



Strengthened floatation of molybdenite using oleate with suitable co-collector

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ABSTRACT

The difference in flotation and adsorption mechanism of mixed sodium oleate (NaOl)/dodecylamine (DDA) and NaOl/cetyl pyridinium chloride (CPC) collectors on molybdenite was comparative studied through micro-flotation, fluorescence emission spectroscopy, zeta potentials measurement, adsorption tests and FTIR measurement. The flotation results show that the best flotation of molybdenite for 2×10^{-4} M NaOl, CPC and DDA is achieved at pH 7, 8 and 10, with corresponding mineral recovery of 64.3%, 40.9% and 44.5%, respectively. It is found that the collecting ability of single collector on molybdenite is in the order of NaOl > CPC > DDA. For mixed system, molybdenite recoveries with NaOl are improved by co-adsorbed DDA from about 75% to 95% with increasing DDA dosage, while no improvement is found in the case of mixed NaOl/CPC collectors. Fluorescence emission spectroscopy investigation displays the critical hemimicelle concentration (CHC) and critical micelle concentration (CMC) of NaOl are 2×10^{-4} M and 2×10^{-3} M, respectively. A larger micro-polarity of molybdenite in mixed NaOl/DDA than that of mixed NaOl/CPC collectors is found. The adsorbed amount of DDA increase with the increasing DDA dosage due to the extra adsorption of DDA cations between the adjacent adsorbed NaOl ions, which leads to the less negative zeta potentials (from about -60 mV to -30 mV) of molybdenite surface for mixed NaOl/DDA collectors. Above phenomenon and corresponding explanation are further confirmed by FTIR findings. Suggested models are presented to interpret the difference in adsorption mechanism of mixed NaOl/DDA and NaOl/CPC collectors on molybdenite.

1. Introduction

Molybdenite (MoO_3), one of the molybdenum oxide minerals, belongs to orthorhombic system (Solferino and Anderson, 2012). If it can be taken full advantage, the Mo resource gap resulted from the reducing supply of molybdenite due to the lasting mining of molybdenum ores for near 100 years (Cao et al., 2017), will be offset to some degree. However, the hydrophilic molybdenite surface results in the not well flotability (Wang et al., 2013; Wang et al., 2015a,2015b; Liu et al., 2015). Mixed anionic and cationic (catanionic system) surfactants are given increasing attention as effective collectors, due to the preferable interface physicochemical performance and widespread applications in paints, dispersion/flocculation, ore flotation and so on, during the flotation of metal oxide minerals (Helbig et al., 1998; Ejtemaei et al., 2011; Khaleghi et al., 2016; Dey et al., 2014). A. Vidyadhar and Rao (2007) reported the adsorption mechanism of mixed dodecylamine and sulphate or oleate collectors on hematite. The first time they found that the presence of anionic collector increases the adsorbed amount of

cationic collector due to a decrease in the electrostatic repulsion between the adjacent adsorbed ammonium headgroups and thus promoting the chain-chain attraction.

In general, it is believed that complex aggregations will be formed when oppositely charged reagents are intermixed together due to the electrostatic interactions between cationic and anionic surfactants' charged bodies (Rao and Forsberg, 1997). Effectively, many recent literatures have been published for the findings of positive synergistic of catanionic system in mineral flotation. Researchers argue that, in mixed collectors system, the electrostatic repulsion between the head groups of a surfactant will decrease, while the lateral tail–tail hydrophobic interactions between hydrocarbon chain increase in the presence of the oppositely charged one (Helbig et al., 1998; Wang et al., 2014; L. Wang et al., 2016; Xu et al., 2013; J. Wang et al., 2016). The performance of collector mixtures depends on the type of bonding of a collector to the mineral surface (electrostatic (Adamczyk, 2003), hydrogen-bonding or chemical adsorption (Pearse, 2005)), the collector and co-collector structures, and the mixing ratio of collectors (Helbig

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et al., 1998; Wang et al., 2014). Helbig found that the adsorption mechanism of sodium N-dodecanoyl sarcosine (chelate linkage over the carboxylate and acid amide group) differs from sodium dodecanate (ionic bonding over the carboxylate group) on fluorite surface due to the insertion of an acid amide group ($-\text{CO}-\text{NH}-$), which results in the different flotation performance of mixed sodium N-dodecanoyl sarcosine/dodecylamine and sodium dodecanate/dodecylamine collectors (Helbig et al., 1998). They argue that the chelation adsorption of N-dodecanoyl sarcosine (equivalent to a big headgroup collector) on fluorite surface would leave space for the adsorption of dodecylamine molecular, while the fluorite surface adsorbed relatively small headgroup dodecanate repulse the adsorption of dodecylamine. The first time the effect of headgroup of collector molecular was proposed in mixed collectors system.

To sum up, cationic system is increasingly at the research fronts in flotation theory and able to strengthen the flotation of refractory minerals. Most of the relevant papers focus on the synergistic effect mechanisms of the mixed collectors on minerals' surfaces, however, that what kind of combination of collectors would have synergy was rarely taken into consideration and discussed in-depth. In this paper, the flotation performance and corresponding mechanism of mixed NaOl/CPC and NaOl/DDA on molybdenite/water interface were comparative studied.

2. Materials and methods

2.1. Materials

Molybdenite was bought from a Mineral Specimens Co., LLC in Beijing. The hand sorted mineral was crushed by a hammer and then ground in a ceramic-grinder. The $+0.074$ mm, $-0.074 + 0.038$ mm and -0.038 mm fractions were obtained by sieving the products of ceramic-grinder using two sieves with aperture size of 0.074 mm and 0.038 mm. The $-0.074 + 0.038$ mm fractions between the two sieves were used for the flotation and adsorption tests. Agate mortar and high speed centrifuge were used to further grind the -0.038 fractions and separate -5 μm or -2 μm fractions by controlling the time of centrifugation. The -5 μm or -2 μm fractions were dried in a vacuum drying oven and prepared for FTIR and zeta potential tests, respectively. The results of X-ray diffraction analysis of molybdenite shows no obvious difference with its PDF card (see Fig. 1).

NaOl was purchased from Qixia TongDa Flotation Reagent Co., Ltd., China. Both analytically pure DDA and CPC were purchased from Sinopharm Chemical Reagent Co., Ltd, and then DDA solution was

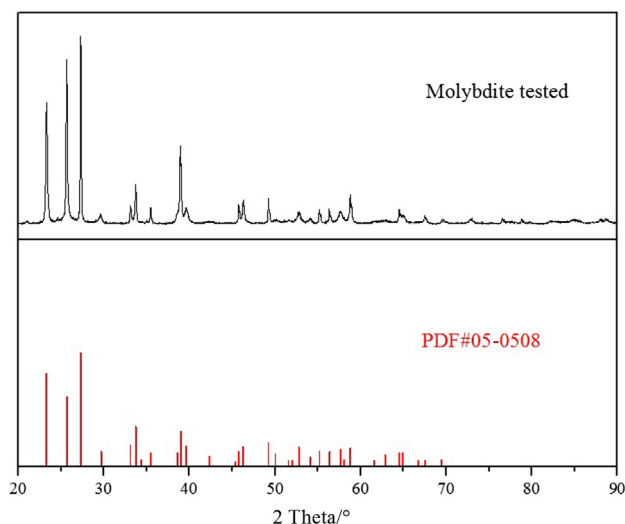


Fig. 1. XRD patterns of molybdenite tested and corresponding PDF.

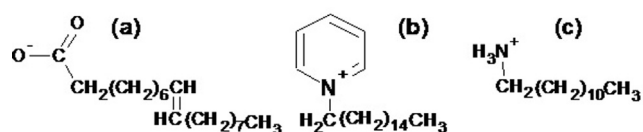


Fig. 2. Structural formulas of (a) NaOl, (b) CPC and (c) DDA.

prepared by adding equimolar dodecylamine into hydrochloric acid solution. Molecular structural formulas of oleate, CPC and DDA was compared in Fig. 2. Analytical grade sodium hydroxide and sulfuric acid were used for pH control. KCl of analytical purity was employed as background electrolyte solution. The water used in all these tests is deionized (DI) water with a resistivity of 18.3 M Ω -cm.

2.2. Flotation tests

Flotation tests were carried out in a micro-flotation cell with an effective volume of 40 ml (Wang, 2017). For each test, 2.0 g of mineral powder samples were placed in the cell after 3 min of cleaning of mineral powder surfaces in ultrasonic cleaner to remove any impurity, and then filled with 35 ml DI water. After 2 min of agitation, the pH value was adjusted to the desired value upon which collector and co-collector were added successively. The conditioning time for pH regulators and collectors are 2 min and 3 min, respectively. After 4 min of flotation, the floated and non-floated fractions were filtered, dried and weighed for the recovery calculation (See Fig. 3).

2.3. Fluorescence emission spectroscopy

The samples for fluorescence emission spectroscopy were prepared through mixing pyrene stock solution with collectors (the addition of collector and co-collector with an interval of 1 h) and mineral pulp, and allowed to stand for 1.5 h to equilibrate. The pyrene steady-state emission spectra were obtained by using a Hitach F-4500 fluorescence spectrophotometer. The pyrene stock solution was prepared by dissolving pyrene in hot water until saturation, then cooled to 25 $^{\circ}\text{C}$, and filtered. The concentration of pyrene in the solution was determined to be 6.53×10^{-7} mol/L. The excitation wave length of pyrene was 335 nm (Wang et al., 2015a,2015b; Xu et al., 2013; Piñeiro et al., 2015).

2.4. Adsorption tests

Collector solution (40 ml) combined with molybdenite powder (2 g) were placed in 100 ml flasks. The pH was adjusted to 7.0 with the addition of HCl and NaOH and to settle for 10 min, then the co-collector was added followed another adjustment of the pH value and maintained another 10 min. The pulp was agitated for 25 min at 200 rpm in a constant temperature incubator shaker. The solutions were centrifuged at 8500 rpm for 20 min, and the concentrations of each component in

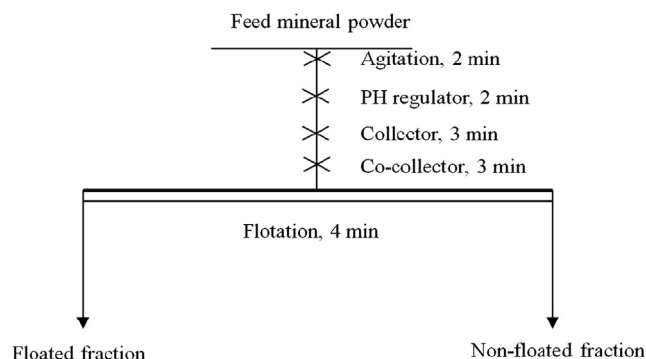


Fig. 3. Flowsheet of pure mineral flotation tests.

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