



Influence of excess sulfide ions on the malachite-bubble interaction in the presence of thiol-collector



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ABSTRACT

In this study, the effects of the type (ammonium sulfide ($(\text{NH}_4)_2\text{S}$) and sodium sulfide (Na_2S)) and amount (8×10^{-5} mol/L and 2×10^{-3} mol/L) of sulfidizing reagents used in malachite flotation with xanthate as a collector on flotation recovery were investigated in a well-controlled Hallimond tube. The results showed that the average flotation recovery of malachite was similar regardless of the type of sulfidizing agent; however, a significant difference was observed when the amount of sulfidizing agents varied. Specifically, malachite had a higher flotation recovery when sulfidized at a low concentration than at a high concentration. This result was not explained by either the differences in the extent of sulfidization or by the electrostatic interaction between xanthate and malachite, which was supported by XPS and XRD analyses, adsorption tests of sulfidizing agents, and zeta potential measurements. Notably, malachite without excess sulfide ions exhibited significantly greater flotation recovery than that with excess sulfide ions regardless of the type of sulfidizing agent. These results were well supported by the results from the potentiometric titration tests, which showed greater xanthate adsorption onto the surface of malachite without excess sulfide ions than that with excess sulfide ions. Therefore, the excessive use of sulfidizing agents was confirmed to inhibit xanthate adsorption onto the malachite surface, and consequently, to decrease the flotation recovery of malachite.

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1. Introduction

Copper (Cu) ores exist either as Cu oxides or Cu sulfides, and Cu sulfides are more easily separated than Cu oxides via flotation. The demand for these minerals is on an increase as industrial development increases; however, mineral resources are limited. Therefore, fundamental and practical studies have been conducted to improve the flotation for Cu oxide recovery [1–6]. The flotation of Cu oxides is usually achieved via several methods. One representative method involves floating Cu oxide minerals using organic complexing agents (e.g., fatty acids, fatty amines, petroleum sulphonates, and 2-ethyl-2-hexenal oxime) as collectors [4,7–9]. Recently, Li et al. [10] reported that hydroxyoctyl phosphinic acid (HPA) could be used as a powerful collector for malachite direct flotation. Their results showed that >80% of pure malachite floated over a wide pH range (pH 5–9). Even though this study is valuable because it is the first attempt to use HPA as a collector, further studies are required to reveal the uncertainty of the selectivity of malachite from complex ore systems. Another method is to

sulfidize the oxide mineral surface using a sulfidizing agent and to conduct selective flotation using sulfhydryl collectors, such as xanthate [5,11–17], which is the most commonly used collector for oxide mineral flotation.

Sulfidization is usually conducted as a pretreatment process for oxide minerals and includes strong chemisorptions of sulfide (S^{2-}) or hydrosulfide ions (HS^-) onto the oxide mineral surface. Accordingly, the chemisorbed sulfide ions allow for xanthate adsorption. Several studies have reported that surface activation (i.e., sulfidization) improves the flotation recovery rate of both Cu oxide minerals and oxidized Cu sulfide minerals [18–20]. However, the opposite trend has also been observed [15,21,22] wherein the flotation efficiency decreased when sulfide ions were excessively used. Even though comparatively little work concerning this issue is available for Cu oxide minerals, an elegant study by Castro et al. [21] revealed a mechanism where the excess sulfide ions in the pulp, as well as the sulfide ions adsorbed onto the Cu oxide mineral surface, were oxidized to form oxy-sulfur species that led to the reduced floatability of the mineral. That study indirectly reveals information about the depression process, which is likely associated with the inhibition of xanthate adsorption onto the mineral surface; however, more useful information concerning

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the correlation between xanthate adsorption and sulfidization flotation was not provided in that study and has not yet been reported elsewhere, even though the process is widely recognized. Therefore, further studies are required to better capture the underlying mechanism.

Sodium sulfide (Na_2S), sodium hydrosulfide (NaHS), and ammonium sulfide ($(\text{NH}_4)_2\text{S}$) are frequently used as agents for sulfidization [4,16,23] and account for a large part of the cost in the flotation process of oxide minerals [3]. However, studies on the sulfidization effects of these different sulfidizing agents are rare. Only a study reported by Kongolo et al. [3], to the best of our knowledge, investigated the effect of the type of sulfidizing agent (NaHS , $(\text{NH}_4)_2\text{S}$, and $\text{NaHS} + (\text{NH}_4)_2\text{S}$) on the flotation of Cu-Co complex oxide ores and observed that there was a significant difference in the recovery and assay of their concentrates. Even though it gives valuable insight into the importance of the type of sulfidizing agent used, that study focused more on practical applications instead of fundamental aspects, therefore implicitly suggesting that further study is necessary to understand the underlying mechanism. It is worth pointing out that no study so far has been reported concerning the different effects of sulfidization with Na_2S and $(\text{NH}_4)_2\text{S}$ on the flotation of malachite.

This study aims to investigate the effect of the sulfidization using different types of sulfidizing agents on the flotation recovery of malachite and includes an examination of the coupled role of sulfide ions and xanthate adsorption on malachite flotation to reveal the underlying mechanism. For this purpose, flotation tests were conducted in a well-controlled Hallimond system using two types of sulfidizing agents (sodium sulfide (Na_2S) and ammonium sulfide ($(\text{NH}_4)_2\text{S}$)) at different concentration levels. In addition, colorimetric and potentiometric titration methods were employed to determine the amount of sulfide ions and xanthate adsorbed onto the malachite surface.

2. Experimental approach

2.1. Materials and reagents

Synthetic malachite (purity >95%, Junsei Chemical, Japan) with a spherical shape containing >55% Cu was used in this study. The size of the as-received malachite ranged from 1 to 100 μm with a median diameter of approximately 30 μm ($d_{50} = 30 \mu\text{m}$). The microflotation study used samples with a particle-size distribution of +45–53 μm (Tyler Standard). Note that, for the microflotation tests, the particle size ranges in this study were found to be optimal to minimize the effect of natural floatability [1,2]. Xanthates were used as collectors, and the sulfidizing agents were used as activators. The xanthates used in this study were potassium amyl xanthate (PAX, $\text{C}_5\text{H}_{11}\text{OCS}_2\text{K}$) with a purity of 90% or higher (Hong Yuan Industry & Trade, China) and potassium ethyl xanthate (PEX, $\text{C}_2\text{H}_5\text{OCS}_2\text{K}$) with a purity of 96% (Sigma-Aldrich). The Na_2S and $(\text{NH}_4)_2\text{S}$ were obtained from Sigma-Aldrich and were used as sulfidizing agents, and stock solutions of the sulfidizing agent and xanthate were prepared daily. Silver nitrate (AgNO_3 , Sigma-Aldrich) was used as a titrant in the titration tests to determine the xanthate concentration in the bulk phase. All reagents were mixed with deionized (DI) water (18.2 $\text{M}\Omega \text{cm}$) to adjust the solution to its desired concentration. To regulate the pH, 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) were obtained from Fisher Scientific Inc.

2.2. Sulfidization

The malachite surface was treated with a sulfidizing agent using a 50-mL centrifugal tube (BD Falcon Co., USA) and an agitator (SLRM-3, Seoulin Bioscience Co., Korea). The Na_2S and $(\text{NH}_4)_2\text{S}$,

which were used as sulfidizing agents, were then mixed with DI water in a 50-mL tube to prepare 40 mL of $8 \times 10^{-5} \text{ mol/L}$ and $2 \times 10^{-3} \text{ mol/L}$ solutions. Next, 1 g of malachite was added and stirred at room temperature for one hour until the mixture reached the equilibrium state. The adsorption tests were conducted using a UV-Vis Spectrophotometer (UV-3300, Humas Co., Korea) to measure the amount of sulfide ion adsorbed on the malachite surface. The sulfidized malachite suspension was consecutively filtered using 0.45-, 0.2-, and 0.02- μm syringe filters (Whatman Co., UK), and then the sulfide concentration, which remained in the filtrate, and the corresponding adsorbed amount were determined via a colorimetric analysis [13].

2.3. Characterization tests

An ELS-Z zeta potential analyzer (Otsuka Electronics Co., Japan) was used to measure the electrophoretic mobility of the malachite treated with sulfidizing agent. Prior to measurement, the malachite sample was mixed with DI water and was ground at 700 rpm for 4 h using an attrition mill (KMDC-1B, Korea Material Development Co., Korea) to obtain particles with an $\sim 3 \mu\text{m}$ particle distribution (Accusizer 780, At Frontier Co., Korea). The surface of the ground malachite was treated using sulfidizing agents with different concentrations. A small amount of the sulfidized malachite was mixed with DI water, and its pH was adjusted before pouring it into the cell. Then, the electrophoretic mobility was measured by obtaining values from four repeated measurements, which were converted to zeta potential using the Smoluchowski equation [24]. The pH of the solution was adjusted using 0.1 mol/L hydrochloric acid (HCl) and sodium hydroxide (NaOH).

X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses were conducted to examine the surface characteristics of the malachite after sulfidization. The sample preparation for the XPS analysis followed the previously reported procedure [25]. The XPS model was a Theta Probe (Thermo Fisher Scientific, UK) using a monochromated Al $K\alpha$ source (15 kV, 150 W) at the KBSI Busan Center. The binding energy was referenced to the natural C1 s peak at 284.6 eV. Wide spectra were collected with a pass energy of 300 eV and a channel width of 1.0 eV, and detailed spectra were collected with a pass energy of 50 eV and a channel width of 0.1 eV. The powder samples treated with $2 \times 10^{-3} \text{ mol/L}$ Na_2S and $(\text{NH}_4)_2\text{S}$ were mounted on the sample holder using a double-sided adhesive copper tape and then transferred to the analysis chamber where the pressure was maintained at $3 \times 10^{-8} \text{ Torr}$. For the XRD analysis, malachite was first grounded using a mortar, and then the ground samples were sulfidized with the Na_2S and $(\text{NH}_4)_2\text{S}$ solutions at a concentration of $2 \times 10^{-3} \text{ mol/L}$. XRD patterns were recorded using an XRD analyzer (X'pert³ Powder, PANalytical, Netherlands) equipped with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.154060 \text{ nm}$, 40 kV).

2.4. Microflotation tests

The microflotation tests were conducted at room temperature using an in-house Hallimond tube [26]. One gram of malachite and 150 mL of DI water were injected into the Hallimond tube, and the contents were mixed at 340 rpm using a bar-shaped magnetic stirrer. Nitrogen gas of 99% or higher purity was injected at a flow rate of 30 mL/min, and the flotation time was fixed at 4 min. The floated and unfloatable malachite were filtered and dried at room temperature for 12 h. The two malachite samples were weighed to calculate the flotation recovery. In addition, potassium ethyl xanthate was used to investigate the effects of the xanthate chain length. Note that all the flotation tests were conducted using samples without residual xanthate in suspension after the xanthate adsorption. The filtration was conducted using a cellulose

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