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# Selective depression effect in flotation separation of copper−molybdenum sulfides using 2,3-disulfanylbutanedioic acid

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**Abstract:** 2,3-disulfanylbutanedioic acid (DMSA) was found to be a selective depressant in the flotation separation of copper−molybdenum sulfides. The flotation results suggest that a low dosage of DMSA has a strong depression effect on chalcopyrite in the pH range between 4 and 12. At pH 6, the recoveries of molybdenum are up to 85%, 75%, and 80% while those of chalcopyrite are 15%, 5%, and 20% respectively when flotation tests are carried out with single minerals, mixed minerals and molybdenum-bearing copper concentrates. Adsorption isotherms measurement indicates that DMSA adsorbs more strongly on chalcopyrite than on molybdenite. The frontier orbital calculation reveals that the two S atoms of DMSA molecule are active centers for the adsorption of the DMSA molecule on chalcopyrite surface. Fermi level calculation shows that chalcopyrite can obtain electrons from the DMSA molecule while molybdenite cannot.

**Key words:** 2,3-disulfanylbutanedioic acid; molybdenite; chalcopyrite; copper−molybdenum separation; frontier orbital

## 1 Introduction

Molybdenite ($MoS_2$) is the most important source mineral to extract molybdenum. It is usually associated with copper sulfide ore as a trace mineral [1−3]. In the flotation of copper−molybdenum sulfide ores, two methods are widely used: 1) the bulk copper−molybdenum flotation, followed by copper−molybdenum separation; 2) the sequential flotation of the copper and molybdenum sulfide minerals. Because the sequential separation usually requires large reagent dosages and complex flowsheet, the bulk copper−molybdenum flotation is commonly used in the commercial process.

Inorganic depressants are routinely used as selective depressants in copper−molybdenum separation due to their low price and good performance, e.g., sodium sulfide (or sodium hydrosulfide) is used to depress chalcopyrite [4]. However, these inorganic depressants are usually toxic or hazardous, and large dosages are usually required which lead to high cost and low selectivity. The alternative is to use organic depressants, which are more environmentally friendly and selective. Moreover, organic depressants can be designed and synthesized to tailor the needs. In fact, an increasing need for alternative depressants has led to extensive research on the use of organic depressants in copper–molybdenum separation.

For molybdenite depression, ANSARI and PAWLIK [5,6] investigated the adsorption and Hallimond tube flotation of chalcopyrite and molybdenite in the presence of lignosulphonates. The results suggested that it is possible to selectively float chalcopyrite from molybdenite over a wide pH range, and that lignosulphonate can be selectively adsorbed on molybdenite and make it hydrophilic. Their results are in line with the results presented by KELEBEK et al [7]. In addition, humus substance and dextrin are also shown to strongly depress molybdenite [8,9].

In terms of chalcopyrite depressants, thioglycolic acid or sodium thioglycollate is commonly considered to be traditional and effective depressant [10]. Sodium thioglycollate was used as the depressant for chalcopyrite and pyrite in the copper−molybdenum separation process of Qingyang molybdenum ore, and the results showed that sodium thioglycollate has a strong depressive effect on chalcopyrite and pyrite, but has relatively little impact

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on molybdenite flotation [11]. Many other new depressants also show depression effect on chalcopyrite. For example, CHEN et al [12] investigated the separation of chalcopyrite and molybdenite using pseudo glycolythiourea acid (PGA), and showed that it is possible to depress chalcopyrite selectively and float molybdenite in the presence of PGA. HUANG et al [13] reported that chitosan selectively depressed chalcopyrite while galena was floated by xanthate.

Many kinds of chalcopyrite depressants are being used in flotation, but more novel and nontoxic depressants need to be found with the increasingly rigid environmental pollution control regulations. A novel selective depressant named 2,3-disulfanylbutanedioic acid (DMSA) was firstly used in copper−molybdenum sulfides separation. DMSA is a white crystalline powder with a smell of sulfhydryl compounds, and every DMSA molecule contains two carboxyl and two sulfydryl groups. It is similar to thioglycolic acid in terms of functional groups, but is more stable and much less toxic than thioglycolic acid [14,15]. Although much work has been done on the copper sulfide ore depressants for copper–molybdenum separation, there is still a lack of understanding on the flotation characteristics of copper−molybdenum sulfides when DMSA is used as the depressant. Thus, the main purpose of this work is to investigate the copper–molybdenum separation characteristics in the presence of DMSA, and to delineate the mechanism of flotation depression.

## 2 Experimental

### 2.1 Materials

2.1.1 Reagents

2,3-disulfanylbutanedioic acid (DMSA) with a reported purity over 99% was purchased from Beshine Chemical Science and Technology (Beijing) Co., Ltd.. The DMSA solution was prepared by dissolving the DMSA in diluted sodium hydroxide solution (0.2 mol/L). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used as pH regulators and were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Kerosene and terpenic oil were provided by Tieling Flotation Reagents Factory, China.

2.1.2 Minerals

High-purity chalcopyrite and molybdenite were obtained from Yunnan and Tibet, China, respectively. They were used as the single mineral samples of copper and molybdenum sulfide minerals in experiments. The lumps of the chalcopyrite and molybdenite were separately crushed manually and hand-picked in order to gain high-purity samples, then further crushed and pulverized in an agate mortar. The particles with size larger than 45 μm and less than 100 μm were screened out for use in the flotation tests. The results of chemical analysis revealed that the purity of chalcopyrite was 95.0% and that of molybdenite was 90.2%.

The mixed minerals of copper and molybdenum were prepared by mixing high-purity chalcopyrite and molybdenite (with a mass ratio of 3:1).

A copper−molybdenum ore sample was obtained from Jiama copper polymetallic deposit in Tibet, which contained 0.90% copper and 0.056% molybdenum. The mineralogical analysis showed that the sulfide minerals consisted mainly of chalcopyrite, molybdenite, as well as minor pyrite, and the gangue minerals were primarily quartz, chlorite and calcite. The screen analysis of the ore showed that 70% of the particles were less then 74 μm after crushing and milling. The molybdenum-bearing copper concentrate was obtained through filtering and drying the concentrate of bulk flotation test as shown in Fig. 1 in the vacuum drying oven at 25 °C. Chemical analysis of the bulk concentrate sample showed that it contained 22.42% copper and 1.96% molybdenum.

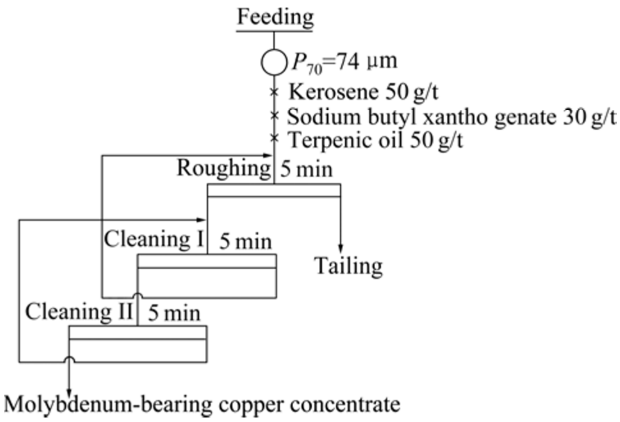


**Fig. 1** Flotation flowsheet of closed circuit experiment to obtain molybdenum-bearing copper concentrate

### 2.2 Methods

2.2.1 Flotation tests

The flotation tests were conducted in a microflotation cell. In a typical test, 2 g of the samples with particle size larger than 45 μm and less than 100 μm were ultrasonically washed in distilled water for 5 min to remove any possible oxides on the mineral surface. Then, the washing solution of samples was decanted, and the remaining part was removed to the microflotation cell and diluted to 30 mL with distilled water. The slurry pH was adjusted by HCl or NaOH. Subsequently, an appropriate amount of DMSA, kerosene and terpenic oil were added in sequence to the cell and conditioned for 2 min each. The conditioned slurry was floated for 5 min. Both the froth product and tailing were collected and dried to calculate mineral recovery in single minerals flotation. In the flotation separation tests of mineral