



Ammonia modification for enhancing adsorption of sulfide species onto malachite surfaces and implications for flotation

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ABSTRACT

In this study, the surface modification of malachite with ammonia was developed as a promising method to enhance the adsorption of sulfide species onto the mineral surface. The flotation recovery of the ammonia-modified malachite was significantly improved under the same flotation condition compared with that of bare malachite. This result can be ascribed to the fact that the adsorbed amount of S species on the mineral surface increased because of the considerable affinity of the ammonia-modified malachite for sulfide ion species in the pulp solution. The negativity of the zeta potential of malachite increased, which implied that more S species was adsorbed onto the surface of the ammonia-modified mineral. This phenomenon facilitated the attachment of the collector. XPS analysis confirmed the enhancement of sulfide ion species adsorption onto the ammonia-modified malachite surface. In addition, the amount of cuprous sulfide species on the modified surface increased. The mechanism by which ammonia modification enhances the sulfidization of malachite was further studied by solution chemistry calculation. The hydrophilic $\text{Cu}(\text{OH})_2$ coated on the malachite surface was detrimental to the adsorption of sulfide ion species, whereas the involvement of $\text{Cu}(\text{NH}_3)_2^{2+}$ changed the surface species distribution and improved the sulfidization of malachite, thereby facilitating its flotation recovery.

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1. Introduction

Copper is a widely used nonferrous metal because of its remarkable malleability, excellent electrical and thermal conductivity, and low resistivity [1,2]. The copper element in nature mainly exists in the form of sulfide and oxide. Copper sulfide minerals include chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), chalcocite (Cu_2S), and covellite (CuS). Copper oxide minerals contain malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), tenorite (CuO), chrysocola ($(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$), cuprite (Cu_2O), and atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$) [3–6]. Copper sulfide minerals are primarily smelted for metallic copper production worldwide. Most copper sulfide mines are associated with copper oxide minerals, and increasing amounts of copper oxide ores are being treated because of the depletion of available copper sulfide resources. Copper oxide minerals are usually difficult to directly float using traditional

collectors due to surface hydroxylation and solubility [7,8]. Hence, copper oxide minerals should be sulfidized for the production of copper sulfide species on the mineral surface to improve their floatability.

Na_2S is used as a typical sulfidizing reagent to provide sulfide ions for the sulfidization of oxide minerals [9–11]. Hydrolysis occurs in Na_2S solution, and its dissociated product depends on the solution pH. For instance, H_2S is the dominating S species at pH lower than 7.0, HS^- is predominant within the pH range of 7.0–13.9, and S^{2-} becomes the primary S species at pH higher than 13.9 [12–14]. Malachite responds well at pulp pH of approximately 9.5. Thus, HS^- primarily interacts with the malachite surface [8]. Copper sulfide compound is produced on the mineral surface when malachite is conditioned with a sulfidizing reagent, and surface sulfidization is a complicated reaction, which may involve the ion-exchange reaction, surface adsorption, and redox reaction [15–17]. Similar to other nonferrous metal oxide minerals, the amount of sulfidizing reagents remains an unmanageable issue with regard to the sulfidization flotation of malachite. The sulfidization control system [12], bioflotation method [18,19], and synthetic collectors [20–22] were developed to avoid the adverse effect of excess

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sulfide ions on the floatability of oxide minerals. However, sulfidization followed by xanthate flotation is still the preferred method to concentrate copper oxide minerals because it considers technical and economic factors. Consequently, sulfidization should be considered because it is a critical step with regard to the sulfidization xanthate flotation of copper oxide minerals.

Nevertheless, surface sulfidization is confronted with some drawbacks, such as inferior sulfidization efficiency, unstable sulfidization products, massive consumption of sulfidizing reagents and collectors, and low flotation recovery. On the basis of the formation of lead chloride complexes, chloride ions are used to modify the surface composition and property of cerussite to increase the number of active sites and enhance the activity of active sites on the mineral surface, thereby improving the sulfidization and floatability of cerussite [23–25]. Kongolo et al. [26] obtained a higher flotation recovery of copper when $(\text{NH}_4)_2\text{S}$ instead of NaHS was used as a sulfidizing reagent to treat copper oxide minerals. The main difference between $(\text{NH}_4)_2\text{S}$ and NaHS is their cations. Dissociation equilibrium exists between ammonium ions (NH_4^+) and ammine (NH_3) in aqueous solution, and copper ions can react with ammine to form highly stable copper ammine complexes [27,28]. Accordingly, ammine species may play an important role in the sulfidization of copper oxide minerals. However, the influence of ammonia modification of malachite surface on its sulfidization behavior and mechanisms remains unclear to date.

In the present work, surface modification with ammonia was performed to facilitate the sulfidization flotation of malachite using xanthate as a collector. The enhanced adsorption of sulfide species onto the malachite surface was evaluated by solution chemistry calculation, microflotation tests, surface adsorption experiments, zeta potential measurements, and X-ray photoelectron spectroscopy (XPS) studies.

2. Materials and methods

2.1. Materials

Malachite samples collected from the Yunnan Province in China were crushed and handpicked to remove all the other gangue minerals. The selected mineral exhibited a high purity with only minor impurities, as characterized by chemical and X-ray diffraction analyses. The purified mineral samples were dry ground using an agate mortar and pestle, and then dry screened using a standard screen. Malachite samples with particle sizes ranging from $-74\ \mu\text{m}$ to $+38\ \mu\text{m}$ were utilized in the microflotation tests, surface adsorption tests, and XPS measurements. A portion with a particle size smaller than $5\ \mu\text{m}$ was adopted to determine the zeta potential. NaOH and HNO_3 solutions were used for pH adjustment. Except for commercial sodium amyl xanthate (NaAX), all reagents used in this work were of analytical grade. Pure deionized water was used in all experiments.

2.2. Microflotation tests

A small-scale flotation machine was used for the microflotation tests at room temperature. Approximately 2 g of pure malachite samples were added into a flotation cell with a volume of 40 mL. The mineral suspension was first conditioned with 1.0×10^{-3} mol/L ammonia stock solution before a desired amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution was poured as necessary. Subsequently, various concentrations of freshly prepared $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solutions were added into the pulp suspension and subjected to sulfidization. Afterward, a certain amount of NaAX, which served as the collector, was added into the flotation system, and the flotation test was conducted. At the end of the test, the overflowed and submerged mineral

particles were collected, dried, and then weighed. The flotation recovery of malachite was calculated according to the weight distribution between the two solid products.

2.3. Surface adsorption experiments

The surface adsorption experiments of sulfide species onto the ammonia-modified and bare malachite surfaces were performed in a thermostatic water bath at 298 K. Pure malachite particles (5 g) were dispersed into 500 mL of aqueous phase in the absence or presence of 1.0×10^{-3} mol/L ammonia. After the mixed suspensions were stirred for a certain time, a freshly prepared $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ stock solution with a needed amount was immediately added to react with the mineral surface. During sulfidization, 5 mL of the mixture was accurately withdrawn at set intervals, and a solid–liquid separation was conducted via centrifugation. The separated liquid was collected to analyze the total S concentrations through inductively coupled plasma-atomic emission spectrometry (ICPS-1000II, Shimadzu, Japan). The adsorbed amounts of S species were expressed using the following equation:

$$\Gamma = C_0 - C, \quad (1)$$

where Γ is the amount of S species adsorbed onto the ammonia-modified or bare malachite surface, C_0 is the initial S concentration, and C is the final S concentration when malachite particles interacted with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ within the desired time.

2.4. Zeta potential measurements

The zeta potential of malachite particles was measured using a Brookhaven ZetaPlus instrument. The KNO_3 background solutions (5×10^{-3} mol/L) were used to maintain the ionic strength of the mineral suspension. The mineral suspension (0.01% mass fraction) was dispersed in electrolyte solutions and magnetically stirred for a desired time by a magnetic stirring apparatus after the required flotation reagent was added. For each measurement, the solution pH was regulated at 9.5 by adding HCl or NaOH stock solution after sulfidization of the malachite surface. Afterward, the fine mineral particles were transferred to the measurement vessel for zeta potential determination at room temperature when the resultant suspension was set for 10 min. Zeta potential measurement was repeated three times with a maximum standard deviation of ± 2.0 mV, and an average value was recorded as the final value.

2.5. XPS measurements

The samples used in this measurement were received at the same experimental condition depicted in Section 2.3. The measured samples were examined using a PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) with a monochromatic Al K_{α} X-ray source. The tested samples were first subjected to a survey scan to determine all existing elements. Subsequently, a high-resolution scan on a specific element was conducted to obtain its precise XPS spectrum. Afterward, the elemental XPS spectra and surface atomic ratios of the measured samples were fitted and analyzed using the MultiPak Spectrum software. The carbon 1s spectrum at 284.8 eV was used as an internal standard to calibrate the measured spectra for charge compensation.

3. Results and discussion

3.1. Effect of ammonia on malachite flotation behavior

The flotation behavior of the ammonia-modified and bare

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