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Copper sulfide species formed on malachite surfaces in relation to flotation

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ABSTRACT

The interaction between sulfide ion species and malachite surfaces in relation to flotation was studied in this work using X-ray photoelectron spectroscopy analysis, surface adsorption, zeta potential determination, and micro-flotation experiments. Results demonstrate that the flotation recovery of malachite was correlated with the contents of sulfidization products and their active components as well as the residual sulfide ion species in pulp solutions. The sulfidization product was composed of cuprous monosulfide, cuprous disulfide, and cuprous polysulfide. Among them, disulfide and polysulfide positively contributed to the activity of the product.

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Introduction

Copper is an important nonferrous metal and is mostly refined from natural copper sulfide minerals in the past [1,2]. The gradual depletion of copper sulfide resources has made copper oxide minerals an alternative source to meet copper market demands [3,4]. Malachite is an abundant copper oxide mineral with CuCO_3 and $\text{Cu}(\text{OH})_2$ components; its flotation behavior with various flotation reagents has been intensively investigated [5–8]. Compared with its corresponding sulfide mineral, copper oxide mineral shows inferior floatability because of its surface hydration and solubility; thus, this mineral cannot be subjected to a direct flotation via a short-chain xanthate collector.

The sulfidization flotation technology is the most practical method for upgrading copper oxide ores [9,10]. In this process, sodium sulfide (Na_2S) and alkyl xanthate are commonly employed as the sulfidizing agent and the collector, respectively. A cautious addition of Na_2S is required because low concentration of Na_2S cannot adequately sulfidize the mineral surface; meanwhile, high concentration of Na_2S can result in the adverse adsorption of xanthate species onto the sulfidized mineral surface [11,12]. Much effort has been made by researchers to address this issue. Gush

[12] designed a control system that can accurately regulate the concentration of sulfide ion species in pulp solutions, thereby facilitating subsequent recovery of oxide minerals. Various chelating collectors have been synthesized to recover copper oxide minerals by direct flotation methods without preliminary sulfidization treatment. Fuerstenau et al. [13] previously assessed the collecting capabilities of different chelating agents to copper oxide minerals. Hope et al. [14] detected the surface products and the bulk copper compounds generated by the interaction of various hydroxamate reagents with copper oxide minerals. They also specially reported the reaction product of *n*-octanohydroxamate and malachite surfaces [15]. Buckley et al. [16] investigated the interaction between *n*-octanohydroxamate collector and copper oxide minerals using secondary ion mass spectrometry. Li et al. [17] synthesized α -hydroxyoctyl phosphinic acid and studied its effect on malachite floatability. Kim et al. [18,19] found that bioflotation is a potential alternative to treat copper oxide minerals using *Rhodococcus opacus*. Other sulfidization techniques, such as mechanochemical sulfidization and hydrothermal sulfidization, have also been applied to copper oxide sulfidization [20,21]. Nevertheless, only the surface sulfidization flotation method has been employed to commercially concentrate copper oxide minerals owing to technical and economic conditions. Consequently, an in-depth study on the surface sulfidization must be conducted.

Surface sulfidization is implemented by adding Na_2S into malachite suspension to render copper sulfide compounds

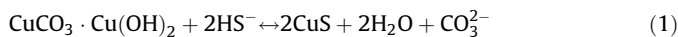
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generated on copper oxide surfaces. Na_2S plays a critical role in malachite sulfidization. The distribution of the effective components of Na_2S in aqueous solution is in control of solution pH; in other words, H_2S is the dominating S species at pH lower than 7.0, HS^- is predominant within the pH range from 7.0 to 13.9, and S^{2-} turns into the primary S species at pH higher than 13.9 [22,23]. The sulfidization reaction of malachite proceeds under mild alkaline conditions; thus, HS^- is a substantial reactant with malachite surfaces. The sulfidization reaction of malachite can be described as follows:



The formation of copper sulfide may be due to the HS^- adsorption onto copper sites on the mineral surface or ion-exchange reaction between HS^- in pulp solutions and carbonate ions/hydroxide ions on the malachite surface. Bessiere et al. [24] indicated that copper sulfide is formed on malachite surfaces after treatment with Na_2S using high-frequency dielectric techniques. Kongolo et al. [25] found that a combined utilization of NaHS and $(\text{NH}_4)_2\text{S}$ can improve the flotation index of copper oxide minerals. Zhou and Chander [9] considered that the sulfidization reaction of malachite cannot be completed in one stage. Specifically, a primary copper sulfide layer is formed in the first stage, and the precipitation of dissolved copper ions and oxidation of sulfide species occur in the subsequent stage. Park et al. [10] systematically studied the effect of the type and concentration of a sulfidization reagent on malachite floatability. They also found that high concentration of a sulfidization reagent is detrimental to the flotation recovery of mineral particles as a result of less adsorption of collector on the sulfidized malachite surface.

Numerous studies on malachite flotation have been conducted; however, they concentrated mostly on collector synthesis, sulfidization conditions, and practical applications, etc. Minimal information is available concerning the interaction products of sulfide ion species and malachite surfaces. Consequently, these vacant studies must be addressed to better understand the underlying mechanism of malachite sulfidization flotation. In this work, X-ray photoelectron spectroscopy (XPS), micro-flotation experiments, surface adsorption, and zeta potential determinations were employed to deeply investigate the formation of sulfidization products and its effects on the flotation behavior of malachite.

Experimental

Materials and reagents

The malachite sample used in all the experiments was obtained from the Yunnan Province in China. For micro-flotation experiments and adsorption measurements, the malachite sample was crushed and dry-ground in an agate torsion mortar; the ground products were then sieved using a standard screen to achieve a particle fraction of $-74+38\ \mu\text{m}$ malachite. The rest of the samples was ground and screened into fractions finer than $5\ \mu\text{m}$ during the zeta potential determination. The chemical analysis shows that the sample contained 57.41% Cu; this value reveals that the sample used had high purity with small quantity of mineral impurities. The X-ray diffraction (XRD) pattern of samples shown in Fig. 1 also shows that only the malachite crystal existed; the diffraction peak of this crystal was in line with the data presented in the JCPDS card (No. 76-0660).

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and sodium amyl xanthate (NaAX) were employed as the sulfidizing agent and the collector, respectively. Potassium nitrate (KNO_3) served as the background solution to keep the ionic strength of measured solutions constant during the zeta potential determination. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to regulate solution pH values. In addition to NaAX of commercial grade, all other reagents employed in this

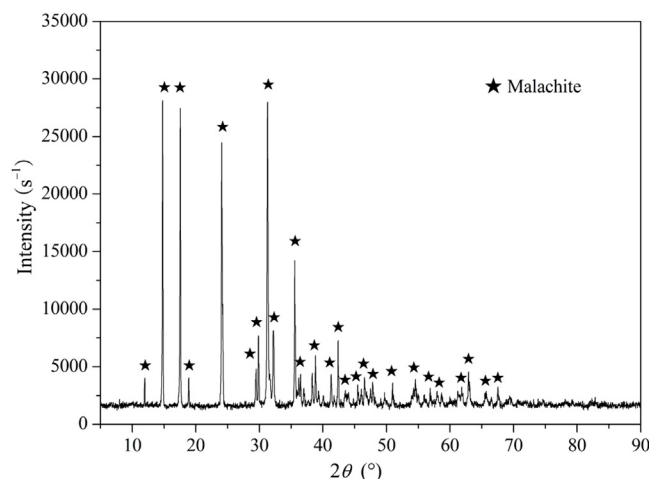


Fig. 1. XRD pattern of pure malachite samples.

work were of analytical grade. Pure de-ionized water was also served during the tests. The Na_2S and NaAX stock solutions were prepared by mixing $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and NaAX into oxygen-free de-ionized water, and they were obtained on the day of usage to avoid oxidation.

Flotation studies

The flotation experiment was conducted at room temperature in a small-scale flotation machine, and 2.0 g of pure malachite samples were added into a 40 mL flotation cell. A fresh $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ stock solution with a desired concentration was prepared. A certain amount of stock solutions were poured into the pulp suspension and conditioned for 5 min prior to the regulation of the solution pH value to 9.5. Subsequently, collectors were added into the pulp and subjected to collection for 5 min. After drying the collected products, the weight distribution between floated and unfloted malachite was used to calculate the flotation recovery.

Adsorption experiments

The adsorption experiments of sulfide onto malachite surfaces were carried out after dispersing 5 g of pure malachite samples into 500 mL of aqueous phase, which was maintained in constant temperature by a thermostatic water bath. The suspensions were magnetically stirred at 650 rpm, and the solution was maintained at 298 K. A fresh $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ stock solution with a desired concentration was injected to interact with mineral surfaces under natural conditions, and a mixed solution with 5 mL was extracted at various time periods for the solid-liquid separation via a centrifuge. The separated liquid was collected to quantitatively analyze the total S concentrations by inductively coupled plasma-atomic emission spectrometry (ICPS-1000II, Shimadzu, Japan). The obtained solid products were thoroughly rinsed with pure de-ionized water to eliminate the weak adsorption of a sulfidizing agent or solution reaction products. This rinsing step is a simulation of the disordered circumstance in a flotation cell to some extent.

Zeta potential determination

The zeta potential was determined using a Brookhaven ZetaPlus instrument. The ionic strength of the malachite suspension in all the measurements was maintained at $5 \times 10^{-3}\ \text{mol/L}$ KNO_3 background solution. The mineral suspension (0.01% mass fraction) was dispersed in electrolyte solutions, which were

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