of malachite, increasing its negative charge.

Compared with Figure 9, xanthate is introduced here to evaluate its adsorption effect, as shown in Figure 10. When NaBX is added alone, the surface potential shifts to a more negative value due to the adsorption of $RCSS^-$ [42]. However, when Na_2S and NaBX are added, the surface potential becomes even more negative and stabilizes at $pH > 8.5$. This suggested that NaBX species were adsorbed on the sulfurized mineral surface [8], which reaches equilibrium and limits further Na_2S adsorption. In contrast, with the $(NH_4)_3PO_4 + Na_2S$ treatment, the surface potential decreases and stabilizes at $pH > 9.5$, primarily due to sulfide ion adsorption. At higher pH, stabilization occurs due to the equilibrium between copper hydroxide formation and sulfide adsorption. This indicates that NaBX adsorbs onto the malachite surface, further lowering its potential. The greater downward shift in surface potential upon adding NaBX with $(NH_4)_2SO_4 + Na_2S$ treatment, compared to $(NH_4)_3PO_4$ pre-treatment, indicates a more negatively charged malachite surface after $(NH_4)_2SO_4 + Na_2S$ treatment. This stronger negative charge enhances NaBX adsorption, confirming the positive effect of $(NH_4)_2SO_4$ on NaBX uptake from the malachite surface. Thus, the increased negative charge from copper sulfide complexes strengthens the attraction of NaBX (a positively charged collector), leading to greater NaBX adsorption.

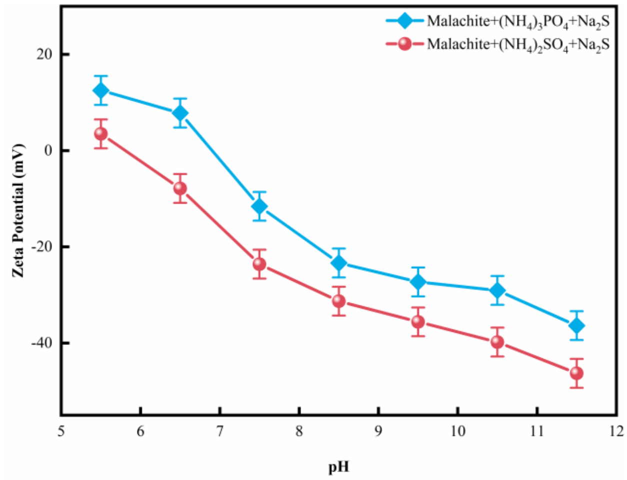

Figure 9. Zeta potential of malachite as a function of pH in the presence of various ammonium salts, and sodium sulfide during sulfurization flotation.

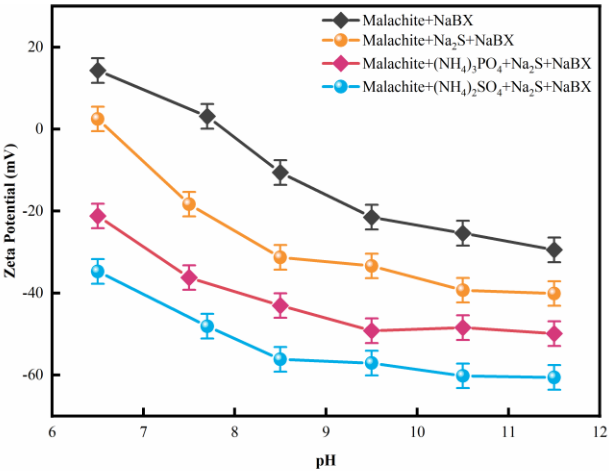

Figure 10. Zeta potential of pure malachite as a function of pH with flotation reagents.

3.6. Malachite-NH3-Na2S system

Ammonium salts are used as a sulfurization accelerator, and ammonium ion (NH_4^+) will undergo a hydrolysis reaction, as shown in Figure 11. This process leads to the dissolution of significant amounts of Cu^{2+} from the surface, resulting in numerous broken bonds. The free copper ions in the solution then react with NH_3 to form a series of copper–ammonium complexes. Meanwhile, copper on the malachite surface also interacts with the remaining NH_3 in the solution, forming a copper–ammonium complex that dissolves into the solution.

The copper-ammonia complex primarily forms as $[Cu(NH_3)]^{2+}$, $[Cu(NH_3)_2]^{2+}$, $[Cu(NH_3)_3]^{2+}$, $[Cu(NH_3)_4]^{2+}$, or $[Cu(NH_3)_5]^{2+}$, depending on the reactant concentration in the solution. This result indicates that $[Cu(NH_3)_5]^{2+}$ is produced when ammonium salts NH_4^+ are present at high concentrations [43, 44, 45]. Nevertheless, the concentrations of NH_4^+ employed in this research may not be sufficient to form $[Cu(NH_3)_5]^{2+}$. Consequently, further chemical calculations showed that $[Cu(NH_3)_5]^{2+}$ had a minimal effect on malachite flotation.

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+ \tag{1}$$

$$2NH_4^+ + 2HS^- \leftrightarrow 2NH_3 + H_2S(aq) + H_2S(g) \tag{2}$$

$$Cu^{2+} + NH_3 \rightarrow [Cu(NH_3)]^{2+} \quad \beta_1 = 1.40\times10^4 \tag{3}$$

$$Cu^{2+} + 2NH_3 \rightarrow [Cu(NH_3)_2]^{2+} \quad \beta_2 = 4.06\times10^7 \tag{4}$$

$$Cu^{2+} + 3NH_3 \rightarrow [Cu(NH_3)_3]^{2+} \quad \beta_3 = 2.96\times10^{10} \tag{5}$$

$$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} \quad \beta_4 = 4.74\times10^{12} \tag{6}$$

$$Cu^{2+} + 5NH_3 \rightarrow [Cu(NH_3)_5]^{2+} \quad \beta_5 = 8.66\times10^{12} \tag{7}$$

Where:

β_1, β_2, β_3, β_4, and β_5 represent the cumulative stability constant of the chemical reaction, respectively. According to the conservation of copper ion mass, the total copper [*TCu*] in the flotation solution was expressed by Eq. (8).

$$T_{Cu} = [Cu^{2+}] + [Cu(NH_3)]^{2+} + [Cu(NH_3)_2]^{2+} + [Cu(NH_3)_3]^{2+} + [Cu(NH_3)_4]^{2+} \tag{8}$$

$$\alpha_0 = \frac{[Cu^{2+}]}{[Cu_T]} = \frac{1}{1 + \beta_1[NH_3] + \beta_2[NH_3]^2 + \beta_3[NH_3]^3 + \beta_4[NH_3]^4} \tag{9}$$

$$\alpha_1 = \frac{[Cu(NH_3)]^{2+}}{[Cu_T]} = \beta_1[NH_3]\alpha_0 \tag{10}$$

$$\alpha_2 = \frac{[Cu(NH_3)_2]^{2+}}{[Cu_T]} = \beta_2[NH_3]^2\alpha_0 \tag{11}$$

$$\alpha_3 = \frac{[Cu(NH_3)_3]^{2+}}{[Cu_T]} = \beta_3[NH_3]^3\alpha_0 \tag{12}$$

$$\alpha_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu_T]} = \beta_4[NH_3]^4\alpha_0 \tag{13}$$

Where:

α_0, α_1, α_2, α_3, and α_4 represent the percentage of Cu^{2+}, $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, and $Cu(NH_3)_4^{2+}$, respectively.

The concentration of ammonium ions (NH_4^+) influences the behavior of copper complexes. At low ammonium concentrations, copper primarily exists as $Cu(NH_3)_n^{2+}$ species, where the specific value of 'n' is dependent on the ammonium concentration. The copper content can exist in several complex forms, including $Cu(NH_3)_4^{2+}$, $Cu(NH_3)_3^{2+}$, $Cu(NH_3)_2^{2+}$, and $Cu(NH_3)^{2+}$, respectively. Notably, the presence of ammonium in the solution affects the complexation behavior of copper, resulting in different copper-ammonia complexes depending on the concentration of ammonium.

3.7. Malachite-(NH4)3PO4 system

$(NH_4)_3PO_4{\cdot}3H_2O$ is a salt that reacts as an intermediate between a strong acid and a weak base, resulting in an aqueous solution. The results shown in Figure 12 reveal that the most advantageous component in the solution at pH 9.0 is the $[HPO_4]^{2-}$ ion. At this pH level, the phosphate radical consumes a large amount of hydrogen ions [H+], thereby accelerating the formation of copper sulfide [35]. However, this rapid formation may hinder the stable adhesion of copper sulfide to malachite, possibly because ammonium phosphate is less effective in promoting malachite sulfurization than ammonium sulfate.

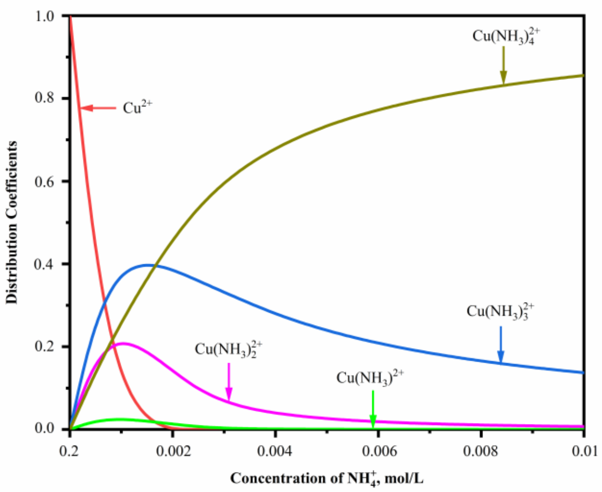

Figure 11. Distribution of Cu^{2+} and $Cu(NH_3)_n^{2+}$ in aqueous solutions as a function of ammonium concentration.

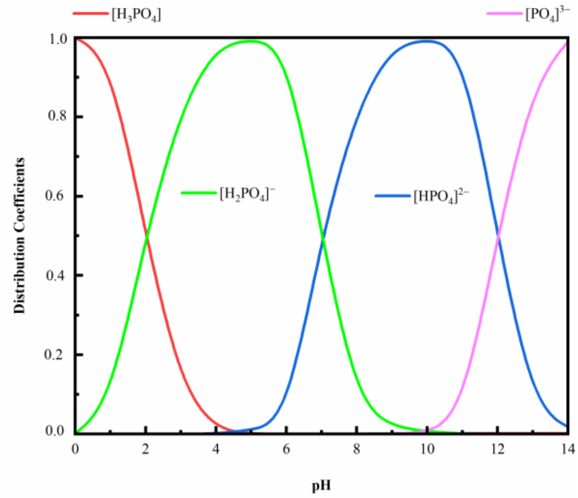

Figure 12. Distribution coefficients of phosphor species as a function of pH value.

Based on the characterization results and flotation analysis, the enrichment mechanism of malachite sulfurization can be explained as follows. Figure 13 illustrates the schematic diagram. Indeed, malachite surface enrichment can occur through a sulfurization reaction with ammonium salts. The sulfur species derived from ammonium salts react with copper ions in malachite to form copper sulfide compounds. These compounds are generated on the surface, increasing sulfur species and some active copper. As a result, this significantly enhances the enrichment of malachite on the surface.

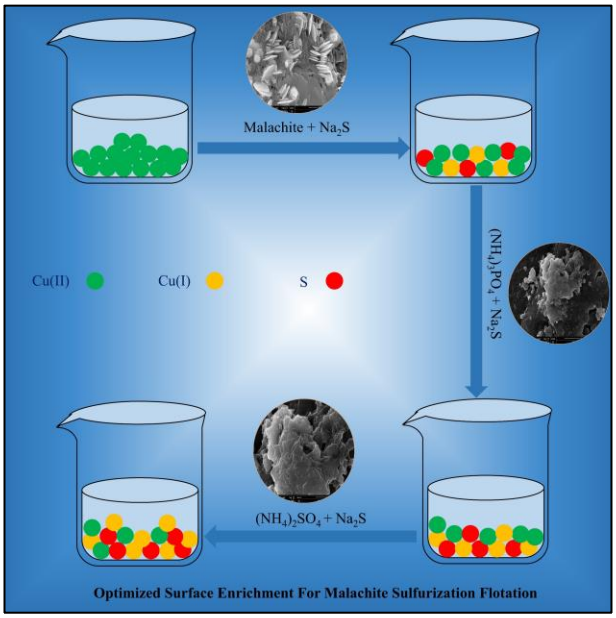

Figure 13. Schematic diagram of surface enrichment on malachite sulfurization.

4. Conclusions

This study optimized surface enrichment for malachite during sulfurization flotation. The sulfurization process modifies the malachite surface, enhancing its flotation properties by forming a sulfur layer that increases hydrophobicity and promotes affinity for air bubbles. The key conclusions from this work are:

1) Malachite flotation results showed that ammonium sulfate enhances flotation recovery more effectively than ammonium phosphate, particularly during sulfurization. NaBX further improves recovery by forming a hydrophobic layer on the malachite surface.

2) The FESEM−EDS analysis confirmed partial sulfurization of malachite with Na_2S. However, compared to $(NH_4)_3PO_4$, $(NH_4)_2SO_4$ enhanced surface reactivity. Ammonium sulfate led to more complete surface modification, with higher concentrations of Cu and S.

3) In ToF-SIMS analysis, the sulfur content detected on the malachite surface significantly increased when $(NH_4)_2SO_4$ was added to the reaction, compared to $(NH_4)_3PO_4$. This enhancement promotes the formation of copper sulfide, thereby improving surface reactivity and flotation properties.

4) In theoretical solution chemistry, sodium and ammonium ions significantly affect the copper species in flotation solutions. $Cu(NH_3)_4^{2+}$ and $Cu(NH_3)_3^{2+}$ remain stable in the malachite-ammonium system, increasing copper concentration by keeping copper in solution and preventing insoluble precipitation.

Declaration of Competing 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.

Acknowledgments

This research project was supported by the National Natural Science Foundation of China (Grant No. 52074138), Yunnan Major Scientific and Technological Projects (Grant NO. 202202AG050015), Basic research project of Yunnan Province (Grant No. 202001AS070030 and 202201AU070099), and Caiyun Postdoctoral Program (Grant No. CG25066E003A).

References

[1]. Ndoro, T., & Witika, L. (2017). A Review of the Flotation of Copper Minerals. *International Journal of Sciences: Basic and Applied Research, 34*(2), 145–165.

[2]. Bulatovic, S. (2007). Flotation of oxide copper and copper cobalt ores. *Handbook of flotation reagents: chemistry, theory and practice, 2*, 47–65.

[3]. Jin, X., Cui, S., Sun, S., Gu, X., Li, H., & Liu, X. (2019). The preparation of a bio-polyelectrolytes based core-shell structure and its application in flame retardant polylactic acid composites. *Composites Part A: Applied Science and Manufacturing, 124*, 105485.

[4]. Khoso, S., Gao, Z., & Sun, W. (2021). Recovery of high-grade copper concentrate from sulfur-rich porphyry ore using tricarboxystarch micromolecule as pyrite depressant. *Minerals Engineering, 168*(4), 106916.

[5]. Yuan, Z., Ji, H., Zhang, L., & Liu, L. (2023). Sustaining the United States' copper resource supply. *Journal of Cleaner Production, 429*(6), 139636.

[6]. Banza, A., & Gock, E. (2003). Mechanochemical processing of chrysocolla with sodium sulphide. *Minerals Engineering, 16*(12), 1349–1354.

[7]. Chen, X., Peng, Y., & Bradshaw, D. (2014). The separation of chalcopyrite and chalcocite from pyrite in cleaner flotation after regrinding. *Minerals Engineering, 58*, 64–72.

[8]. Zhang, Q., Wen, S., Feng, Q., & Zhang, S. (2020). Surface characterization of azurite modified with sodium sulfide and its response to flotation mechanism. *Separation and Purification Technology, 242*, 116760.

[9]. Feng, Q., Zhao, W., Wen, S., & Cao, Q. (2017). Copper sulfide species formed on malachite surfaces in relation to flotation. *Journal of Industrial and Engineering Chemistry, 48*, 125–132.

[10]. Zuo, Q., Wu, D., Cao, J., Wang, Z., Shi, Y., & Huang, L. (2022). A DFT-based method to determine the ammonium-induced activation and sulfidation pathway of tenorite. *Journal of the Taiwan Institute of Chemical Engineers, 132*(2), 104221.

[11]. Yin, Z., Sun, Q., Li, D., Tang, Y., Fu, Y., & Yao, J. (2019). Mechanism and application on sulphidizing flotation of copper oxide with combined collectors. *Transactions of Nonferrous Metals Society of China (English Edition), 29*(1), 178–185.

[12]. Canpolat, G., & Ziyadanoğullari, R. (2023). Recovery of Copper From Complex Copper Oxide Ore by Flotation and Leaching Methods. *Advanced Physical Research, 5*(2), 103–116.

[13]. Bai, X., Wen, S., Feng, Q., Liu, J., & Lin, Y. (2019). Utilization of high-gradient magnetic separation–secondary grinding–leaching to improve the copper recovery from refractory copper oxide ores. *Minerals Engineering, 36*, 77–80.

[14]. Zhang, Q., Wen, S., Feng, Q., & Wang, H. (2022). Enhanced sulfidization of azurite surfaces by ammonium phosphate and its effect on flotation. *International Journal of Minerals, Metallurgy and Materials, 29*(6), 1150–1160.

[15]. Rao, & Ramachandra, S. (2013). Surface chemistry of froth flotation. 2nd ed. *Springer Science & Business Media,* 385–575.

[16]. Bulatovic, S. (2007). Handbook of flotation reagents: chemistry, theory and practice: Volume 1: flotation of sulfide ores. *Elsevier*, *1*, 45–129.

[17]. Wills, B., & Finch, J. (2015). Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery. *Butterworth-Heinemann*, *8*, 285–374.

[18]. Rao, X., Zhang, C., Sun, W., Chen, J., & Zhang, H. (2025). Malachite sulfidation flotation mechanism: Cu-S co-deposition insights. *Separation and Purification Technology, 364*, 132476.

[19]. Cecile, J., Cruz, M., Barbery, G., & Fripiat, J. (1981). Infrared spectral study of species formed on malachite surface by adsorption from aqueous salicylaldoxime solution. *Journal of Colloid And Interface Science, 80*(2), 589–597.

[20]. Liu, Y., Fu, X., Sun, W., & Yue, T. (2025). Application and interaction mechanisms of sodium methyl-phosphonate sulfonate as novel selective depressant in the flotation separation of dolomite from malachite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 719*, 137033.

[21]. Wu, D., Ma, W., Wen, S., Deng, J., & Bai, S. (2017). Enhancing the sulfidation of smithsonite by superficial dissolution with a novel complexing agent. *Minerals Engineering, 114*, 1–7.

[22]. Yu, X., Yin, Z., Chen, Y., Shen, P., Wang, H., & Mao, Y. (2024). Experimental and DFT study of modified malachite with 2,5-dimercapto-1,3,4-thiadiazole and its response to sulfidization-xanthate behavior. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 693*, 134057.

[23]. Shen, P., Liu, D., Zhang, X., Jia, X., Song, K., & Liu, D. (2019). Effect of $(NH_4)_2SO_4$ on eliminating the depression of excess sulfide ions in the sulfidization flotation of malachite. *Minerals Engineering, 137*, 43–52.

[24]. Castro, S., Goldfarb, J., & Laskowski, J. (1974). Sulphidizing reactions in the flotation of oxidized copper minerals, I. Chemical factors in the sulphidization of copper oxide. *International Journal of Mineral Processing,* 1(2), 141–149.

[25]. Castro, S., Soto, H., Goldfarb, J., & Laskowski, J. (1974). Sulphidizing reactions in the flotation of oxidized copper minerals, II. Role of the adsorption and oxidation of sodium sulphide in the flotation of chrysocolla and malachite. *International Journal of Mineral Processing, 1*(2), 151–161.

[26]. Lee, K., Archibald, D., Mclean, J., & Reuter, M. (2009). Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Minerals Engineering, 22*(4), 395–401.

[27]. Zhou, R., & Chander, S. (1993). Kinetics of sulfidization of malachite in hydrosulfide and tetrasulfide solutions. *International Journal of Mineral Processing, 37*(3), 257–272.

[28]. Park, K., Park, S., Choi, J., Kim, G., Tong, M., & Kim, H. (2016). Influence of excess sulfide ions on the malachite-bubble interaction in the presence of thiol-collector. *Separation and Purification Technology,* 168, 1–7.

[29]. Yu, X., Yu, B., Wang, H., Shen, P., & Liu, D. (2024). Evolution of sulfur species on malachite surfaces in the presence of calcium and magnesium ions and implications for xanthate flotation. *Advanced Powder Technology, 35*(7), 104538.

[30]. Zhang, Q., Wen, S., Zuo, Q., & Feng, Q. (2023). Density functional theory calculation of catalytic sulfidization on the azurite (0 1 1) surface by ammonium salts and its effect on flotation. *Separation and Purification Technology, 309*, 122993.

[31]. Liu, R., Liu, Z., Li, J., Ao, S., Pei, B., & Liu, D. (2020). Reexamining the Role of Ammonium Ions in the Sulfidization, Xanthate-Flotation of Malachite. *Minerals, 10*(6), 537.

[32]. Qiu, Z., Fang, J., Liu, D., He, H., Peng, L., & Qin, S. (2024). Flotation activation mechanism of trithiocyanuric acid to malachite. *Advanced Powder Technology, 35*(6), 104469.

[33]. Cai, J., Su, C., Yu, X., Peng, R., Liu, R., Zhang, X., Shen, P., & Liu, D. (2022). Understanding the mechanism for promoting azurite sulfurization with ammonium sulfate. *Minerals Engineering, 177*, 107368.

[34]. Shen, P., Liu, D., Xu, X., Jia, X., Zhang, X., & Song, K. (2020). Effects of ammonium phosphate on the formation of crystal copper sulfide on chrysocolla surfaces and its response to flotation. *Minerals Engineering*, *155,* 106300.

[35]. Ibrahim, AM., Jia, X., Su, C., Cai, J., Shen, P., & Liu, D. (2022). Effect of Ammonium Sulfide on Sulfidization Flotation of Malachite. *Minerals, 12*(10), 1–14.

[36]. Cai, J., Su, C., Ma, Y., Yu, X., Peng, R., Li, J., Shen, P., & Liu, D. (2022). Role of ammonium sulfate in sulfurization flotation of azurite: Inhibiting the formation of copper sulfide colloid and its mechanism. *International Journal of Mining Science and Technology, 32*(3), 575–584.

[37]. Lu, W., Wen, S., Liu, D., Wang, H., & Feng, Q. (2023). A novel method for improving sulfidization xanthate flotation of malachite: Copper–ammonium synergistic activation. *Applied Surface Science*, *618*, 156660.

[38]. Jia, X., Song, K., Cai, J., Su, C., Xu, X., Ma, Y., & Liu, D. (2023). Effect of oxygen and sodium sulfide on flotation of cuprite and its modification mechanism. *Transactions of Nonferrous Metals Society of China (English Edition), 33*(4), 1233–1243.

[39]. Ibrahim, AM., Wang, H., Yousif, J., Elhadi, M., Shen, P., & Liu, D. (2025). Improved activation of malachite sulfurization flotation by thiourea's $(CS(NH_2)_2)$: Performance and mechanism study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 705*, 135643.

[40]. Liu, R., Liu, D., Li, J., Li, J., Liu, Z., Jia, X. (2020). Sulfidization mechanism in malachite flotation: A heterogeneous solid-liquid reaction that yields Cu_xS_y phases grown on malachite. *Minerals Engineering, 154*, 106420.

[41]. Ibrahim, AM., Jia, X., Cai, J., Su, C., Yu, X., Zheng, Q., & Liu, D. (2023). Role of ammonium phosphate in improving the physical characteristics of malachite sulfidation flotation. *Physicochemical Problems of Mineral Processing, 59*(1), 1–13.

[42]. Yu, X., Shen, P., Yin, Z., Wang, L., Wang, H., & Liu, D. (2023). Surface modification of malachite using DMTD and its effect on xanthate adsorption. Colloids and Surfaces A: Physicochemical and Engineering Aspects, *679*, 132560.

[43]. Shen, P., Dan, L., Zhang, X., Jia, X., Song, K., & Liu, D. (2019). Effect of $(NH_4)_2SO_4$ on eliminating the depression of excess sulfide ions in the sulfidization flotation of malachite. *Minerals Engineering, 137*, 43–52.

[44]. Wang, C., Sun, L., Wang, Q., Wang, Y., Cao, Y., & Wang, X. (2022). Adsorption mechanism and flotation behavior of ammonium salt of N-Nitroso-N-phenylhydroxyamine on malachite mineral. *Applied Surface Science*, *583*, 152489.

[45]. Margl, P., & Ziegler, T. (1999). Solvation of Cu^{2+} in Water and Ammonia. Insight from Static and Dynamical Density Functional Theory. *The Journal of Physical Chemistry A, 103*(48), 9693–9701.

انجمن مهندسی معدن ایران

نشریه مهندسی معدن و محیط زیست

نشانی نشریه: www.jme.shahroodut.ac.ir

دانشگاه صنعتی شاهرود

غنی‌سازی سطح در فلوتاسیون سولفوریزاسیون مالاکیت: مکانیسم‌های جذب و بهینه‌سازی عملکرد

ایمان ام. ابراهیم[۱،۲،۳]، هان وانگ[۱*]، نزار مکاوی[۳]، جابر ای. یوسف[۴]، عمادالدین آدم[۵]، الفاروق النور[۵]، محمد کباشی[۵] و دیانون لیو[۱]

۱ .آزمایشگاه کلیدی ایالتی بهره‌برداری پاک از منابع فلزی غیرآهنی پیچیده، یون‌نان آزمایشگاه کلیدی جداسازی سبز و غنی‌سازی منابع فلزی استراتژیک، دانشکده مهندسی منابع زمین، دانشگاه علوم و فناوری کونمینگ، کونمینگ ۶۵۰۰۹۳، یون‌نان، جمهوری خلق چین
۲ .گروه مهندسی معدن، دانشکده علوم مهندسی، دانشگاه نیالا، نیالا ۶۳۳۱۱، جمهوری خلق سودان
۳ .گروه مهندسی معدن، دانشکده مهندسی، دانشگاه خارطوم، خارطوم ۱۱۱۱۵، جمهوری خلق سودان
۴ .گروه مهندسی معدن، دانشکده مهندسی، دانشگاه الداین، الداین ۶۳۳۱۲، جمهوری خلق سودان
۵. گروه مهندسی معدن، دانشکده علوم مهندسی، دانشگاه اسلامی امدورمان، ۱۴۴۱۱، خارطوم، جمهوری خلق سودان

اطلاعات مقاله

تاریخ ارسال: ۲۰۲۵/۰۴/۲۹
تاریخ داوری: ۲۰۲۵/۰۶/۰۶
تاریخ پذیرش: ۲۰۲۵/۰۸/۱۹

DOI: 10.22044/jme.2025.16134.3115

کلمات کلیدی

مالاکیت
واکنش هیدرولیز
کمپلکس مس-آمونیوم
غنی‌سازی سطحی
جذب

چکیده

این کار به بررسی غنی‌سازی سطحی مالاکیت در طول فلوتاسیون سولفوریزاسیون برای افزایش بازیابی مس می‌پردازد. هدف، بهبود راندمان فلوتاسیون با اصلاح خواص سطحی مالاکیت از طریق سولفوریزاسیون، با استفاده از سولفید سدیم به عنوان عامل سولفورساز است. اثرات واکنشگرهای پیش تصفیه بر بازیابی فلوتاسیون، با تمرکز بر تأثیر آنها بر شیمی سطح مالاکیت، ارزیابی شد. یافته‌ها نشان داد که مالاکیت تصفیه شده با سولفات آمونیوم ((NH4)2SO4) در مقایسه با فسفات آمونیوم ((NH4)3PO4) بازیابی فلوتاسیون بهتری نشان می‌دهد و به نرخ بازیابی بهینه ۸۷.۵٪ دست می‌یابد. آنالیزهای FESEM-EDS و ToF-SIMS افزایش قابل توجهی در گونه‌های گوگرد روی سطح را نشان دادند که باعث تشکیل لایه‌های نازک سولفید مس (CuS) و افزایش واکنش‌پذیری این ماده معدنی در طول فلوتاسیون می‌شود. محاسبات نظری شیمی محلول، این یافته‌ها را تأیید کرد و نشان داد که تیمارهای نمک آمونیوم، تشکیل کمپلکس‌های مس-آمونیوم را تسهیل می‌کنند، یون‌های مس را در محلول تثبیت می‌کنند و از رسوب آنها به صورت هیدروکسیدهای مس یا کربنات‌ها جلوگیری می‌کنند. این کمپلکس‌ها با حفظ مس در یک فرم واکنش‌پذیر پایدار، راندمان شناورسازی را بهبود می‌بخشند. هم محاسبات نظری و هم مشاهدات تجربی تأیید می‌کنند که تثبیت یون‌های مس برای افزایش شناورسازی، تضمین در دسترس ماندن مس برای تعامل با معرف‌های شناورسازی و در نهایت، بهبود بازیابی مس، بسیار مهم است. ادغام رویکردهای نظری و تجربی، درک فرآیند گوگردسازی را افزایش می‌دهد و روشی بهینه برای بهبود عملکرد شناورسازی و بازیابی مس ارائه می‌دهد..

نویسنده مسئول مکاتبات: *wanghankmust@126.com* (ه. وانگ)