

Article

Reexamining the Role of Ammonium Ions in the Sulfidization, Xanthate-Flotation of Malachite

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Abstract: Ammonium ions have positive effects on the sulfidization flotation of malachite; however, the underlying mechanisms remain poorly understood. In the present work, micro-flotation tests, field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and solution analysis for ammonium nitrogen were carried out. The flotation results showed positive effects of ammonium on the sulfidization flotation of malachite. Macroscopically, the sulfidized malachite produced with ammonium exhibited a darker color than that without ammonium, whereas the opposite appeared to be true for their corresponding residual liquids. FESEM images highlighted the larger particle size and higher converge density of the sulfidization product when the presence of ammonium. Furthermore, XPS results indicated a higher sulfur concentration on malachite surfaces when the presence of ammonium. XRD results showed that $\text{Cu}_{31}\text{S}_{16}$ (djurleite) and Cu_7S_4 (anilite) comprised the sulfidization products, regardless of the presence or absence of ammonium. However, neither EDS nor XPS analysis showed nitrogen on malachite surfaces; moreover, the residual-ratio results for ammonium nitrogen clearly demonstrated that most ammonium continued to be held in solution before and after malachite sulfidization. Based on these findings, we inferred that ammonium ions may mediate the nucleation and growth of sulfidization product during malachite sulfidization, rendering larger sulfidization product particles. The larger size of sulfidization products may result in a darker, stabler and denser sulfidization product coating layer, and then may reduce the generation of colloidal copper sulfide in the residual liquids. Ultimately, ammonium facilitates better performance of sulfidization flotation of malachite.

Keywords: malachite; sulfidization; flotation; ammonium ions; FESEM

1. Introduction

Sulfidization converts the surface of oxide minerals of base metals into their sulfide counterparts, and then greatly improves the flotation performances [1–4]. It is obvious that the sulfidization of oxide minerals is a phase-transition process [5–8]. Thus, sulfidization process involves dissolution, diffusion, adsorption and chemical reaction [9]. In this communication, research and practice have shown that ammonium ions can further enhance the sulfidization flotation of copper oxide minerals [10–13], and eliminate the depression of malachite with excess sulfide ions to some degree [14]. In addition, recent studies have demonstrated that ammonium ions can also enhance smithsonite (ZnCO_3) sulfidization and improve its flotation performance [15,16].

Previously, Zhang et al. [10] concluded that ammonium sulfate played multiple significant roles in the sulfidization flotation of malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$), including: (1) catalytic effect, i.e., accelerating the rate and increasing the degree of sulfidization; (2) stability effect, i.e., rendering the sulfidization product layer more stable; (3) hydrophobic effect, i.e., improving the adsorption rate and adsorption ability of xanthate on sulfidized malachite surfaces, thereby making the malachite surfaces more hydrophobic. Recently, Wu et al. [11] studied the effect of ammonium ions on the sulfidization flotation of malachite using X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS), discovering that the concentration of sulfur on malachite surfaces treated with sulfide ions and ammonium ions was higher than that of malachite surfaces treated with sulfide ions alone. More recently, Feng et al. [12] also confirmed the enhancement of sulfur concentration on the malachite surfaces by ammonium ions, based on XPS analysis and sulfur residual concentration data.

Indeed, these researchers have gained some important insights into the role of ammonium ions on the sulfidization and flotation of malachite [10–14]. However, the underlying mechanisms remain poorly understood. It is clear that understanding the sulfidization mechanism of malachite is required to determine the action mechanism of ammonium ions on malachite sulfidization. However, most of the previous studies have only focused on the adsorption of sulfide/hydrosulfide ions on mineral surfaces and ignored the subsequent chemical reaction process [17]. Based on density functional theory (DFT) calculations, Wu et al. [18] concluded that ammonium could be adsorbed on the malachite surface, and then could enhance the adsorption of sulfide on malachite surfaces, thereby improving the sulfidization flotation; a similar standpoint was proposed by Feng et al. [12], according to solution calculations. Nevertheless, the DFT calculations overlook the impact of water, which has been proven to have a significant effect on the calculation results [19,20]; the thermodynamic data of copper species in aqueous solution were used as those at the malachite–aqueous solution interface [12]. However, more importantly, there continues to be no empirical evidence that ammonium ions can be adsorbed on the malachite surfaces before and after sulfidization.

On the other hand, the information on the morphology, crystal phase, etc., of sulfidized malachite produced with ammonium is still limited. Overall, this topic does need to be reexamined. In this communication, two primary questions still require elucidation before the mechanism can be understood:

1. What are the actions of ammonium during malachite sulfidization?
2. What are the differences between the sulfidized malachite produced with and without ammonium?

In the present work, we attempted to answer these two questions. In this regard, microflotation tests, field emission scanning electron microscopy (FESEM), EDS, XPS, X-ray diffraction (XRD) and solution analysis for ammonium nitrogen were carried out. Our results challenge the previous standpoint and provide new insights into the role of ammonium ions in the sulfidization flotation of malachite.

2. Materials and Methods

2.1. Mineral and Reagents

A high-purity malachite sample was ground in an agate mortar and then screened to obtain a size fraction of 38–75 μm for use in this work. X-ray fluorescence result shows that the sample contained 53.91 wt% Cu, indicating a purity of 93.7% $\text{Cu}_2(\text{OH})_2\text{CO}_3$; and the main impurity is aluminosilicate mineral.

$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was used as a sulfidizing agent, and $(\text{NH}_4)_2\text{SO}_4$ served as an ammonium source. In the flotation tests, the pulp pH was adjusted by NaOH and HCl. All the aforementioned reagents were of analytical purity (AR) grade. Industrial butyl xanthate (NaBX) was used as a collector. All aqueous solutions were prepared with deionized water.

2.2. Flotation Tests

To investigate the effects of ammonium ions on the sulfidization flotation of malachite, flotation tests were carried out in a 50 mL modified Hallimond tube as showed in Figure S1. Prior to flotation, the pulp was prepared by dispersing 0.5 g malachite sample in a known volume of deionized water in a 50 mL beaker. After being stirred for 1 min, various flotation reagents were injected into the pulp in turn: $(\text{NH}_4)_2\text{SO}_4$ (if needed, stirring for 3 min), Na_2S (stirring for 3 min), pH regulators (stirring for 1 min) and NaBX (stirring for 3 min). After treatment, the 50 mL pulp was moved to the flotation tube to float. Finally, the floating and sunken materials were collected, dried and weighed to calculate the flotation recovery. Each test was carried out three times and their average value and standard deviation are presented.

2.3. Characterization

The sulfidization treatment of sample for characterization was same as that for flotation tests: after being stirred for 1 min, $(\text{NH}_4)_2\text{SO}_4$ (if needed) and Na_2S solutions were injected into the pulp in sequence. After sulfidization, the sample was washed with deionized water thrice and dried in a vacuum-drying oven. XPS spectra were recorded by the use of a PHI5000 Versa Probe II (Al $K\alpha$ X-ray source; ULVAC-PHI, Kanagawa, Japan). The C1s peak at 284.8 eV was used for a charge correction reference. FESEM-EDS analyses were carried out using a Nova NanoSEM 450 field emission electron microscope equipped with an energy dispersive spectrometer (EDS, Oxford, London, UK); before analyses, the samples were deposited with platinum on the surfaces.

The crystal phase of sulfidization product was determined using an X'Pert³ Powder XRD system (Malvern Panalytical, Almelo, The Netherlands) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$; scanning speed: $0.2^\circ/\text{s}$). The sulfidization product samples for XRD analyses were prepared using the method of our previous work [8].

2.4. Analysis of Ammonium Ion Actions

The ammonium nitrogen concentrations in solution were determined by Nessler's reagent colorimetric method. Experiments were carried out in a thermostatic water bath at 298.15 K. For the treatment with ammonium ions alone, 0.5 g malachite was added into deionized water; after agitation for 1 min, ammonium sulphate solution with the concentration of 10^{-3} M NH_4^+ was added; after treatment for 3 min, 10 mL of the resulting solution was sampled and filtered; and the passed solution was analyzed for residual ammonium. For the treatment with ammonium ions and sulfide ions, a $5 \times 10^{-4} \text{ M Na}_2\text{S}$ solution was further added into the mineral suspension that had been treated with ammonium solution as stated above; after sulfidization for 3 min, a liquid sample obtained by filtering was analyzed. The residual ratio (R) of ammonium nitrogen in solution was expressed as

$$R = \frac{C}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial ammonium nitrogen concentration, determined by Nessler's reagent colorimetric method to be $0.964 \times 10^{-3} \text{ M}$; and C is the final ammonium nitrogen concentration after malachite particles interacted with the reagent solution.

The solid-to-liquid ratio was kept at 1:100 after the addition of reagents. Each test was carried out thrice, and their mean value and standard deviation were plotted.

3. Results and Discussion

3.1. Flotation Tests

As depicted in Figure 1a, the recoveries of sulfidized malachite without and with ammonium both increased with increasing NaBX concentration. More importantly, recovery for sulfidized malachite

with ammonium was higher over the entire range of NaBX concentrations than for sulfidized malachite without ammonium. As shown in Figure 1b, sulfidized malachite has a higher flotation rate in the presence of ammonium. These results indicated the positive effects of ammonium on the sulfidization flotation of malachite. Previously, Park et al. [21] had also observed that the average recovery of malachite sulfidized with $(\text{NH}_4)_2\text{S}$ appeared slightly higher than that sulfidized with Na_2S .

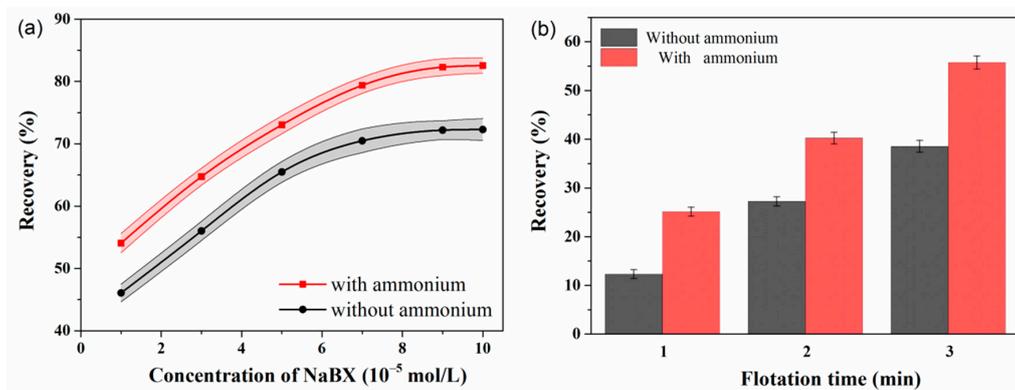


Figure 1. (a) Flotation recovery of sulfidized malachite with and without ammonium as a function of NaBX concentration, the flotation time was 10 min. (b) Flotation recovery of sulfidized malachite with and without ammonium as a function of flotation time. $C(\text{Na}_2\text{S}) = 5 \times 10^{-4}$ M, $C(\text{NH}_4^+) = 10^{-3}$ M, $C(\text{NaBX}) = 1 \times 10^{-4}$ M, $\text{pH} = 10.0 \pm 0.05$.

3.2. Characterization of Sulfidized Malachite

3.2.1. Macroscopic Observation

Figure 2a–e show photographs of malachite particles treated at different conditions. The unsulfidized malachite suspension was light green (Figure 2a). After sulfidization, the particles turned darker (Figure 2b–e). However, at the same sodium sulfide concentration, the sulfidized sample with ammonium exhibited a darker color than the sulfidized sample without ammonium (Figure 2b vs. Figure 2d; Figure 2c vs. Figure 2e).

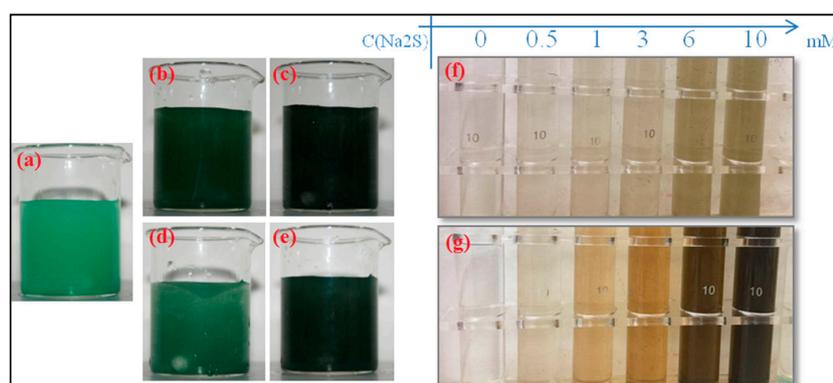


Figure 2. (a–e) Malachite particles in deionized water, after treatment with (a) deionized water alone, (b) 5×10^{-4} M Na_2S and 5×10^{-4} M NH_4^+ , (c) 3×10^{-3} M Na_2S and 6×10^{-3} M NH_4^+ , (d) 5×10^{-4} M Na_2S alone, and (e) 3×10^{-3} M Na_2S alone. (f,g) Residual liquids after treatments at different conditions (f) with ammonium and (g) without ammonium; the concentrations of ammonium ions were twice those of sulfide ions shown above the photo.

Figure 2f,g show photographs of residual liquids after treatments at different conditions. In the absence of ammonium, residual liquids increasingly darken with increasing sodium sulfide dose (Figure 2g). As suggested in previous work [22], this phenomenon of residual liquids is understood in

terms of colloidal copper sulfide particle formation. In contrast, there was no clear tendency of residual liquids to darken in the presence of ammonium (Figure 2f).

3.2.2. FESEM-EDS Analysis

Previously, Wu et al. [11] and Shen et al. [14] had studied this topic using SEM-EDS. However, nothing interesting was observed, because of the limited magnification and resolution. Herein, FESEM with high magnification and high resolution was used to observe the morphology of sulfidized malachite produced with and without ammonium. Figure 3a1,a2 shows FESEM images of malachite treated only with 5×10^{-4} M sodium sulfide solution. The malachite surfaces appeared to be coated with a layer of mud-like material. EDS results in Figure 4a show that the mud-like material contained sulphur (Spot 2 in Figure 3a1), while no sulphur was detected in the surrounding areas (Spot 1 in Figure 3a1), indicating that these mud-like materials were a solid sulfidization product.

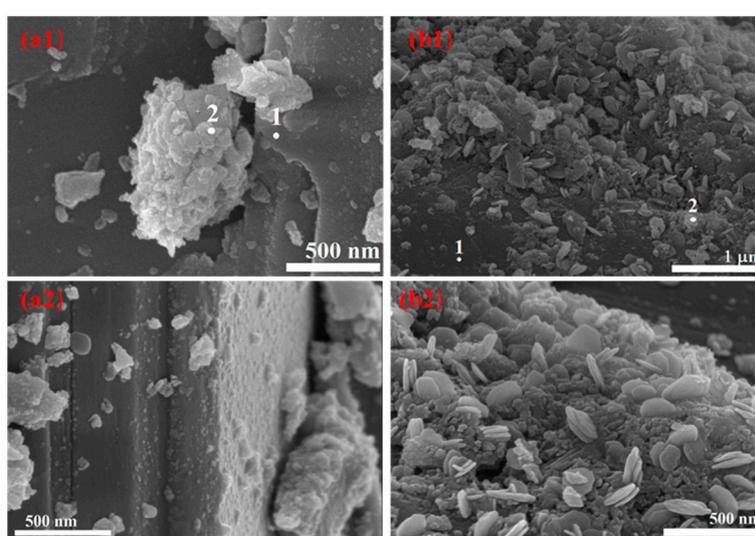


Figure 3. FESEM images of sulfidized malachite (a1,a2) without ammonium ions and (b1,b2) with ammonium ions. $C(\text{Na}_2\text{S}) = 5 \times 10^{-4}$ M, $C(\text{NH}_4^+) = 10^{-3}$ M.

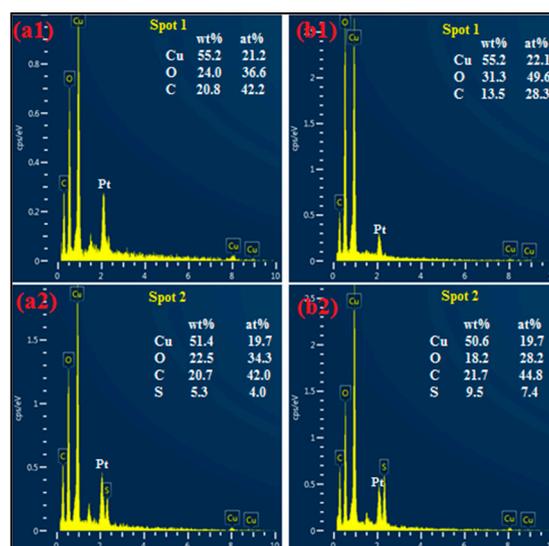


Figure 4. EDS results for sulfidized malachite produced (a1,a2) without of ammonium and (b1,b2) with ammonium, corresponding to Figure 3a,b, respectively.

In contrast, a large quantity of elliptical nanoparticles grew on the malachite treated both with ammonium ions and sulfide ions. Similarly, EDS results in Figure 4b indicated that these elliptical nanoparticles were the solid sulfidization product formed in the presence of ammonium.

As depicted in Figure 5, increasing the sodium sulfide concentration to 3×10^{-3} M produced more sulfidization product in both samples, thereby greatly changing the morphologies. As expected, the presence vs. absence of ammonium produced significant morphological differences in sulfidization products.

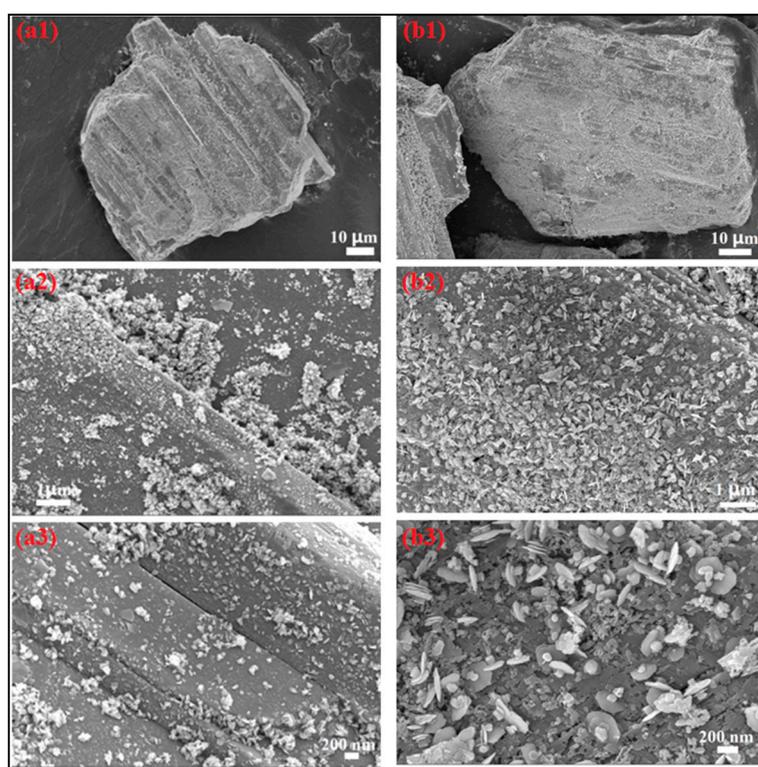


Figure 5. FESEM images of sulfidized malachite (a1,a2,a3) without ammonium and (b1,b2,b3) with ammonium. $C(\text{Na}_2\text{S}) = 3 \times 10^{-3}$ M, $C(\text{NH}_4^+) = 6 \times 10^{-3}$ M.

FESEM images (Figures 3 and 5) clearly show that the sulfidization product produced in the presence of ammonium had a larger particle size and a higher converge density than that produced in the absence of ammonium. To the best of our knowledge, high-magnification and high-resolution FESEM images were obtained for the first time, highlighting the effect of ammonium on the morphology of sulfidization product of malachite.

3.2.3. XRD Measurement

Figure 6 shows the XRD patterns of the sulfidization products that were extracted from the malachite treated with 5×10^{-4} M Na_2S . The results showed that both $\text{Cu}_{31}\text{S}_{16}$ (djurleite) and Cu_7S_4 (anilite) comprised the sulfidization products, regardless of the presence or absence of ammonium. However, the proportion of $\text{Cu}_{31}\text{S}_{16}$ was higher in the presence of ammonium. When the concentration of sodium sulfide was increased to 3×10^{-3} M, similar results were obtained (Figure 7). The XRD results show that the sulfidization products of malachite were the copper-deficient Cu_{2-x}S phases, regardless of the presence or absence of ammonium.

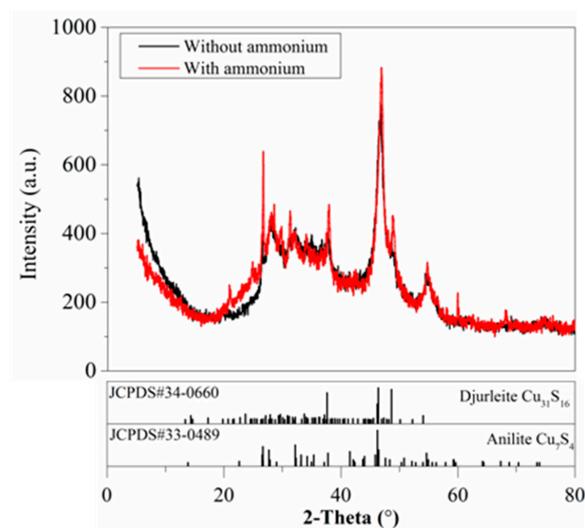


Figure 6. XRD patterns of sulfidization products without and with ammonium. $C(\text{Na}_2\text{S}) = 5 \times 10^{-4}$ M, $C(\text{NH}_4^+) = 1 \times 10^{-3}$ M.

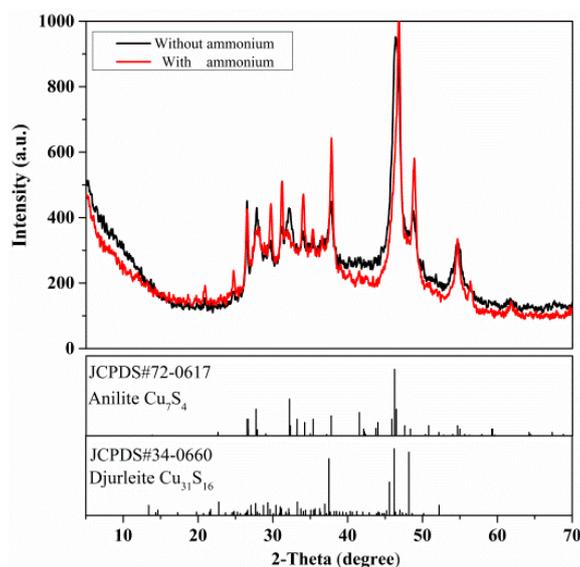


Figure 7. XRD patterns of sulfidization products without and with ammonium. $C(\text{Na}_2\text{S}) = 3 \times 10^{-3}$ M, $C(\text{NH}_4^+) = 6 \times 10^{-3}$ M.

3.2.4. XPS Study

Figure 8 shows the XPS survey spectra and high-resolution N1s spectra of malachite treated at different conditions. S2s and S2p peaks are observed for all sulfidized malachite sample surfaces regardless of the absence or presence of ammonium, clearly showing that sulfidization occurred on all malachite samples surfaces. However, no sample surfaces showed a N1s peak.

The atomic concentrations of sulphur on four sample surfaces were calculated on the basis of their high-resolution S2p spectra (Figure 9). Sulfidized malachite surfaces with ammonium showed sulphur concentrations substantially higher than sulfidized malachite surfaces without ammonium, a pattern consistent with previous work [11,12].

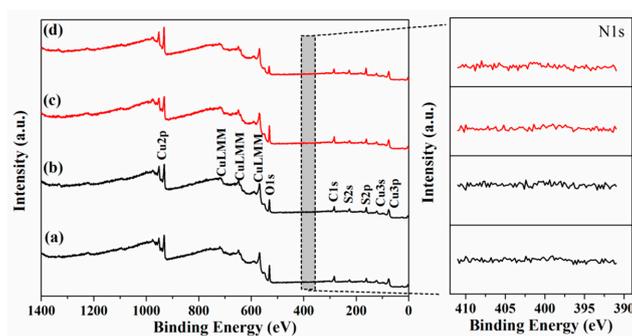


Figure 8. XPS survey spectra (left) and corresponding high-resolution N1s spectra (right) of malachite treated with (a) 5×10^{-4} M Na_2S alone, (b) 3×10^{-3} M Na_2S alone, (c) 5×10^{-4} M Na_2S and 1×10^{-3} M NH_4^+ , (d) 3×10^{-3} M Na_2S and 6×10^{-3} M NH_4^+ .

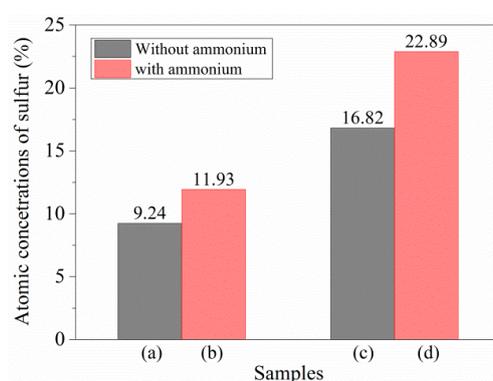


Figure 9. Atomic concentration of sulfur at the sulfidized malachite's surface treated with (a) 5×10^{-4} M Na_2S , (b) 5×10^{-4} M Na_2S and 1×10^{-3} M NH_4^+ , (c) 3×10^{-3} M Na_2S , and (d) 3×10^{-3} M Na_2S and 6×10^{-3} M NH_4^+ .

3.3. Ammonium Actions

The actions of ammonium during malachite sulfidization remain to be determined, so this question was further studied using solution analysis. Figure 10 shows the residual ratio of ammonium nitrogen in solution. After treatment with ammonium solution for 3 min, the residual ratio of ammonium nitrogen still remained at 96.8%. After treatment with ammonium and sulfide in sequence, the residual rate still remained high at 93.0%.

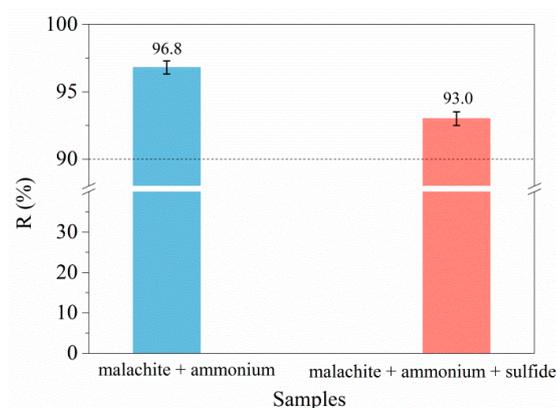


Figure 10. Residual ratio of ammonium nitrogen in solution for malachite suspension treated with ammonium solution (malachite + ammonium), or with ammonium and sulfide solution in sequence (malachite + ammonium + sulfide).

3.4. Role of Ammonium

As stated in Section 1, two primary questions require elucidation:

1. What are the actions of ammonium during malachite sulfidization?
2. What are the differences between sulfidized malachite produced with and without ammonium?

For the first question, neither EDS nor XPS analysis found no nitrogen on malachite surfaces for any treatment. Considering the detection limit, they do not provide conclusive proof that ammonium cannot be adsorbed onto malachite surfaces. However, the results of residual ratio of ammonium nitrogen demonstrated clearly that most ammonium continued to be held in solution before and after malachite sulfidization. Overall, these results challenge the previous viewpoint that the adsorption of ammonium could enhance the adsorption of sulfide ions on malachite surfaces.

For the second question, the property differences between the sulfidized malachite produced with and without ammonium were explored. Macroscopically, the sulfidized malachite with ammonium exhibited a darker color than the sulfidized malachite without ammonium, while the opposite appeared to be true for their corresponding residual liquids. Further, FESEM-EDS and XPS analyses provide stronger evidence for the role of ammonium, showing that the presence of ammonium induces more sulfidization product coatings and higher sulphur concentrations on malachite surfaces. These results demonstrate that ammonium can reduce the formation of colloidal copper sulfide in residual liquids while enhancing the degree of sulfidization of malachite surfaces. More importantly, the presence vs. absence of ammonium produced significant morphological differences in sulfidization products.

The findings of this study suggest that we do require to rethink the mechanism of ammonium ions on malachite sulfidization. According to our characterizations and analyses, regardless of the presence or absence of ammonium, malachite sulfidization is clearly a heterogeneous solid-liquid reaction in which the solid product attaches to the unreacted malachite, and sulfidization products on malachite are not a monatomic layer but a solid polyatomic layer. Hence, malachite sulfidization, i.e., the formation of copper-deficient Cu_{2-x}S phases on malachite surfaces, involves heterogeneous nucleation and growth. FESEM images highlight the larger particle size and greater stability of sulfidization products produced in the presence of ammonium. Thus, we can infer that ammonium plays a key role in mediating the nucleation and growth of sulfidization product crystals during malachite sulfidization, producing larger sulfidization product particles. The larger size of sulfidization product may result in a darker, stabler and denser sulfidization product-coating layer, which is noticeably detached to reduce the formation of colloidal copper sulfide in the residual liquids. Ultimately, ammonium facilitates better performance of sulfidization flotation of malachite. Based on the above results and discussion, a schematic diagram of the sulfidized malachite produced without and with ammonium is proposed (Figure 11). However, further work is required to determine the mediation mechanisms of ammonium on the nucleation and growth of the sulfidization product.

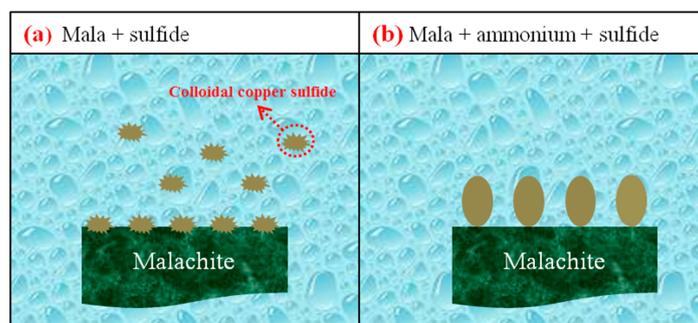


Figure 11. Schematic of sulfidization products grown on malachite without (a) and with (b) ammonium ions. The brown floccules and elliptical plates represent the sulfidization products without and with ammonium, respectively.

4. Conclusions

In this work, a variety of analytical techniques were applied to determine the actions of ammonium during malachite sulfidization and get more information on the sulfidized malachite produced with ammonium. The results of EDS, XPS and residual ratio of ammonium nitrogen analyses clearly demonstrated that most ammonium continued to be held in solution before and after malachite sulfidization. Regardless of the presence or absence of ammonium, the sulfidization product grown on malachite were the copper-deficient Cu_{2-x}S phases, FESEM images highlighted that the sulfidization product produced in the presence of ammonium had a larger particle size and a higher converge density than that produced in the absence of ammonium, which was consistent with the macroscopic observation and XPS analyses.

The findings of this study suggested that malachite sulfidization is clearly a heterogeneous solid-liquid reaction in which the solid product attaches to the unreacted malachite. Malachite sulfidization involves heterogeneous nucleation and growth of the solid sulfidization product. We inferred that ammonium may mediate the nucleation and growth of the sulfidization product during malachite sulfidization, rendering larger product particles. The larger size of sulfidization products may result in a darker, stabler and denser sulfidization product coating layer, and then may reduce the generation of colloidal copper sulfide in the residual liquids. Ultimately, ammonium ions facilitate the better performance of sulfidization flotation of malachite.

This study challenges the previous standpoint and provides new insights into the role of ammonium ions in the sulfidization flotation of malachite.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/6/537/s1>, Figure S1: Schematic diagram of flotation devices.

Author Contributions: Conceptualization, D.L. and J.L.; Formal analysis, J.L.; Funding acquisition, D.L.; Investigation, R.L. and J.L.; Methodology, R.L.; Project administration, D.L.; Resources, Z.L. and S.A.; Software, J.L.; Supervision, D.L.; Validation, B.P.; Visualization, J.L.; Writing—original draft, R.L.; Writing—review & editing, J.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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