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FLOTATION OF MOLYBDENITE IN THE PRESENCE OF MICROEMULSIFIED COLLECTOR

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Abstract: In this paper molybdenite flotation using microemulsified collector was reported. The flotation performance of microemulsified collector and conventional diesel was compared. This study is a preliminary investigation which uses pure molybdenite mineral in a modified Hallimond tube. The pH tests showed that the highest recovery of molybdenite in the presence of diesel and microemulsion was obtained at pH=6, reaching the recoveries of 93% and 90%, respectively. In the case of obtaining similar results, it was observed that the microemulsion consumption was lower in comparison to diesel. In the flotation tests with microemulsified collector the recovery slightly decreased because too large collector amount caused formation of more unstable bubbles. The contact angle measurements showed that the microemulsified collector was more effective for increasing the hydrophobicity of molybdenite surface. An adsorption model was proposed and it was suggested that the non-ionic surfactant present in the microemulsified collector formed a continuous bimolecular layer, resulting in the increased surface hydrophobicity. The accomplishment of this research demonstrated the viability of the use of microemulsified collector in molybdenite flotation, attempting to simplify the molybdenite flotation process, especially replace the conventional emulsified collector with high energy consumption and difficult storage.

Keywords: *molybdenite, flotation, microemulsified collector, diesel*

Introduction

The recovery of molybdenite from the ores is usually simple since this mineral is naturally hydrophobic (Pearse, 2005). The natural hydrophobicity of molybdenite results from its layered crystal structure. The sulfur and molybdenum atoms within each layer are held together by strong covalent bonds, while the bonds between adjacent layers are weak van der Waals bonds between sulfur atoms. The weak sulfur–sulfur bonds provide excellent cleavage characteristics parallel to the sulfur sheets causing natural hydrophobicity of mineral (Ansari and Pawlik, 2007a, 2007b). The hydrophobicity of molybdenite depends on its origin and surface preparation. The values of contact angles vary from 20 to 75° (Chander and Fuerstenau, 1972; Kowalczuk and Drzymala,

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2011). The kerosene, vapor oil, fuel oil, transformer oil and other hydrocarbons are often employed in molybdenite flotation as a collector which is used to increase the hydrophobicity of molybdenite surface (Yuan et al., 2007; Yin et al., 2010; Gerson et al., 2012). The collector is dispersed into droplets in the pulp, and these droplets collide with, adhere to, and coat the molybdenite particles to increase their hydrophobicity (Polat et al., 2003). Dispersing these hydrocarbons is often difficult with traditional mechanical agitation, and thus the size of oil droplets is usually large (He et al., 2011). This results in high collector consumption and poor flotation performance.

Hydrocarbons can be dispersed into smaller droplets by emulsification (Song et al., 2012). Many types of surfactants were used as emulsifiers. One of them was Artic Syntex L which was a sulfated monoglyceride made from coconut oil. This surfactant could enable the grinding fineness to reduce from 55% to 40% at Climax Molybdenum Co., which could make the Climax operation function economically (Ronzio, 1970). Although the emulsified collector achieved some success, it is well known that the emulsion is thermodynamically unstable and demulsification usually takes place during storage. Demulsification of collectors significantly reduces their separation efficiency. In addition, a special emulsification device with a complex structure and high energy consumption has been reported, so its application in the molybdenite flotation industry is not popular (Li and Lu, 2011, Zhang and Zhong, 2010).

Microemulsions are systems composed of water, oil, surfactant and a short chain alcohol as a co-surfactant (Winsor, 1968). The average droplet size of microemulsion is 5-100 nm, compared with hundreds of microns for emulsions (Huibers, 1996). Microemulsions are kinetically and thermodynamically stable, so can be formed spontaneously (Vollmer and Vollmer, 2001). Oils can be dispersed into smaller droplets by microemulsification and spontaneous formation reduces the difficulty and energy consumption associated with preparation.

This work attempts to investigate the application of microemulsion as a collector for molybdenite flotation. This study is a preliminary investigation which used only pure molybdenite mineral as model systems to optimize the flotation using microemulsified collector.

Material and methods

Materials

Molybdenite sample used in this work was obtained from Jinxin Mines Ltd. (Chifeng, China), which was received in chunks of particles of up to 150 mm diameter. The mineral was hammered, and then ground using a ceramic mill. After grinding, a shaking table was used to obtain molybdenite concentrate. Then, the samples were dry sieved to obtain particles with a size from 75 to 150 μm. The samples were washed with distilled water to remove fine particles and dried at 80 °C for 4h prior to flotation. The chemical analysis showed that the concentration of molybdenum in the concentrate was 56.94%.

Reagents were nonylphenol ethoxylated 10/NP-10 (Laurenthall Enterprises, A.R. grade), pentanol (Merk, A.R. grade), MIBC (Merk, A.R. grade), NaOH (Kemiou, A.R. grade), H_2SO_4 (Kemiou, A.R. grade) and diesel. NaOH and H_2SO_4 were used as pH modifiers. Diesel was commercially obtained, and had a density of 0.83 g/cm^3 and viscosity of 4.5 mPa·s. Doubly distilled deionized water was used in experiments.

The microemulsified collector was prepared by phase inversion emulsification, and the methodology was described elsewhere (Bellocq and Roux, 1987). The reagents (NP-10, surfactant) and pentanol (cosurfactant) were mixed at a mass ratio of 3:2 to form the surfactant phase (SA). SA, diesel and water were mixed at a mass ratio of 3:5:6 with a magnetic stirrer for 3 min at 25 °C. The microemulsified collector was determined to be an O/W (oil in water) microemulsion by staining. The size of dispersed diesel droplets in microemulsion was measured with a Malvern Zetasizer, and the average size was about 31 nm (Li et al., 2013).

Methods

The flotation experiments were carried out in a 200 cm^3 modified Hallimond tube (Fig. 1), which was constructed by Hallimond (1944) and modified by Fuerstenau et al. (1957).

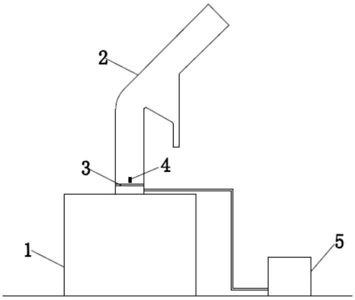

Fig. 1. Schematic diagram of experimental setup: 1 – magnetic stirrer, 2 – Hallimond tube, 3 – porous plate, 4 – magnetic stirring bar, 5 – compressor

Molybdenite sample (1.5 g) was conditioned with 100 cm^3 distilled water in a 150 cm^3 glass beaker for about 2 min. Firstly, the pH of the pulp was adjusted. Afterwards, the collector (either pure diesel or microemulsion) was added to achieve suitable collector dosage and the mixture was conditioned for 5 min with a micro sample injector (2.0 cm^3). Then, the frother (MIBC) was added. The frother enhanced the kinetics of mineral flotation while stabilizing the formation of smaller, more uniform-in-size gas bubbles. The collector/frother (MIBC) agent ratio was held constant at 2, and the MIBC dosage was determined by bubble diameter (about 0.5 mm). A required amount of MIBC was added to the beaker, and then conditioned for 5 min. After conditioning, the whole mixture was transferred to the modified Hallimond tube, and the pulp was mechanically mixed in the tube for about 20 s. All the tests were performed using compressed air. The flotation time was 90 s to minimize the mechanical carryover of poorly floating particles, while the air-flow rate was maintained at 50 cm^3/min. The products of froth were dried in an oven at 100 °C. The weights of the flotation products were used for the calculation of mineral recovery.

Contact angle measurements were used to determine the hydrophobicity of molybdenite in the presence of water and collectors. Double distilled water was used as the test liquid. The molybdenite sample was pressed into a pellet with an SH-1 tablet making machine produced by the Henan Ruida Mechanical Instrument company, Ltd. The sample weight was 10 g, the pressure on the tablet was 24.5 MPa and the diameter of the tablet was 20 mm. The surface of the resulting pellet was flat and smooth.

The soaking method was used for making a surface film of the collector. A blank copperplate paper was cut to 20 mm×20 mm and dipped into the collector (diesel or microemulsion) solution for about 1 min, and then stored in a silica gel desiccator for about 24 h before use.

The contact angle of the test liquid on the solid surface was measured using a JJC-I wetting angle measurement instrument produced by the Changchun Optics Instrument factory. A micro sample injector (2.0 cm^3) was used to carefully drop the test liquid from a distance of 3 mm perpendicularly onto the solid surface to form a droplet. The droplet volume was 3–5 mm^3, the diameter was 1–2 mm and the measurement time was no longer than 1 min. The average of ten measurement values was taken to be the contact angle of the droplet. All the measurements were performed at room temperature (25 °C).

Results and discussion

Effect of pH

The aim of this experiment was to analyze the effect of changing behavior of pulp pH. The pH was varied, covering a range of 3-12. The dosages of collector and frother were 200 mg/dm^3 and 100 mg/dm^3, respectively.

As seen from Fig. 2, the flotation in the presence of diesel and microemulsified collector showed similar trends as a function of pulp pH. The highest flotation levels with microemulsion and diesel were achieved at pH=6, reaching the recoveries of 93.21% and 90.18%, respectively. A significant decrease in flotation was observed at higher and lower pH values. Chander and Fuerstenau (1972) determined that the relative flotation of molybdenite was at a maximum in the pH range of 5.5~6.5, which was consistent with this experiments. In acidic solution, the poor separation efficiency was attributed to MoO_3 deriving from oxidation of molybdenite surface. However, in alkaline solution, adsorption of MoO_4^{2-} and OH^- to molybdenite surface caused lower recovery with dissolving of MoO_3.

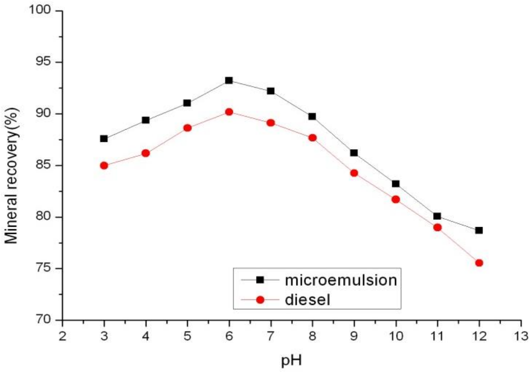

Fig. 2. Effect of pH on mineral recovery

Effect of collector type

Figure 3 shows that two mineral recovery curves were similar. At the initial stage, the mineral recovery of microemulsion and diesel increased significantly with the increasing of collector dosage. The stable recoveries were almost obtained at the microemulsion and diesel amounts of 200 mg/dm^3. Surprisingly, the recovery decreased slightly with the further increase of collector dosage, it was possibly that too large amount of collector caused more unstable bubbles. It also could be seen from Fig. 2 that the lower amount of microemulsion collector produced similar recovery to diesel, likely because of the smaller oil droplets which increased the probability of collision between molybdenite and collector particles, and shortening the attachment period (Rubio et al., 2007). After microemulsification, the amount of oil adsorbed on the surface of molybdenite particles decreased, on the premise of similar coverage area. On the other hand, it is probably that the surfactant played the role of flotation promoter or collector.

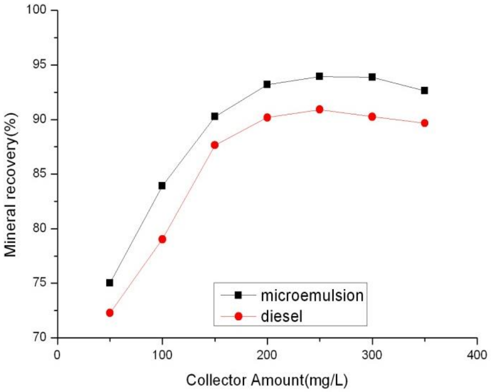

Fig. 3. Effect of collector amount on mineral recovery
(collector/frother agent ratio = 2, pulp pH = 6)

Contact angle

The contact angle measurement in the presence and absence of collector (diesel or microemulsion) is shown in Table 1. It can be seen that the presence of either diesel or microemulsion causes an increase in the contact angles from that measured in pure water. This suggests that the adsorption of the both collectors increased the hydrophobicity of the molybdenite surface. In addition, it was observed that the contact angle of microemulsion was higher than diesel. This result indicated stronger interaction between the molybdenite surface and microemulsified collector, which was consistent with the flotation results.

Table 1. Measured contact angle of molybdenite sample

Type of collector	Water	Diesel	Microemulsion
contact angle [°]	74.2	79.6	84.7

Collector adsorption

The contact angle and Hallimond tube flotation results can be used to formulate an adsorption model for two collectors on the molybdenite surface. It is well known that the diesel spreads on the molybdenite surface rendering its hydrophobicity. The increased values of contact angles in the presence of microemulsion were mainly caused by the presence of non-ionic surfactant (NP-10). NP-10 is a typical non-ionic surfactant. Non-ionic surfactants carry no electrical charge and their water solubility is derived from the presence of polar functionalities capable of significant hydrogen bonding interaction with water (Furlong and Aston, 1982). They are physically adsorbed, rather than chemisorbed (Aktas and Woodburn, 1994).

For hydrophobic solids, such as molybdenite, methylated silica and low-ash bituminous coal, there are several theories regarding the molecular orientation of the surfactants during adsorption on the solid surfaces. Adsorption takes place with the nonpolar alkyl-aryl hydrocarbons in contact with the surface, while the polyoxyethylene groups are projected toward the aqueous phase. The orientation of adsorbate initially may be either parallel, perpendicular or slightly angled to the surface of the solid with the hydrophobic group close to the surface (Giles et al., 1974a, 1974b). At very low concentrations, the adsorbed non-ionic surfactant is thought to be orientated parallel to the interface (Gellan and Rochester, 1985). At higher concentrations (near the critical micelle concentration, CMC), the adsorbed layer is thought to resemble a monomolecular layer with the surfactant orientated perpendicular to the surface. As the concentration is further increased, which is at a concentration approximately twice that of the surfactant CMC, strong co-operative adsorption leads to the formation of aggregates (hemi-micelles) on the surface, and the adsorbed phase is thought to resemble a continuous bimolecular layer or two dimensional micellar phases (Levitz et al., 1984a; 1984b). The hydrophobic tails of the second layer are extended into the aqueous solution whilst those in the first layer are orientated to the solid surface. This adsorption model explains the higher degree of contact angle for the microemulsified collector.

Conclusions

It was shown that microemulsified collector could be used with a good efficiency in the molybdenite flotation. The best results were obtained at pH=6. Due to the nanometer-sized oil droplets, microemulsified collector provided better separation efficiency at lower dosage. The contact angle measurements demonstrated that the microemulsified collector was more effective for increasing the hydrophobicity of the molybdenite surface. An adsorption model was proposed, and it was suggested that the non-ionic surfactant (NP-10) in the microemulsified collector formed a continuous bimolecular layer, resulting in increased surface hydrophobicity.

This work opens the way to the use of microemulsified collector in molybdenite flotation, which attempts to simplify the molybdenite flotation process, especially replace the conventional emulsified collector with high energy consumption and difficult storage using microemulsified collector.

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