



Effect of copper ions on the flotation separation of chalcopyrite and molybdenite using sodium sulfide as a depressant



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ABSTRACT

Copper ions are unavoidable in the process of copper-molybdenum flotation separation. The flotation response of chalcopyrite and molybdenite in the presence of copper ions was investigated through single mineral flotation tests and flotation separation tests. The influence mechanism was studied by adsorption experiments, zeta-potential measurements, and X-ray photoelectron spectroscopy (XPS) analysis. Flotation results indicated that copper ions dramatically reduced the recoveries of copper and molybdenum, and increased the inhibition effect of sodium sulfide; that is, the flotation separation of chalcopyrite and molybdenite was seriously hindered by copper ions. The adsorption experiments demonstrated that copper ions were adsorbed on molybdenite and chalcopyrite, and the adsorption amounts increased in the presence of sodium sulfide. The results of zeta-potential measurements confirmed that the floatability of the minerals was deteriorated by the adsorption of copper hydroxides ($\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$) and the subsequent adsorption of hydrosulfide ions (HS^-). Moreover, XPS analysis verified that the adsorbed copper hydroxides reacted with hydrosulfide ions, producing Cu(I)-S species on the surface of chalcopyrite and molybdenite. The adsorbed Cu(I) ions provided additional reaction sites and promoted the formation of a hydrophilic layer by the attachment of excessive hydrosulfide ions. Based on these analyses, a possible inhibition model for the interactions among the mineral surface, copper ions, and sulfide ions is proposed.

1. Introduction

Copper minerals and molybdenum minerals have closely paragenetic relationships, and approximately half of molybdenum production comes from Cu-Mo sulfide ores as a by-product (Hirajima et al., 2014). Porphyry copper deposits are one of the primary resources for the extraction of copper and molybdenum, in which chalcopyrite and molybdenite are the dominant valuable minerals. The typical flotation process for this type of ore involves the bulk flotation in the first stage and the separation of molybdenite from Cu-Mo bulk concentrate in the second stage (Ansari and Pawlik, 2007). However, the residual collectors in the bulk concentrate and the similar floatability of chalcopyrite and molybdenite make the separation process challenging. Therefore, increasing and maintaining the floatability difference between chalcopyrite and molybdenite is imperative for successful separation results. For porphyry copper ore, this is usually achieved by using the selective inhibition effect of depressants on chalcopyrite. Various depressants have been synthesized and applied to depress chalcopyrite by removing the adsorbed collectors or forming a hydrophilic layer on its surface (Deng et al., 2014; Li et al., 2015a; Li et al., 2015b; Yin et al., 2017a).

Furthermore, most depressants are designed to react with the exposed copper and iron ions on chalcopyrite surface. Hence, theoretically, the floatability of molybdenite is almost unaffected, owing to the absence of reaction sites.

In practical flotation processes, however, the surface properties of minerals and the function of reagents might be significantly affected by various ions in the process water. Generally, metal ions such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Pb^{2+} , Al^{3+} , Fe^{3+} , and Cu^{2+} are released from the added reagents or dissolved from the mineral surface during comminution and flotation (Ikumapayi et al., 2012; Raghavan and Hsu, 1984). For instance, lime is widely used as the pH regulator in bulk flotation and could release Ca^{2+} into the pulp. To understand the effect of Ca^{2+} on the floatability of molybdenite, many relevant studies at different pH have been studied. It has been found that Ca^{2+} may act as a promoter in acidic media or a depressant in alkaline media for the flotation of molybdenite (Chander and Fuerstenau, 1972; Hoover, 1980). Due to the Cu-Mo separation process is carried out at neutral or weakly alkaline pH, systematic studies have revealed that Ca^{2+} and $\text{Ca}(\text{OH})^+$ ions are strongly adsorbed on molybdenite, and the adsorption amount increases with increasing pH (Castro et al., 2016; Hirajima

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et al., 2016). In addition, it has been reported that $\text{Ca}(\text{OH})^+$ ions could not only adsorb at the edges of molybdenite particles, but also on the basal planes (López-Valdivieso et al., 2012). Similar phenomena and mechanisms have been extensively studied for the Cu-Mo separation process at pH 9.5–10.0 in seawater, which contains high levels of Ca^{2+} and Mg^{2+} (Laskowski et al., 2014; Yin et al., 2017b). The depression effect takes place in the approximate pH range where magnesium hydroxide ($\text{Mg}(\text{OH})_{2(s)}$) starts precipitating, because there is significantly more Mg^{2+} hydrolysis than that of Ca^{2+} at the same pH (Castro et al., 2014; Laskowski et al., 2014). Furthermore, the hydrophilic metal hydroxides adsorb on the surface of minerals without selectivity and reduce the floatability of both chalcopyrite and molybdenite during separation (Hirajima et al., 2016; Qiu et al., 2016; Somasundaran et al., 2000). Consequently, the hydrophilic shells composed of metal hydroxides constitute a barrier to the adsorption of inhibitors and collectors (Castro, 2012; Hirajima et al., 2016). However, some metal ions are also prone to adsorption on the surface of minerals, providing reaction sites. For instance, Cu^{2+} is generally regarded as the activator for some sulfide minerals such as sphalerite, pyrite and even chalcopyrite when xanthates are used as collectors (Chandra and Gerson, 2009; Chandra et al., 2012). The activation mechanism is commonly considered to be that the copper ions adsorb on the surface of minerals, increasing the number of active sites for xanthate molecules, thereby improving the floatability (Ejtemaei and Nguyen, 2017; Liu et al., 2014; Yin et al., 2010). Nevertheless, in the presence of depressants for chalcopyrite and when using non-polar oil as the collector during Cu-Mo separation, the adsorption of copper species on chalcopyrite and molybdenite might result in inhibited sites instead of active sites and make adverse effects on Cu-Mo separation. These effects are rarely involved in the reported literatures.

Therefore, a systematic investigation concerning the effect of Cu^{2+} on the flotation separation of chalcopyrite and molybdenite using sodium sulfide as a depressant was conducted by various methods: flotation tests, adsorption experiments, zeta potential measurements and X-ray photoelectron spectroscopy (XPS) analysis.

2. Experimental

2.1. Materials

Pure chalcopyrite and molybdenite were procured from Dayao Copper Mine and China Molybdenum Co., Ltd., respectively. The samples were carefully hand-picked, crushed and ground in a laboratory porcelain mill. Then, the products were sieved with standard screens to obtain samples of different fineness and stored in sealed jars to minimize oxidation. The $-100 + 43 \mu\text{m}$ size fractions were used in single mineral flotation tests, and the $-5 \mu\text{m}$ size fractions were used for chemical analysis, X-ray diffraction (XRD) analysis, adsorption experiments, zeta-potential measurements, and XPS analysis. The chemical analysis results demonstrated that the pure chalcopyrite sample contained 34.23% Cu, 29.09% Fe, and 35.93% S; and the pure molybdenite sample contained 58.23% Mo, 38.86% S, 1.49% Cu, 1.13% Fe and traces of quartz. The XRD results (Fig. 1) reconfirmed that the main minerals in the pure samples were chalcopyrite and molybdenite, respectively. Therefore, the samples were sufficiently pure to meet the requirement for all experiments.

A representative sample of Cu-Mo bulk concentrate was obtained from Jiama Dressing Plant located in Tibet, China. It contained 25.74% Cu, 1.98% Mo and some silica impurities. The mineralogical data verified that copper minerals and molybdenum minerals mainly existed in the form of chalcopyrite and molybdenite, respectively. The samples were reground with a porcelain mill to obtain $-100 + 43 \mu\text{m}$ size fraction for flotation separation tests.

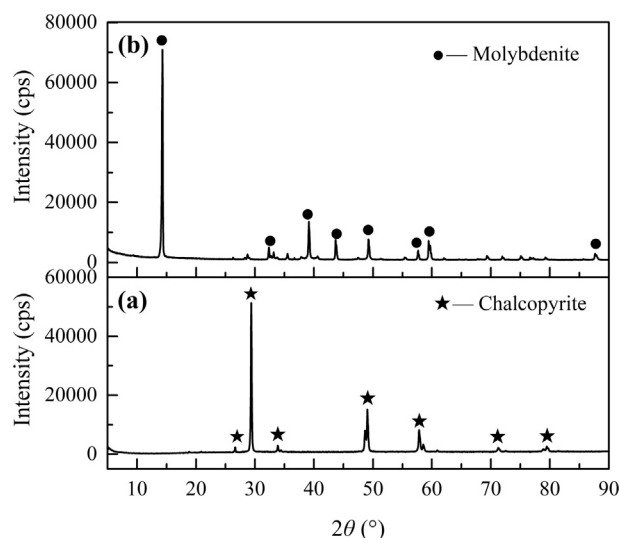


Fig. 1. X-ray diffraction patterns of chalcopyrite (a) and molybdenite (b).

2.2. Reagents

Chemically pure cupric chloride (CuCl_2) and sodium sulfide non-anhydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) were purchased from Kermel Chemical Reagent Co., Ltd., China. The solutions of copper ions and sulfide ions were prepared at a ion concentration of 1 g/L and used in all tests. Industrial pure kerosene and terpenic oil were used as the collector and frother, respectively. Before adding into the pulp, the collector and the frother were diluted with distilled water and treated with ultrasound for 5 min to enhance the dispersion. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions (0.1 mol/L) were used to adjust the slurry pH. Distilled water was used in all experiments.

2.3. Flotation tests

Single mineral flotation tests were conducted in a 30 mL XFG₁₁₅ flotation cell with a fixed impeller speed of 1260 rpm. In a typical test, 2 g samples were cleaned with an ultrasonic cleaner for 2 min and then transferred into the flotation cell. Before the slurry pH was adjusted to the required value, different concentrations of Cu^{2+} and/or S^{2-} were added into the suspension and stirred for 3 min. Then, the collector (10 mg/L kerosene) and frother (5 mg/L terpenic oil) were introduced into the cell in that order with a 2 min conditioning time. After flotation for 5 min, the floated and the submerged fractions were separately collected, filtrated, and dried. For single mineral flotation, the recovery was calculated on the basis of the solid weight distributions of the two products. To ensure the accuracy of flotation tests, the average recovery of at least three parallel tests under each condition was calculated and reported along with the standard deviation.

Flotation separation tests were implemented with the aid of an XFD_{III} flotation machine equipped with a 1 L flotation cell, manufactured by Jilin Prospecting Machinery Factory, China. During the conditioning process, the pulp was prepared with 350 g Cu-Mo bulk concentrate and 500 mL distilled water. The addition sequence and the dosage of flotation reagents were established as follows: cupric chloride (CuCl_2 , variable), pH regulators (pH = 7.5–8.0), depressant (5000 g/t Na_2S), collector (100 g/t kerosene), and frother (50 g/t terpenic oil). The conditioning time for each reagent was 2 min, and then the pulp density was adjusted to about 33% before flotation. The flotation was conducted for a total of 5 min. After flotation, both the Mo concentrate and the Cu concentrate were filtered, weighed and assayed, respectively. The recoveries of Cu and Mo in Mo concentrate were calculated based on the weight and grade. All tests were conducted at room temperature of approximately 293 K.

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