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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.

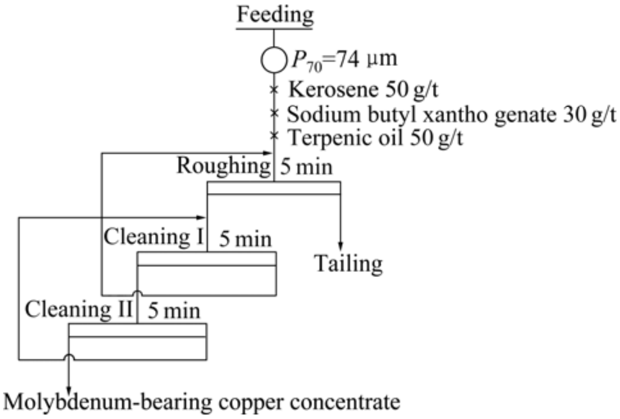

Fig. 1 Flotation flowsheet of closed circuit experiment to obtain molybdenum-bearing copper concentrate

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 mixtures and molybdenum-bearing copper concentrate, the metal contents of copper and molybdenum in the froth and tailing were calculated based on chemical analysis.

2.2.2 Adsorption isotherms measurement

For the adsorption tests, 2 g mineral powder was transferred to a glass conditioning vessel and made up to 30 mL after the addition of desired amounts of DMSA solution of known concentration and pH. Then, the suspensions were stirred continuously 0.5 h using a magnetic stirrer at 25 °C [16]. After equilibration, the solution was centrifuged for 5 min at 5000 r/min. The supernatant liquid was then clarified using 2 μm filter paper and analyzed for the reagent concentration by spectrophotometric method [17].

2.2.3 Quantum chemistry calculation

The geometry optimizations and frontier orbital calculations of minerals were conducted by the CASTEP [18] and DMol3 modules in Material Studio calculation software, while the structure optimization and frontier orbital calculation on the DMSA were performed using DMol3 module. The DMol3 was set with GGA-PW91 [19,20] method, DNP basis set, effective core potentials, a fine quality, and SCF convergence threshold of 1.0×10^{-6} eV/atom.

3 Results and discussion

3.1 Flotation of single minerals

The flotation recoveries of chalcopyrite and molybdenite in single mineral flotation tests with and without DMSA as a depressant at different pH values are presented in Fig. 2 and Fig. 3, respectively. In the absence of DMSA, chalcopyrite and molybdenite are floatable with a high flotation recovery of more than 85% and 70%, respectively, in the tested pH range. Furthermore, both the flotation recoveries of chalcopyrite and molybdenite are enhanced with the increase of pH from 4 to 8, but gradually decreased above pH 8. The flotability of chalcopyrite becomes significantly poor while the recovery of molybdenite decreases slightly, when 46.7 mg/L DMSA is added into the system. Between pH 4 and 8, the recovery of chalcopyrite dropped from over 70% in the absence of DMSA to less than 10% in the presence of 46.7 mg/L DMSA as shown in Fig. 3.

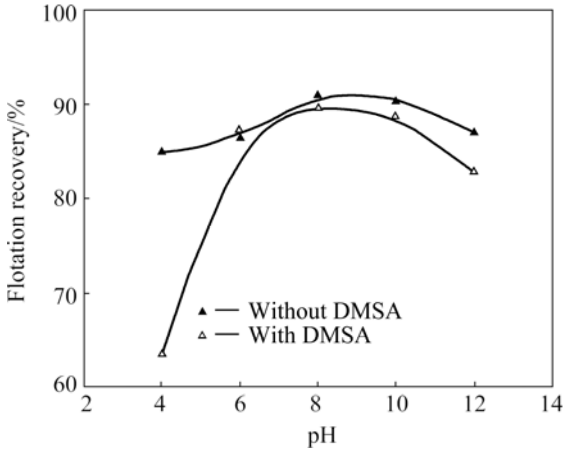

Fig. 2 Flotation recoveries of molybdenite as function of pH by collector kerosene (8.3 mg/L) with or without DMSA (46.7 mg/L) depressant

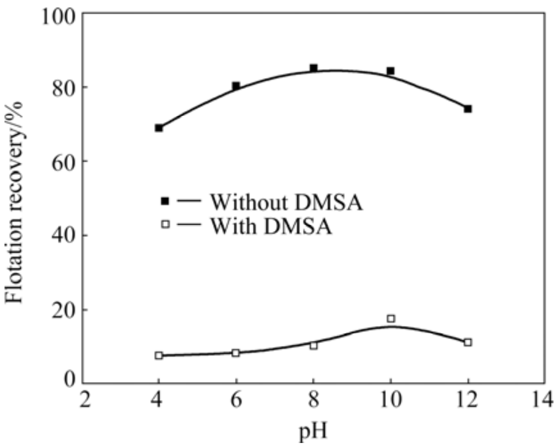

Fig. 3 Flotation recoveries of chalcopyrite as function of pH by collector kerosene (8.3 mg/L) with or without DMSA (46.7 mg/L) depressant

Figure 4 shows the recoveries of chalcopyrite and molybdenite at different DMSA concentrations. As shown in this figure, the recovery of chalcopyrite decreases rapidly from 56.2% to 6.3% with the increase in DMSA concentration from 6.7 mg/L to 66.7 mg/L. However, the recovery of molybdenite is not affected and remains around 90% in the entire tested DMSA concentration range.

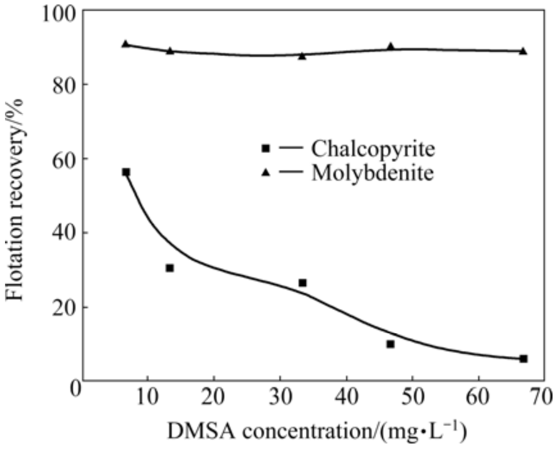

Fig. 4 Flotation recoveries of chalcopyrite and molybdenite as function of DMSA concentration at pH 6 by collector kerosene (8.3 mg/L)

3.2 Flotation of copper−molybdenum mineral mixtures

The flotation tests of single minerals prove the possibility of using DMSA as a selective depressant in the copper−molybdenum separation. Based on the results of single mineral flotation tests as above, the differential flotation tests of chalcopyrite−molybdenite mixtures (chalcopyrite and molybdenite with mass ratio of 3:1) were conducted at different pH values and DMSA concentrations. It can be seen in Fig. 5 that the recoveries of copper and molybdenum metals in froth are about 5% and 75% respectively at pH 6. They both increase with increasing pH below 10, and decrease with further increasing pH over 10. This recovery tendency of mixed minerals is similar to that of the single minerals.

As shown in Fig. 6, the recovery of copper in froth decreases slightly with the increase of DMSA concentration, while the recovery of molybdenum in froth has no significant change in the range of DMSA dosage from 6.7 mg/L to 66.7 mg/L, which indicates that DMSA dosage has little effect on the flotability of molybdenite. There is a interesting phenomenon that the recoveries of molybdenum in whole concentration range are a little lower than that in single minerals flotation. The low floatability can be ascribed into the adsorption of copper ion which comes from the dissolution of chalcopyrite on molybdenite surface.

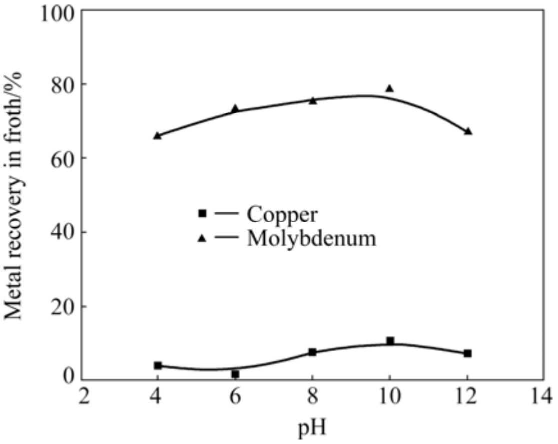

Fig. 5 Recoveries of copper and molybdenum in froth as function of pH by collector kerosene (8.3 mg/L) with DMSA depressant (46.7 mg/L)

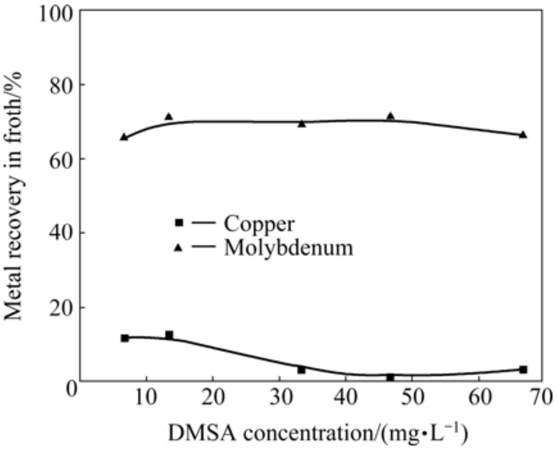

Fig. 6 Recoveries of copper and molybdenum in froth as function of DMSA concentration at pH 6 by collector kerosene (8.3 mg/L)

3.3 Flotation of molybdenum-bearing copper concentrate

The effects of slurry pH value on the recoveries of copper and molybdenum in the molybdenum-bearing copper concentrate were investigated and the results are shown in Fig. 7. With the increase in pH values from 4 to 8, the recovery of molybdenum in froth increases rapidly from about 15% to 75% then decreases gradually when pH is over 8. The recovery of copper in froth is below 20% and also varies with pH in a similar fashion as that of molybdenum.

The influence of DMSA concentration on the molybdenum-bearing copper concentrate separation was further tested. Figure 8 shows that both the recoveries of copper and molybdenum in froth decrease slowly with the increase of DMSA concentration. The recoveries of copper and molybdenum declined from about 25% to 15% and 85% to 75% in the tested DMSA concentration range, respectively. The average recovery difference between copper and molybdenum is about 60% in the tested DMSA concentration range, which indicates that DMSA is effective for the copper−molybdenum separation of molybdenum-bearing copper concentrate.

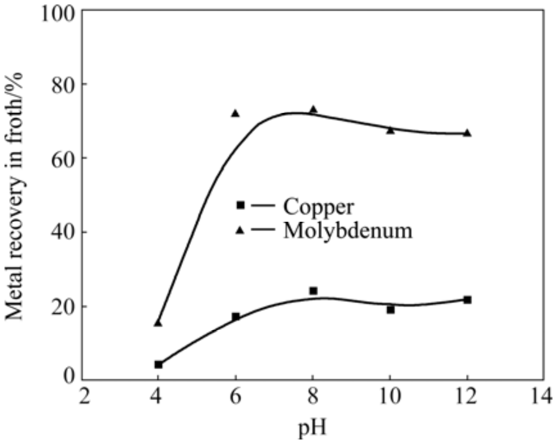

Fig. 7 Recoveries of copper and molybdenum in forth as function of pH for molybdenum-bearing copper concentrate flotation by collector kerosene (8.3 mg/L) with DMSA (46.7 mg/L)

3.4 Adsorption isotherms measurement

The effects of pH on the adsorption density of DMSA onto chalcopyrite and molybdenite are plotted in Fig. 9. As can be seen, the solution pH has little effect on the adsorption capacity of DMSA on molybdenite. But the pH clearly influences the adsorption capacity of DMSA on chalcopyrite: the adsorption of DMSA rises sharply with increasing pH from 4 to 6, and then maintains a high level when pH increases from 6 to 8, but drops gradually when pH is over 8. This tendency is consistent with the results of the flotation test (Fig. 2).

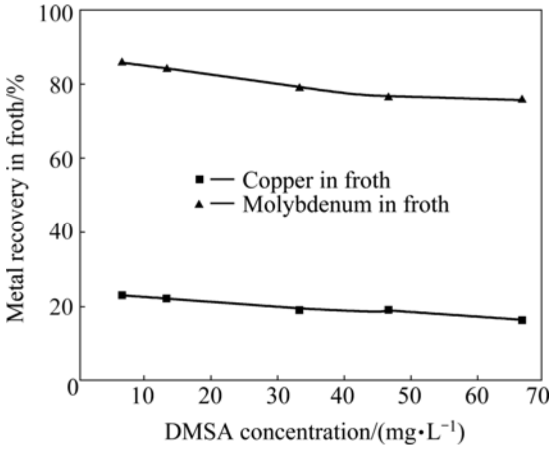

Fig. 8 Recoveries of copper and molybdenum in forth as function of DMSA concentration for molybdenum-bearing copper concentrate at pH 6 by collector kerosene (8.3 mg/L)

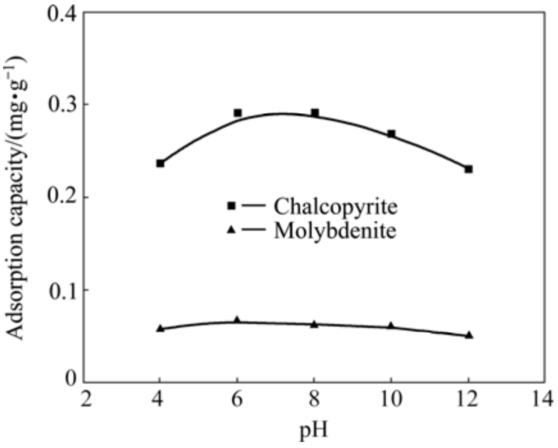

Fig. 9 Adsorption capacity of DMSA on chalcopyrite and molybdenite as function of pH

Figure 10 shows the adsorption capacity of DMSA on chalcopyrite and molybdenite as a function of DMSA concentration at pH 6. It is obvious that the adsorption capacities of DMSA on chalcopyrite and molybdenite increase together. But the increasing adsorption amount with chalcopyrite is faster compared with molybdenite, which is in agreement with the result of the flotation test (Fig. 3).

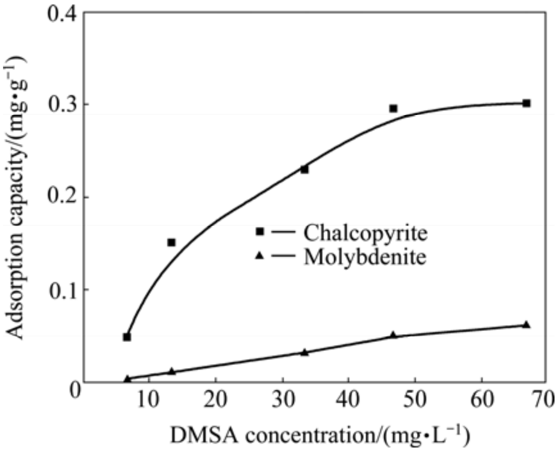

Fig. 10 Adsorption capacity of DMSA on chalcopyrite and molybdenite as function of DMSA concentration (pH=6)

3.5 Calculation results of frontier orbital and atomic orbital coefficients

According to the frontier molecular orbital theory, the electrons belonging to the highest occupied molecular orbital (HOMO) of the molecule show the greatest activity. There are two ways to predict the potential reaction atoms between molecules. In the first way, a larger electron density means a greater reactivity of the HOMO. Therefore, the atom with the largest electron density is most likely to play a role in the reaction between molecules. In the second way, the atomic orbital coefficients can be used to assess the contribution of atoms to the frontier orbital. A greater absolute value of coefficient indicates a greater contribution of the atom to the frontier orbital. It can be seen apparently in Fig. 11(b) that the shadow surrounding the atoms shows the electron density of the HOMO of DMSA molecule, which is mainly located on S atoms.

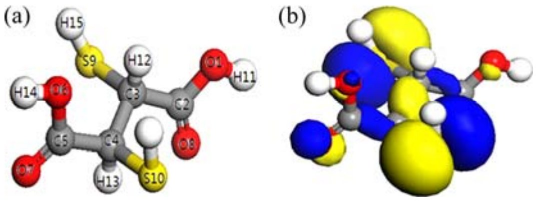

Fig. 11 Molecular structure (a) and HOMO (b) of DMSA

The calculated composition of HOMO for DMSA molecule can be expressed as follows:

$$-0.00042C_2(2p)+0.300708C_3(2p)-0.303535C_4(2p)+0.057074C_5(2p)+0.144537O_1(2p)+0.0729O_6(2p)-0.044869O_7(2p)+0.162322O_8(2p)-0.952129S_9(3p)+0.903523S_{10}(3p)+0.039769H_{11}(1s)+0.025784H_{12}(1s)+0.008413H_{13}(1s)+0.023838H_{14}(1s)-0.003767H_{15}(1s)+0.004075H_{16}(1s)$$

The calculation result reveals that S_9 and S_{10} atoms have the greatest orbital coefficients (0.952129 and 0.903523), while the coefficients of other atoms are quite small. This suggests that S_9 and S_{10} atoms are most likely the reactive sites between DMSA and mineral.

The Fermi level represents the average chemical potential of electrons in the system, and the direction of electron transfer is always from a high energy level to a low energy level. The organic depressants with a strong reducibility mainly depress minerals by transferring electrons from the depressants to the minerals surface [21]. The Fermi level values of chalcopyrite, molybdenite and DMSA were calculated to be −6.1097, −4.3531 and −5.5725 eV, respectively, indicating that chalcopyrite can easily obtain electrons from DMSA while molybdenite cannot. Therefore, it can be concluded that DMSA only reacts with chalcopyrite by electrons transfer which is consistent with the results of adsorption capacity test of DMSA on chalcopyrite and molybdenite as shown in Fig. 10.

4 Conclusions

1) DMSA was investigated as a depressant of chalcopyrite in the flotation separation of copper–molybdenum sulfide minerals. The flotation tests of single minerals, mixed minerals, and molybdenum-bearing copper concentrates indicated that DMSA has a strong depression effect on chalcopyrite in the pH range between 4 and 12. The maximal recovery difference was obtained at pH 6, where the recoveries of molybdenite were as high as 85%, 75% and 80%, respectively, while those of chalcopyrite were depressed with low recoveries of 15%, 5% and 20%, respectively for the separation of single minerals, mixed minerals, and molybdenum-bearing copper concentrates.

2) Adsorption isotherms measurement showed that the adsorption capacity of DMSA on chalcopyrite (0.29 mg/g) is much higher than that on molybdenite (0.05 mg/g) when DMSA concentration is 46.67 mg/L.

3) The frontier orbital calculation for DMSA molecule indicated that the two S atoms are active centers. The analysis of Fermi level energies of DMSA (−5.5725 eV), chalcopyrite (−6.1097 eV) and molybdenite (−4.3531 eV) showed that the Fermi; level of DMSA is higher than that of chalcopyrite but lower than that of molybdenite, which revealed that the depression of DMSA can be ascribed by the transfer of electrons.

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2,3-二巯基丁二酸在铜−钼硫化矿浮选分离过程中的选择性抑制作用

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摘　要：2,3-二巯基丁二酸(DMSA)是一种铜−钼硫化矿分离浮选抑制剂。浮选试验结果表明，在 pH 4−12 的范围内少量的 DMSA 可对黄铜矿产生强烈的抑制作用。在 pH 6 条件下对单矿物、人工混合矿、含钼铜精矿进行浮选分离试验，钼的浮选回收率分别为 85%、75%和 80%，同时铜的回收率仅为 15%、5%和 20%。吸附量试验结果显示，DMSA 在黄铜矿上的吸附作用明显强于辉钼矿。前线轨道计算表明，DMSA 分子中的两个硫原子是药剂分子与黄铜矿表面作用的活性中心。费米能级计算结果显示黄铜矿可以从 DMSA 分子获得电子而辉钼矿不能。

关键词：2,3-二巯基丁二酸；辉钼矿；黄铜矿；铜−钼分离；前线轨道

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