



Effective recovery of chalcopyrite at low temperatures using modified ester collector

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Received 12 January 2021; accepted 25 August 2021

Abstract: The effect of a modified ester collector named as BL on the flotation of chalcopyrite at low temperatures was investigated by micro-flotation tests, contact angle measurements, adsorption experiments, laser particle size analysis, cryogenic transmission electron microscopy (Cryo-TEM) and Fourier transform infrared (FTIR) analyses. Micro-flotation tests proved that the collecting ability of BL for chalcopyrite was significantly better than that of N,N-diethyl dithiocarbamate propionitrile ester (ester-105) at low temperatures. Combined with laser particle size, Cryo-TEM and FTIR analyses, it was found that the particle size of BL in water was smaller than that of ester-105, and the distributed density of BL was higher than that of ester-105 at low temperatures, indicating that BL dispersed well at low temperatures. Therefore, BL was more easily adsorbed on the chalcopyrite surface and improved the surface hydrophobic degree of chalcopyrite, which were also confirmed by the contact angle measurements and adsorption experiments.

Key words: modified ester collector; chalcopyrite flotation; collecting ability; dispersivity; low temperature; reagent synthesis

1 Introduction

Chalcopyrite (CuFeS_2), as the main source of copper, is the most extensively used copper sulfide mineral, and froth flotation is the commonly used technology for its recovery [1–2]. It is well known that suitable collectors play a vital role in the flotation of chalcopyrite. For recovering chalcopyrite, various types of collectors, such as xanthates, thionocarbamates, dithiocarbamates, and dithiophosphates, have been extensively used in different conditions [3–6].

In recent years, with the continual exploration of copper-rich ores, the effective recovery of

chalcopyrite from the closely associated minerals, such as pyrite, arsenopyrite, and galena, has become increasingly difficult [7–9]. To resolve this problem, collectors with high selectivity have been commonly used. N,N-diethyl dithiocarbamate propionitrile ester (ester-105), which is a type of nonionic collector, has attracted extensive attention because of its good selectivity in the flotation of copper sulfide minerals [10,11]. However, numerous studies have shown that the collecting ability of ester-105 is sensitive to pulp temperatures and becomes quite poor at low temperatures. It is well known that the freezing point of ester-105 is approximately 295 K; thus, when the temperature is below 295 K, it is difficult to disperse ester-105

well in the pulp, which will further affect its effectiveness in collecting copper sulfide minerals. In order to improve the collecting ability of ester-105, either increasing the dosage at low temperatures or improving the pulp temperature is the commonly used method. However, the high production costs in plants limit their extensive use, particularly in cold areas. Therefore, it is necessary to study other methods to improve the dispersivity and reduce the dosage of ester-105 for chalcopyrite flotation at low temperatures.

In traditional industrial production, ester-105 is generally produced by the reaction of diethyl amine, acrylonitrile, and carbon disulfide in a certain proportion. However, with the exception of poor dispersivity, the requirements of the equipment for synthesizing ester-105 by this method are usually very stringent because of the strong reaction between diethyl amine and carbon disulfide. Dimethyl sulfoxide (DMSO), as a cheap and versatile solvent, has been extensively used in the synthesis of chemical reagents [12]. Previous studies have shown that DMSO can accelerate and catalyze the chemical reactions between reagents and change the dissolution properties of synthetic reagents [13–16]. FENG et al [13] showed that DMSO can act as a promoter for the nucleation of zeolitic imidazolate framework crystals and that the synthetic crystal sizes using DMSO as a solvent are significantly smaller than those using other typical solvents. These can be attributed to DMSO having a high dielectric constant, which promotes the solubility of the reactants and interferes with the chemical equilibrium of the formation of the crystals. HE et al [15] reported that DMSO can promote the homogenization of methyl silsesquioxane gels by dissolving the cyclic and cage-like structures. Moreover, it can improve the solubility of cellulose by changing the solvent viscosity and the surface tension in the fabrication of hydrophobic silica–cellulose aerogels. Therefore, DMSO may serve as a potential solvent to increase the solubility of the reagents at low temperatures during the synthesis of ester collectors.

In this study, a modified ester-105, which was named as BL, was synthesized using DMSO as the solvent. The collecting performance of BL at low temperatures was investigated by microflotation experiments, and the underlying mechanism was

analyzed via FTIR, contact angle measurement, adsorption experiments, laser particle size analysis, and cryogenic transmission electron microscopy (Cryo-TEM). The findings of this study can provide new ideas for achieving the effective recovery of chalcopyrite at low temperatures.

2 Experimental

2.1 Material and reagents

The chalcopyrite samples were obtained from a copper zinc mine (Guangxi, China). After being carefully selected, crushed, and ground with a grinding miller, the samples were further sieved to obtain the required particle sizes. The sample below 0.074 mm was used for the microflotation test. X-ray diffraction (XRD) pattern (see Fig. 1) showed that the chalcopyrite was of high-purity, which was approximately 99.15% further calculated from the chemical element analysis results (see Table 1).

In this study, diethyl amine, carbon disulfide, acrylonitrile, and DMSO were used as the reaction reagents for the synthesis of BL, and were all in analytical reagent grade. Ester-105 (75% in purity) and terpenic oil was respectively used as the collector and frother and were all in industrial grade. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used as the pH regulators, and were in analytical reagent grade.

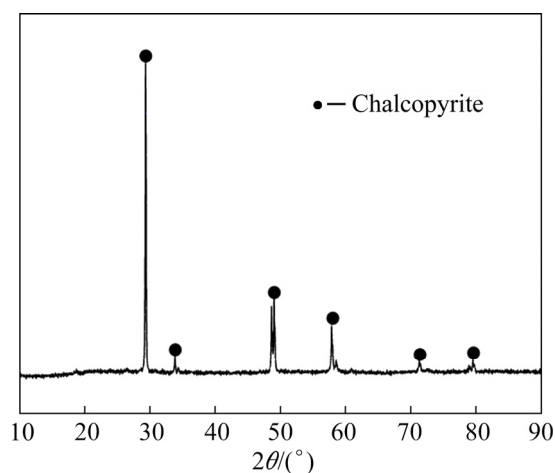


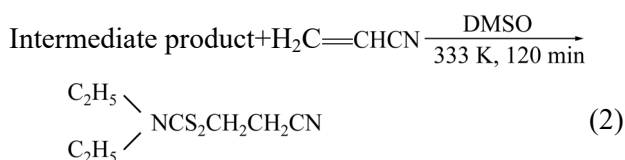
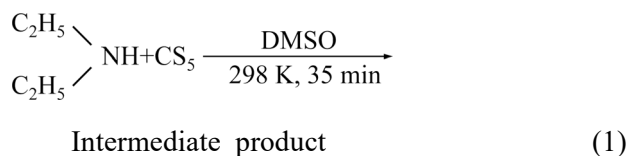
Fig. 1 XRD pattern of chalcopyrite

Table 1 Main chemical element contents of chalcopyrite (wt.%)

Cu	Fe	S
34.31	30.25	34.58

2.2 Reagent synthesis

The synthetic route of BL is shown in Eqs. (1) and (2). The 0.5 mol diethyl amine, carbon disulfide and a certain amount of DMSO were mixed in the same mole ratio in a three-necked flask equipped with a condensing reflux tube and continuously stirred for 35 min at room temperature (298 K). Subsequently, the temperature was increased to 333 K, and 0.5 mol acrylonitrile was added to the solution. Finally, a crimson liquid named as BL was synthesized with continuous stirring at 333 K for 120 min.



2.3 Microflotation tests

The flowchart of the flotation experiment is illustrated in Fig. 2. The tests were conducted in an XFD/FGC flotation machine with the stirring speed of 1700 r/min (Jilin Prospecting Machinery Plant, China). For each experiment, 10 g of chalcopyrite and 50 mL of deionized water were mixed and stirred for 3 min in the flotation cell. The pulp pH value was regulated by 0.1 mol/L NaOH and HCl, and subsequently the required collector and the frother were added in sequence. The stirring periods after adding the regulator, collector, and frother were 2, 3, and 3 min, respectively. Moreover, the flotation time was 5 min. During the tests, terpenic oil dosage was fixed at 3.6 mg/L. At last, the foam products and tailings were dried and weighed to

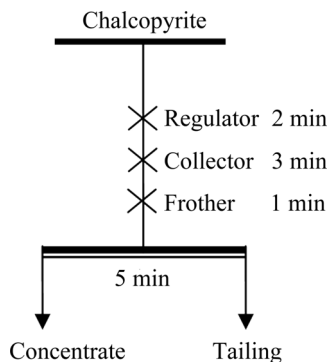


Fig. 2 Flowchart of flotation tests

calculate the recovery. Each test was conducted at least thrice. The mean values and the standard deviations were calculated.

2.4 FTIR spectra measurements

The molecular structures of the collector samples were analyzed using an FTIR spectrometer manufactured by Nicolet Instruments (Thermo Scientific, Waltham, MA, USA) in the wavenumber range of 500–4000 cm^{-1} . Pure organic liquid samples were tested using the liquid membrane method, in which a thin film of liquid was sandwiched between two KBr plates. Appropriate amounts of the reagents were dissolved in carbon tetrachloride solvent for preparing organic solutions. The FTIR spectra of the organic solutions were measured at the same concentration and thickness.

2.5 Contact angle measurements

A JY-82 contact angle instrument (Harke Instruments, Beijing, China) was used to measure the contact angles of the chalcopyrite surface at 298 K based on the drop method. The samples were ground and polished using an abrasive paper and a polishing machine to smoothen the surface and subsequently, they were washed with deionized water. After removing the samples, they were washed with deionized water thrice and subsequently dried in a vacuum oven at 313 K. Finally, the dried samples were placed on the contact angle instrument for the measurements. Each measurement was conducted at least five times independently. The average values and standard deviations were calculated. Concurrently, the contact angle was calculated directly using a connected computer.

2.6 Adsorption experiments

The adsorption amounts of the collectors on chalcopyrite surface were measured using a total organic carbon (TOC) analyzer (Aotao Science and Technology Co., Ltd., Beijing, China). Chalcopyrite samples (0.3 g) were added to a 50 mL conical flask, following which the pH was regulated and the desired collectors were added based on the microflotation tests. After vibrating to achieve adsorption equilibrium, the solutions were transferred for centrifugal separation, and the supernatant was detected using the TOC analyzer. Deionized water and alcohol were used as blank

groups, and their TOC values were calculated using the following formula [17,18]:

$$\Gamma = \frac{(C_0 - C_x)V}{m} \quad (3)$$

where Γ represents the adsorption amount, C_0 represents the initial concentration, C_x represents the residual concentration, V represents the initial pulp volume, and m represents the mass of the sample.

2.7 Laser particle size analyses

The particle size distributions of the collectors were measured using a Mastersizer 3000 laser particle size instrument (Malvern Panalytical Instruments, Malvern, UK). During each measurement, 800 mL of water and 1 mL of the collector were placed in a sample processor, and subsequently the sample treatment pump was opened at a fixed speed of 2000 r/min. To investigate the dispersivity of the collectors at low temperatures, the water used should be stored at 283 K in a refrigerator before the measurement.

2.8 Cryo-TEM analyses

The particle sizes of collectors were measured directly by an FEI Talos F200C Cryo-TEM instrument (Thermo Fisher Scientific, Waltham, MA, USA) with a point resolution of 0.3 nm and a limit information resolution of 0.15 nm. Liquid nitrogen and a quick-freezing agent were used for the sample preparation [19]. Concurrently, the distinctive copper mesh for Cryo-TEM was treated to be hydrophilic before the tests. The samples were diluted with deionized water at the desired temperatures, and their volume fraction was 5%. An appropriate amount of the sample solution was dropped onto the copper mesh, which was rapidly frozen in the quick-freezing agent. The quick-frozen copper mesh was preserved in a four-hole sample box cooled by liquid nitrogen until it was transferred to the sample preparation chamber of the Cryo-TEM instrument for testing.

3 Results and discussion

3.1 FTIR analyses of BL and ester-105

To characterize the main group structure of the synthesized BL and its similarities and differences with ester-105, FTIR analyses of BL and ester-105

were conducted. As shown in Fig. 3, the peaks at 2977 and 2934 cm^{-1} correspond to the C—H asymmetrical stretching vibrations of —CH₃ and —CH₂, respectively [20]. The peak at 2875 cm^{-1} corresponds to the C—H symmetrical stretching vibration of —CH₃. The peak at 1460 cm^{-1} is attributed to the stretching vibration of —CN. Moreover, the peak at 1381 cm^{-1} is related to the symmetrical bending vibration of —CH₃. The peaks at 930 and 834 cm^{-1} correspond to the stretching vibrations of —CH₃ and C—C, respectively. In addition, there are numerous peaks in the ranges of 1570–1395, 1420–1260, and 1140–940 cm^{-1} , arising from the wide adsorption region of C=S and its combination with the nitrogen atom. Based on previous studies, the peaks at 1516, 1396, 1283, 1015, and 778 cm^{-1} correspond to characteristic peak of —N—C=S comprising the superimposed effect of the adsorption vibrations of these peaks [21]. In conclusion, the FTIR spectra of BL and ester-105 are nearly the same except for the peaks at 3441 and 1643 cm^{-1} , which are related to the stretching vibration and variable-angle vibration of —OH.

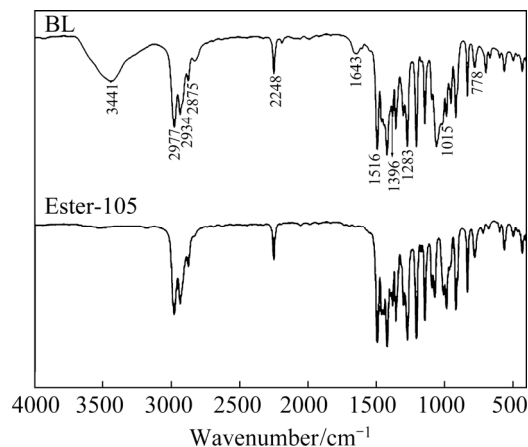


Fig. 3 Infrared spectra of ester-105 and BL

3.2 Microflotation

The effect of DMSO dosage during the synthesis of BL on the recovery of chalcopyrite at 283 K was investigated, and the results are shown in Fig. 4. It can be seen that the recovery of chalcopyrite gradually increased at first with the increase of DMSO dosage, and then decreased when DMSO dosage was above 0.5 mol. Therefore, the maximum recovery of 82.1% could be obtained when DMSO dosage was 0.5 mol. Besides, after finishing the synthesis of BL with the optimum

DMSO dosage, mass fractions of active ingredient (N,N-diethyl dithiocarbamate propionitrile ester) and DMSO were 69.13% and 27.54%, respectively. When DMSO dosage was 0.2 and 0.3 mol, the recoveries of chalcopryrite were less than 77%, which could be attributed to the weak solubilization of low-dosage DMSO. However, the low recovery of chalcopryrite when DMSO dosage was 0.7 mol was due to the lack of active ingredient, because the main components of BL are active ingredient and DMSO, and the content of active ingredient gradually decreased with the increase of DMSO dosage when BL dosage was fixed during the flotation.

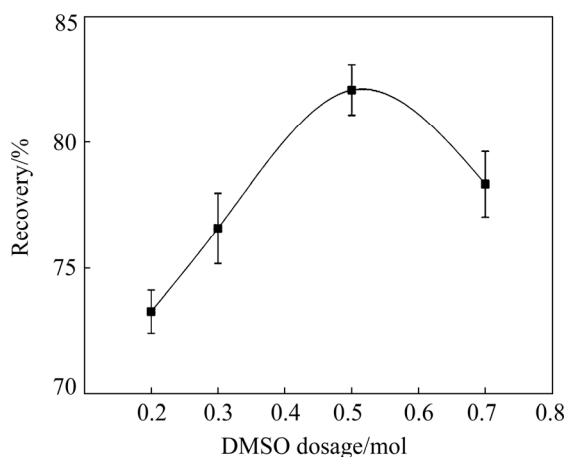


Fig. 4 Effect of DMSO dosage during synthesis of BL on recovery of chalcopryrite (total collector dosage: 18 mg/L; pH: 10.0; temperature: 283 K)

The flotation of chalcopryrite is sensitive to the pulp pH; thus, its effect on the recovery of chalcopryrite with BL or ester-105 as the collector was investigated. As can be seen from Fig. 5, the overall recoveries when using BL as the collector are higher than that when using ester-105 in the measured pH range, particularly under strong alkaline conditions. When the pH value was above 10.0, the recovery of chalcopryrite decreased when using BL or ester-105 as the collector, which is related to the oxidation of chalcopryrite under strong alkaline conditions [22,23]. Based on the molecular hybrid orbital theory, the ability of the thiocarbonyl groups in BL and ester-105 molecules to form a feedback bond by combining with the copper atoms on the chalcopryrite surface is significantly strong. In addition, the electronegativity of the sulfur atoms from the thiocarbonyl in BL and ester-105 molecules was strong enough to enable

their combination with the copper atoms on the chalcopryrite surface [24,25]. Therefore, BL and ester-105 were mainly adsorbed on chalcopryrite via chemisorption.

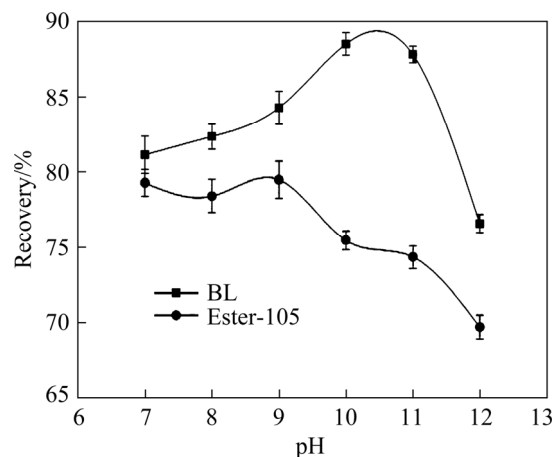


Fig. 5 Recovery of chalcopryrite as function of pH (collector dosage: 18 mg/L; temperature: 298 K)

The effect of temperature on the recovery of chalcopryrite using BL or ester-105 as the collector is shown in Fig. 6. The results show that with the increase in the temperature, the recovery of chalcopryrite gradually increased, whereas the difference in the recoveries gradually decreased when using either BL or ester-105 as the collectors. When the temperature was 298 K, the recoveries of chalcopryrite using BL and ester-105 as the collectors were 90.9% and 87.51%, respectively. This indicated that these two collectors present the same properties at high temperatures. However, when the temperature was 283 K, BL showed superior properties than ester-105; specifically, the recovery of chalcopryrite was 82.1% with BL and

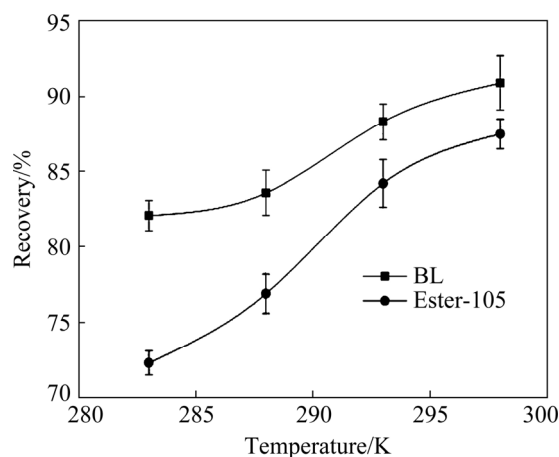


Fig. 6 Recovery of chalcopryrite as function of temperature (collector dosage: 18 mg/L; pH: 10.0)

72.35% with ester-105. This indicated that BL possessed significant adaptability to low temperatures in the flotation of chalcopyrite.

Figure 7 shows the recovery of chalcopyrite as a function of the BL and ester-105 dosage at low temperatures. It can be seen that the collecting property of BL is stronger than that of ester-105 in the used collector dosage range. When using BL as the collector, the recovery of chalcopyrite initially increased from 72.61% to 82.1% when the collector dosage increased from 9 to 18 mg/L and subsequently reached a plateau with the further increase in collector dosage. However, when using ester-105 as the collector, the recovery of chalcopyrite significantly increased with the increase in the collector dosage. When the ester-105 dosage was 31.5 mg/L, recovery of 80.74% could be obtained, which was similar to the flotation results using BL as the collector. This indicated that to realize the effective recovery of chalcopyrite at low temperatures, large amounts of ester-105 must be used.

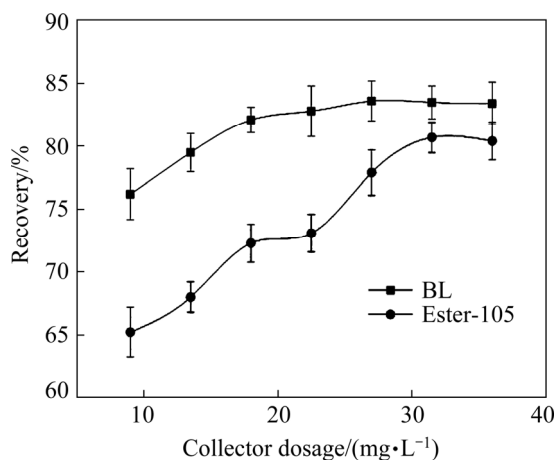


Fig. 7 Recovery of chalcopyrite as function of collector dosage at low temperatures (temperature: 283 K; pH: 10.0)

3.3 Contact angle

The floatability of minerals can be directly attributed to changes in surface wettability. This can be evaluated by contact angle measurements [26–29]. Figure 8 presents the effects of BL and ester-105 on the hydrophobicity of chalcopyrite as a function of pH at different temperatures. It can be seen that the contact angles are all above 90° when using BL or ester-105 as the collector at 298 K in the measured pH range, indicating that the chalcopyrite surface is strongly hydrophobic. When the temperature

decreased from 298 to 283 K, all the contact angles decreased to different degrees for BL and ester-105. However, the contact angles when using BL as the collector were still larger than those when using Ester-105, particularly under strong alkaline conditions. The contact angles were approximately 89° when using BL as the collector, whereas they were approximately 83° when using ester-105 at pH>10.0. This further indicated that chalcopyrite could be easily floated using BL as the collector at low temperatures, consistent with the results shown in Fig. 8.

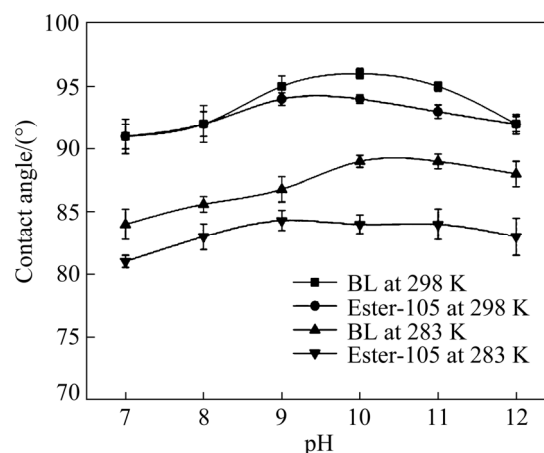


Fig. 8 Effects of BL and ester-105 on hydrophobicity of chalcopyrite as function of pH at different temperatures (collector dosage: 18 mg/L)

3.4 Adsorption

The floatability of chalcopyrite is closely connected with the adsorption amount of a collector on the surface [30–32]. Thus, the adsorption amounts of BL and ester-105 on the chalcopyrite surface at different temperatures were investigated. As can be seen from Fig. 9, the adsorption amount on the surface at 283 K is less than that at 298 K when either BL or ester-105 is used as the collector. Therefore, the recoveries at low temperatures were all lower than those at high temperatures. However, it can also be seen that the adsorption amount at 283 K when using BL as the collector is 4.36 mg/g, which is significantly higher than that when using ester-105. This was one reason that BL could improve the floatability of chalcopyrite at low temperatures.

3.5 Particle size

It is generally known that the collecting ability of ester collectors for copper sulfide minerals

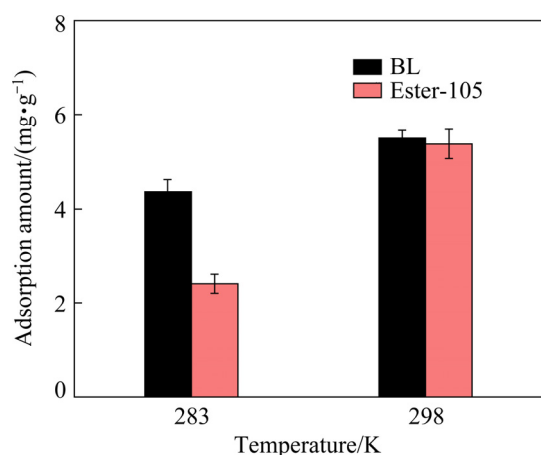


Fig. 9 Adsorption amounts of BL and ester-105 on chalcopyrite surface as function of temperature (initial collector dosage: 18 mg/L; pH: 10.0)

mainly depends on the temperature. Moreover, ester collectors are difficult to disperse well into solutions at low temperatures, which will further result in low collision probabilities and reaction rates between the collector and the mineral particles. Therefore, the dispersivity of BL and ester-105 at different temperatures was analyzed by investigating the particle size distribution of the reagents in the solutions. And the smaller the particle size is, the better the particle dispersivity is.

It can be seen from Fig. 10 that the particle size at high temperatures is smaller than that at low temperatures when using either BL or Ester-105 as the collector. When the temperature decreased from 298 to 283 K, with BL, the D_{50} value increased from 124.41 to 154.75 μm and the D_{90} value increased from 203.49 to 252.12 μm . For ester-105, the D_{50} value increased from 134.85 to 180.15 μm and the D_{90} value increased from 230.84 to 294.61 μm . In addition, it can also be seen that the particle size of BL is significantly smaller than that of ester-105, even at 283 K, indicating the better dispersivity of BL at low temperatures. Therefore, BL was more easily adsorbed on the surface of chalcopyrite at low temperatures, thus further improving the floatability of chalcopyrite.

3.6 Cryo-TEM analyses

To directly determine the dispersivity of the reagents, the particle size and concentration per unit space of BL and ester-105 were further analyzed via Cryo-TEM. As can be seen from Fig. 11, the concentrations of BL and ester-105 distributing per

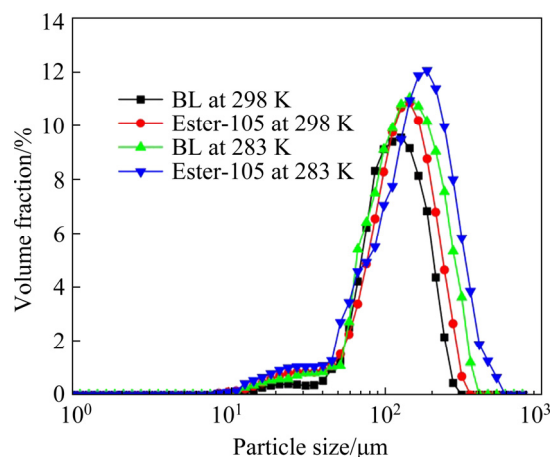


Fig. 10 Particle size distributions of BL and ester-105 at different temperatures

unit space at 283 K are remarkably lower than those at 298 K, whereas the average particle sizes at 283 K is larger than those at 298 K, indicating better dispersivity of BL and ester-105 at high temperatures. The dispersivity of the reagents in solutions was mainly related to their solubility and thermal motion at different temperatures [33–35]. At 298 K, which is higher than the freezing points of ester-105 and BL, the solubility of the reagents significantly increased. Concurrently, the mean kinetic energy of the reagent molecules also increased, which further resulted in their severe thermal motion and better dispersivity. Therefore, the collision probability between the reagents and the mineral particles increased, and the reagents were more easily adsorbed on the surface of samples, which further improved the flotation of chalcopyrite at high temperatures. However, by comparing Figs. 11(c) and 11(d), it can also be seen that the dispersivity of BL is significantly better than that of ester-105 at 298 K, which is mainly related to the easy agglomeration characteristics of ester-105.

When the temperature was 283 K, it can be seen from Figs. 11(a) and (b) that the concentration of BL distributing per unit space is higher than that of ester-105, indicating better dispersivity of BL at low temperatures. DMSO has been extensively used as a solvent in the synthesis of reagents, and numerous studies have shown that DMSO can change the solubility of synthetic reagents. Therefore, the better dispersivity of BL at low temperatures is mainly related to the solubilization action of DMSO in the synthesis of BL.

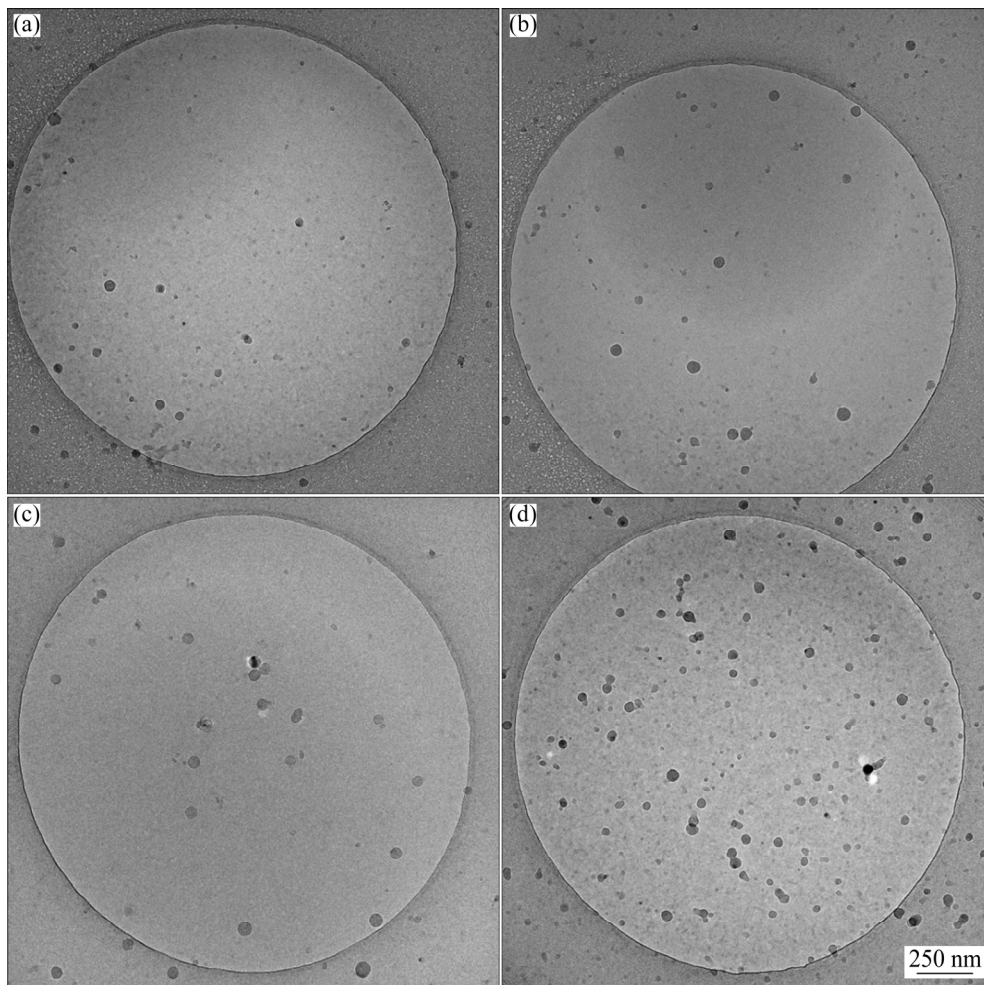


Fig. 11 Cryo-TEM images of collectors at different temperatures: (a) Ester-105 at 283 K; (b) BL at 283 K; (c) Ester-105 at 298 K; (d) BL at 298 K

3.7 Adsorption mechanisms of collectors on mineral surface

Based on the above discussion, the adsorption diagrams of ester-105 and BL on the surface of chalcopyrite at different temperatures are illustrated in Fig. 12. The adsorption amount of ester-105 on the chalcopyrite surface was similar to that of BL at 298 K. Despite this, the effect of BL on the floatability of chalcopyrite was still slightly better than that of ester-105 because the particle size of BL was smaller, as shown in Fig. 12(b). However, the characteristics of these two collectors and their adsorption on the surface of chalcopyrite were significantly different. In contrast to the results shown in Figs. 12(c, d), the ester-105 particles easily formed large-sized agglomerates, resulting in poor adsorption capacity on the surface of chalcopyrite. However, the BL particles were dispersed well in the pulp at low temperatures; thus, BL mainly existed as small-sized particles. It is well

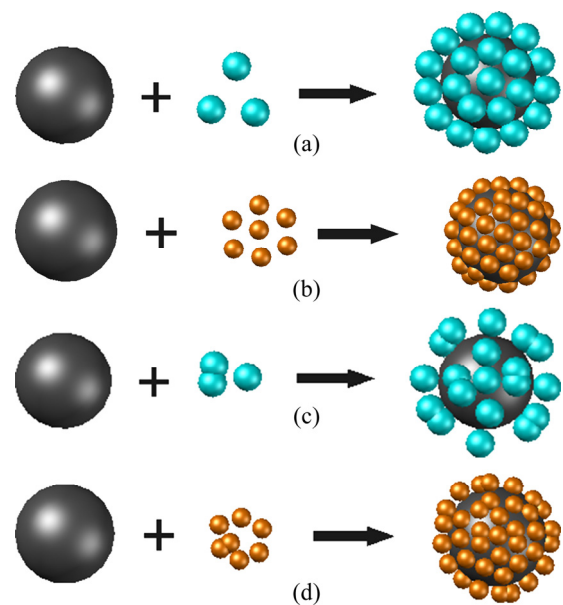


Fig. 12 Schematic of adsorption mechanism of ester-105 and BL on surface of chalcopyrite at different temperatures: (a) Ester-105 at 298 K; (b) BL at 298 K; (c) Ester-105 at 283 K; (d) BL at 283 K

known that a smaller particle size of a collector is associated with a high probability of collision and adsorption with minerals in the pulp. Therefore, BL is more easily adsorbed on the surface of chalcopyrite than ester-105. In addition, small collector particles can react with minerals to achieve a high adsorption density on the surface. However, large collector particles can only adsorb on the surface weakly, which further results in a weak interaction between the collector and the mineral. Therefore, the collection performance of BL is better than that of ester-105 at low temperatures.

4 Conclusions

(1) BL and ester-105 presented almost the same collecting ability at high temperatures in the flotation of chalcopyrite, whereas BL possessed superior properties than ester-105 at low temperatures. To realize the effective recovery of chalcopyrite at low temperatures, larger amounts of ester-105 must be used.

(2) The adsorption amount of BL on the surface of chalcopyrite at low temperatures was significantly larger than that of ester-105, and thus the contact angles when using BL as the collector were larger than those when using ester-105. This is one reason that BL could improve the floatability of chalcopyrite at low temperatures.

(3) BL particles were dispersed well in the pulp at low temperatures and can react with minerals to achieve a high adsorption density on the surface, thus resulting in a strong interaction between the collector and the mineral particles. However, the ester-105 particles mainly existed as large-sized agglomerates, resulting in poor adsorption capacity on the surface of chalcopyrite. Therefore, the collecting ability of BL was better than that of ester-105 at low temperatures.

Acknowledgments

The authors are grateful for the financial supports from the National Natural Science Foundation of China (No. 52074206), the Talent Science and Technology Fund of Xi'an University of Architecture and Technology, China (No. ZR19062), the Open Foundation of State Key Laboratory of Mineral Processing, China (No. BGRIMM-KJSKL-2021-19), the Natural Science

Basic Research Plan in Shaanxi Province of China (No. 2021JQ-507), the Special Research Project of Shaanxi Education Department, China (No. 21JK0731), the Key Program for International S&T Cooperation Projects of Shaanxi Province, China (No. 2021KWZ-16), and the Natural Science Foundation of Qinghai Province, China (No. 2021-ZJ-975Q).

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采用改性酯类捕收剂在低温条件下有效回收黄铜矿

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摘 要: 通过单矿物浮选试验、接触角测试、药剂吸附量试验、粒度分析、冷冻透射电镜和红外光谱分析, 考察改性酯类捕收剂(BL)在低温条件下对黄铜矿浮选的影响。单矿物浮选试验结果表明, 在低温条件下, BL 对黄铜矿的捕收能力明显优于酯 105。结合粒度分析、冷冻透射电镜及红外光谱分析结果, 在低温条件下, BL 在水溶液中的粒度小于酯 105 的, 而分布密度大于酯 105 的, 这表明 BL 在低温条件下分散性更好。因此, BL 更容易吸附在黄铜矿表面, 从而提高其表面疏水程度, 该结果也通过接触角测试和药剂吸附量试验得以证实。

关键词: 改性酯类捕收剂; 黄铜矿浮选; 捕收能力; 分散性; 低温; 药剂合成

(Edited by Bing YANG)