



## Interaction of gangue minerals with malachite and implications for the sulfidization flotation of malachite

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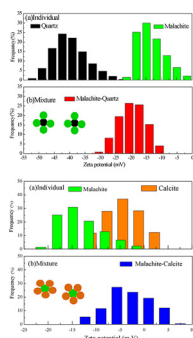
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### GRAPHICAL ABSTRACT

The interaction of quartz-malachite and calcite-malachite are present by zeta potential distribution.



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### ABSTRACT

The role of gangue minerals including quartz and calcite slimes in the sulfidization flotation of malachite was investigated by micro-flotation tests, sedimentation analysis, zeta potential distribution measurements and DLVO calculations. The micro-flotation results showed that calcite slime depressed malachite flotation at pH 9.5 while quartz slime does not appear to influence malachite flotation. Sedimentation tests showed that hetero-coagulation occurred in both of malachite-calcite and malachite-quartz systems. The zeta potential distribution of individual minerals and mixed minerals measurements were used to describe the observed depression of sulfidization flotation of malachite by calcite but not quartz slime addition. DLVO calculation can be explained the hetero-coagulation in malachite-calcite system but not in malachite-quartz system, this may be attributed to the dissolved species of malachite adsorbed on quartz surface in malachite-quartz system.

### 1. Introduction

Sulfide minerals such as chalcopryrite, chalcocine, etc. are main

sources for the extraction of copper. Most valuable copper sulfide minerals are associated with copper oxide minerals, and available copper sulfide resources are becoming depleting. Therefore, beneficiation of

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oxidized copper ore is becoming increasingly attractive [1–4]. Malachite is a typical copper oxide mineral and possesses a naturally hydrophilic surface which does not respond well to traditional collectors for copper sulfide flotation, such as xanthate [5,6]. Currently, sulfidization-xanthate flotation is a commonly used method for the beneficiation of malachite and other oxidized copper, lead, and zinc minerals [7–12]. Sulfidization reaction is an important factor for the sulfidization-xanthate flotation of malachite. The optimal pulp pH for the sulfidization of malachite is approximately 9.5. At this pH value,  $\text{HS}^-$  is the dominant species that interacts with the copper site and forms copper sulfide complex at malachite surface, and consequently the surface hydrophobicity of malachite is improved [5]. Hence, increased effective adsorption of sulfide species ( $\text{HS}^-$ ) at malachite surface will improve the flotability of malachite.

Quartz and calcite are common gangue minerals in copper oxide ores [13]. Calcite is easy to become slimed during grinding process due to its low hardness, and a part of quartz also can be slimed in ground slurries although its degree of hardness is great. The quartz and/or calcite slimes may influence the sulfidization-flotation properties of malachite. Currently, very little research has been conducted concerning the interaction of malachite and calcite or malachite and quartz, as well as its implications for malachite sulfidization-flotation. The interaction mechanism is unclear. Hence, a better understanding of the interaction between malachite and its gangue minerals is of fundamental importance for the sulfidization-flotation of malachite.

In this work, the interaction between malachite and its gangue minerals (calcite and quartz) and implications for sulfidization flotation of malachite were studied. This was accomplished through the use of a series of experiments and analytical techniques, including micro-flotation tests, sedimentation tests, zeta potential distribution measurements and DLVO calculations.

## 2. Experimental

### 2.1. Samples and reagents

Malachite and calcite samples used for the experiments were obtained from Yunnan Province of China. The samples were crushed and ground using an agate mortar. Size fractions of  $-10\ \mu\text{m}$ ,  $-10\ \mu\text{m}$  and  $-74 + 38\ \mu\text{m}$  were utilized for the micro-flotation tests of calcite, quartz and malachite, respectively. The  $-5\ \mu\text{m}$  size fractions were prepared for zeta potential measurements. The X-ray diffraction analysis results and chemical compositions for these samples were shown in Fig. 1 and Table 1, respectively. X-ray diffraction analysis and chemical composition results demonstrate that the purities of samples are very high.

Sodium butyl xanthate (SBX) with 88% purity was obtained from Zhuzhou Flotation Reagent Company, and was used as the collector.  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and methyl isobutyl carbinol (MIBC) were of analytical-grade, and were used as sulfidizing reagent and frother, respectively. NaOH and HCl (analytical-grade) were utilized as pH modifiers in the experiments. Distilled water with a minimum resistivity of  $18.2\ \Omega\ \text{cm}$  was used for all the tests.

### 2.2. Micro-flotation tests

The flotation tests were carried out in a mechanically agitated flotation machine. Pure mineral particles (2 g) and distilled water (40 ml) were mixed in the plexiglass cell and the pulp was fixed at a temperature of 298 K. When needed, calcite was added prior to the conditioning of malachite. A fresh prepared  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  solution with a desired dosage was added to sulfidize the malachite surface for 5 min, and the pulp pH was adjusted by NaOH and/or HCl. SBX as a collector and MIBC as a frother were added into the suspension in sequence, and conditioned for 3 min and 1 min, respectively. The time for froth collection was 4 min. For individual mineral tests, both the floated and

sunk products were filtered, dried, and weighed, and the recovery was calculated based on the dry weight of the product. In the case of an artificial binary mineral mixture (malachite-calcite or malachite-quartz) tests, the concentrates (floated) and tailings (sunk) were assayed for Cu, and the recovery was calculated based on the Cu contents and dry weights in concentrates and tailings. Each micro-flotation test was measured for three times, and the average was reported as the final value.

### 2.3. Sedimentation tests

The sedimentation rate of samples was characterized by turbidity. Sedimentation tests were performed using a Turb 555 IR nephelometer. 0.1 g of calcite or quartz samples were added to a certain volume (100 ml) of distilled water (298 K). When needed, 0.5 g malachite was added in the calcite or quartz suspension. The suspension was stirred for 3 min using a magnetic stirrer. 25 ml supernatant was pipetted out for turbidity measurement. The nephelometer is connected to a computer which collects the data at sedimentation time of 3 min.

### 2.4. Zeta potential distribution measurements

For the zeta potential measurements of individual mineral system, a suspension of 0.05% (by weight) sample was prepared in the  $1 \times 10^{-3}\ \text{M}$  KCl background electrolyte solution. The suspensions of sample were magnetically stirred in a beaker for 10 min at pH 9.5. After settling for 10 min, the pH value of the suspension was recorded and the supernatant was collected for zeta potential distribution measurements. For the binary mineral mixture, the suspension for a binary malachite-calcite or malachite-quartz mixture was prepared by mixing equal volumes of the individual mineral suspensions, and then was stirred with an magnetic stirrer for about 15 min. The pH value of 9.5 was selected for zeta potential distribution measurements for mixed binary minerals.

Zeta potential distribution measurements were carried out by a Zetaphoremeter III (SEPHY/CAD), which was equipped with a rectangular electrophoresis cell, a pair of hydrogenated palladium electrodes, a laser-illuminator and a CCD camera. The system requires an accurate positioning of the stationary layer, where the electrophoretic mobility can be measured accurately. The movement of 50–100 particles in the stationary layer was recorded with the CCD camera. The captured images were then analyzed by the built-in image processing software. The electrophoretic mobility distribution histogram and the corresponding average values were determined, and the data were then converted to zeta potential distributions.

## 3. Results and discussion

### 3.1. Micro-flotation results

Micro-flotation tests were performed in order to investigate the flotation performance of individual minerals and binary mineral systems. Fig. 2 shows the flotation recovery of the three minerals in the absence and presence of sodium sulphide when  $8 \times 10^{-4}\ \text{mol/L}$  SBX was used as a collector. As shown in Fig. 2, in the absence of  $\text{Na}_2\text{S}$ , the flotability of malachite using the SBX collector is poor, and a maximum recovery of approximately 20% was obtained at pH 9.5. This finding is mainly attributed to the fact that xanthate cannot adsorb stably on malachite surface, and also the collecting capacity of the SBX collector is low because of its short carbon chain length [5,14,15]. In the presence of  $\text{Na}_2\text{S}$ , the flotation recovery of malachite increases with the increase of pH and reaches a maximum value of approximately 80% at pH of about 9.5. This is due to the sulfidization of malachite by  $\text{Na}_2\text{S}$ , which improves hydrophobicity of malachite surface, as reported by Feng et al. [5]. Different from malachite, calcite and quartz remain poor flotability with and without  $\text{Na}_2\text{S}$  in the pH range of 7–11, indicating that  $\text{Na}_2\text{S}$  does not influence the surface properties of quartz and calcite.

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