



Partial replacement of sodium oleate using alcohols with different chain structures in malachite flotation

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ABSTRACT

The sodium oleate collector used in malachite flotation usually exhibits low selectivity. By partially replacing sodium oleate with alcohols, this study presents a method for increasing the selectivity of sodium oleate-based collectors in malachite flotation. By combining 3×10^{-5} mol/L alcohols, such as 1-octanol, 2-ethylhexanol, and α -terpineol, with 1×10^{-5} mol/L sodium oleate, malachite floatability values higher than 98% are achieved. Contact angle and zeta potential measurements reveal that the co-adsorption of alcohols with sodium oleate may be resulted from the hydrophobic interactions between their hydrocarbon chains. The co-adsorption of methyl isobutyl carbinol, along with its shorter hydrocarbon chain, makes it more difficult to render the malachite surface highly hydrophobic. However, the co-adsorption of straight-chain and branched-chain alcohols with sodium oleate shows the ability consistently to induce high malachite floatability.

1. Introduction

Malachite, which usually results from the weathering of copper ores, is a typical carbonate copper mineral that is employed in the mineral processing industry. The flotation of malachite has attracted much attention (Li et al., 2015, 2017; Yang et al., 2017; Liu et al., 2018), particularly with the depletion of easy-to-process sulfide copper ores. It has been found that malachite responds poorly to sulfhydryl collectors (Gaudin, 1957). Consequently, sulfide activators are used for the sulfidisation of malachite before flotation with sulfhydryl collectors (Feng et al., 2017). However, it is not easily controlled in industries as its effectiveness is highly dependent on dosage, and the use of high dosages often leads to poor flotation performance (Herrera-Urbina et al., 1999; Park et al., 2016; Li et al., 2017). Therefore, oxhydryl collectors such as carboxylates (Bulatovic, 2010; Choi et al., 2016), hydroxamates (Lee et al., 1998, 2009; Bulatovic, 2010; Marion et al., 2017) and phosphinic acids (Li et al., 2015) have been studied for the flotation of malachite, but their industrial applications are limited because of several shortcomings. Carboxylates such as fatty acids have affinities to most types of cations, and they therefore have inherently low selectivity in mineral flotation (Nagaraj and Ravishankar, 2007). Furthermore, some commonly dissolved species in the slurry of

malachite flotation have detrimental effects on its flotation with carboxylates collectors. For example, in the flotation of synthetic malachite using sodium oleate as a collector, Choi et al. (2016) reported that the malachite floatability decreased sharply at elevated Ca^{2+} concentrations because of the presence of the hydration layer of adsorbed Ca^{2+} in the oleate-malachite interface. Hydroxamates have been reported as promising chelating collectors for oxide minerals, and a few commercial applications of hydroxamate were achieved with Russian hydroxamate of IM50 and similar compounds produced in China (Bulatovic, 2010). However, the large-scale usage of hydroxamates is limited owing to their practical guidelines, efficacy, and cost in plants (Lee et al., 1998; Phetla and Muzenda, 2010).

There have been studies to develop a collector mixture that can be manufactured economically for oxide flotations. Alcohols combined with collectors have been reported to co-adsorb on the mineral surface through the interaction of the hydrocarbon chain (Liu and Peng, 1999; Filippov et al., 2010). For example, neutral dodecyl alcohol was mixed with dodecyl amine in quartz flotation. It was reported that the contact angle of quartz with a mixture of dodecyl amine and dodecyl alcohol was 10° higher than that with dodecyl amine alone, indicating the co-adsorption of dodecyl alcohol and dodecyl amine (Smith, 1963). Similarly, the mixture of dodecyl amine and hexanol has been found to

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improve the floatability of KCl significantly (Monte and Oliveira, 2004). El-Shall et al. (2000) studied the mixture of polyglycol alcohol (15–30 ppm) and fatty acid in the column flotation of Florida phosphate, and it produced concentrates that have good recovery (99%) and high grade (29–31% P_2O_5). Sis and Chander (2003) reported that fatty acids mixed with non-ionic surfactants have a number of synergistic advantages over the use of a single surfactant in phosphate flotations.

The usage of mixtures of alcohols and collectors in oxide flotations may have the following advantages. First, the mixture of collectors and alcohols is more economical compared to the single oxhydroly collector with a high molecular weight (e.g., fatty acid and sodium oleate). The unit price of the alcohols is usually lower than that of the collectors (Nagaraj and Ravishankar, 2007); for example, in 2016, sodium oleate and 2-ethylhexanol were equal to around 0.7 and 0.17 dollars/mol in China. In addition, as reported by Liu and Peng (1999) in the flotation of rutile with the mixture of styryl phosphonic acid and octanol, the use of only 0.1–1% of emulsifier in the mixture was required for the emulsification. Secondly, the replacement of the oxhydroly collector (e.g., sodium oleate) with alcohol reduces its dosage, which may increase its sensitivity and selectivity.

In the present work, the flotation of malachite was studied with a fatty acid type collector (sodium oleate) partially replaced by four types of alcohols, namely 1-octanol, 2-ethylhexanol, α -terpineol, and methyl isobutyl carbinol (MIBC). These alcohols are different with respect to the length and branching of their chain structures. The work was aimed at illustrating the effect of the chain structure of alcohols on the replacement of the sodium oleate collector in malachite flotation.

2. Experimental

2.1. Materials

A natural malachite sample was obtained from the Lupe mine, Puebla, Mexico. The sample was crushed, hand-sorted and dry-ground to obtain different fractions for different applications, namely, lumps for contact angle measurements, particles of $-75 + 38 \mu\text{m}$ for micro-flotation tests, and fine particles for zeta potential measurements. The size distribution of the fine particles fraction was measured using a Shimadzu SALD-1100 laser diffraction analyser (Japan) with d_{50} and d_{85} values of 3.4 and 8.7 μm , respectively. A Bruker D8 (USA) X-ray diffraction (XRD) meter was used to obtain the XRD pattern of the malachite sample, which was operated with Cu K α radiation, a 40-keV accelerating voltage, and a 0.1 s/step (0.01945°/step) scan rate for the 2θ range of 5–100°. The XRD pattern showed high purity malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) with very small amounts of pseudomalachite ($\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$). A chemical analysis using atomic absorption spectroscopy (AAS) measurements assayed the sample of 54% Cu and 0.46% P. Based on the XRD characterisation, the P and Cu were assumed to be from pseudomalachite and combination of malachite and pseudomalachite, respectively; thus, it could be determined that 4.3% of pseudomalachite, 90% of malachite, and 5.7% of other impurity minerals were in the sample. The XRD pattern showed high-purity calcite was used in mixed mineral flotation. Sodium oleate (ACS reagent grade) purchased from Aladdin Industrial, China, was used as the malachite collector in the micro-flotation. Alcohols of 1-octanol, 2-ethylhexanol, α -terpineol, and MIBC obtained from Aladdin Industrial were used to partially replace the sodium oleate. The molecular structures of the alcohols are given in Fig. 1, where the MIBC has short branched hydrocarbon chain, while the 1-octanol has straight hydrocarbon chain. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) with reagent grade ACS were used to modify the pH of the solution. Distilled water was used in all the experiments.

2.2. Methods

A 150 mL Hallimond tube equipped with a 20 μm frit and a

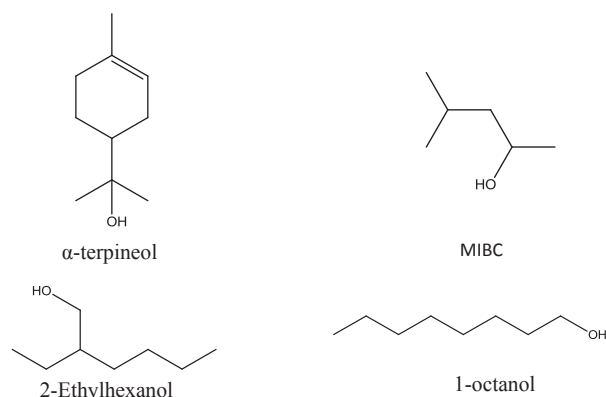


Fig. 1. Molecular structure of the alcohols used in micro-flotation.

magnetic stirrer was used to test the malachite floatability with different reagent mixtures. In each flotation, 3 g of the malachite sample ($-75 + 38 \mu\text{m}$) or mixed mineral (malachite : calcite = 1:1) was conditioned for 2 min in 130 mL of distilled water, and the solution was adjusted to the desired pH by using HCl or NaOH. Then, a given amount of reagents was added and conditioned for 3 min. After that, the conditioned slurry was transferred to the Hallimond tube, and the flotation was performed for 10 min with nitrogen gas at a flow rate of 20 mL/min. The floated (concentrate) and unfloated (tailing) products were separately collected, dried and weighed, and the recovery was calculated based on the percentage of floated product/(mass of floated product + unfloated product). In the micro-flotation tests, the variables used were the pH of the slurry, concentration of sodium oleate and alcohols from 0 to 6×10^{-5} mol/L, and a mixture of sodium oleate and alcohols.

The contact angle of the malachite sample was measured by a goniometer (DSA-25, Kruss, Germany) The DSA-25 goniometer was equipped with a CM4210 optics module with a zoom lens, and was operated using the sessile drop method in the software ADVANCE. In the measurements, lumps of the prepared mineral samples were loaded on the goniometer stage and 1.5 μL of distilled water was dropped on them. The advancing and receding contact angles were then reported. When the difference was less than 1% of the receding contact angle, the average value of these two angles was reported as the contact angle. For each condition (e.g., sodium oleate concentration: 1×10^{-5} mol/L), at least four measurements were performed and the average contact angle was reported in this work. The lumps of the malachite samples were first wet-polished with 80, 400, 800, and 1200 grit SiC paper, and then with 1 μm of alumina powder suspensions. After that, in order to obtain a given pH or reagent condition for the surface, the polished malachite lump was immersed in solutions with different pH values and reagent concentrations for 30 min, and then washed with water.

A ZetaProbe Analyzer (Colloidal Dynamics, Australia) with electroacoustic technology was used to determine the zeta potential of the malachite particles in aqueous solutions for various pH values and reagent concentrations. The zeta potential was calculated from the stimulated electro-acoustic sonic amplitude (ESA) values from the malachite particles using the O'Brien equation (O'Brien, 1990; Rao et al., 2009). In a typical measurement, 5 g of malachite sample and a given amount of sodium oleate and/or alcohol were conditioned with 250 mL KCl (1×10^{-3} mol/L) solutions in the cell of the ZetaProbe for 10 min. Then, the zeta potential values were reported by the equipment. In some cases, changes in the pH were accomplished automatically by the equipment through the addition of 0.1 mol/L KOH and HCl solutions.

3. Results and discussion

Fig. 2 shows the floatability of malachite with sodium oleate (5×10^{-5} mol/L) as a function of the pH. For pH values of 6–12, the

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