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Mechanism study on flotation separation of molybdenite from chalcocite using thioglycollic acid as depressant

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ABSTRACT

Effects of collectors (butyl xanthate (BX), O-isopropyl-N-sulfur ethyl carbamate (Z-200) and emulsified kerosene), dereagent (sodium sulfide) and depressant thioglycollic acid (TGA) on the flotation of chalcocite and molybdenite were investigated through flotation. The first principle theory was adopted to understand the difference of their surfaces and reaction between minerals and reagents. Results of flotation tests revealed that selectivity of emulsified kerosene is the best of three collectors in separation of chalcocite and molybdenite, though the others also display excellent collecting properties. Sodium sulfide can effectively remove collectors adsorbed on chalcocite surface, and TGA is an effective depressant of chalcocite at pH 8–9. Through first principle study, molybdenite displays relatively stronger covalence property while bonding interaction between copper atoms in chalcocite enhanced its ionicity. Bonding interaction is weaker in reaction of TGA and molybdenite, so it shows higher hydrophobicity and better flotability. Therefore, TGA is an effective inhibitor in the separation.

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1. Introduction

Although as an important strategic metal in the industrial sector since 2004, molybdenite concentrate is commonly obtained as a by-product in the treatment of copper porphyry ores in which the molybdenite is a minor constituent [1]. It is reported that approximately 50% of the world's molybdenum production comes from Cu-Mo ore as a by-product [2]. On the other hand, the high grade ore is gradually exhausted due to ceaseless exploitation of resources in the world. The existing low-grade and finer-embedded ores are difficult to be separated and extracted.

Shirley, Sutulov and Hernlund had summarized some of the factors that might affect the floatability of molybdenum from porphyry ores at industrial scale, they were: mineralogy of ore deposits, slime coatings, optimizing copper metallurgy at the expense of molybdenum, grinding, liberation and flotation reagents [3,4]. Traditionally, three flotation approaches, bulk flotation followed by separation, selective Cu flotation followed by bulk flotation and then separation, and preferential Mo flotation followed by Cu flotation, can be adopted in the separation of Mo-Cu ore [5–7]. The first flotation process is adopted in this study. Focusing on separation of chalcocite and molybdenite after bulk flotation, sodium sulfide is used as dereagent due to its property of

desorbing the reagents absorbed on mineral surface, especially collectors. According to literature, sodium sulfide plays its role effectively as dereagent focused on three aspects: resolving the coverage of the mineral surface, inhibiting mechanism of sulfide, and modulating ion composition of slurry [8]. Results of literature published by Yin et al. also showed better recovery and grade of the molybdenum are obtained using sodium sulfide as modifying agent in kerosene-sodium silicate flotation system [9].

Depressant is another important factor in the flotation [10]. Generally, thioglycollic acid (TGA) is employed as depressant in copper-aluminium flotation, it is also a good substitute for sodium cyanide as copper sulfide depressant with less usage and more environmental friendly. -SH and -COOH are effective groups of thioglycollic acid when reacting with sulfide deposit [11]. The supposed mechanisms are: it is absorbed on the mineral surfaces chemically or physically, meanwhile competitive absorption with collectors such as xanthate. On the other hand, -COOH absorbs on the mineral surface and forms a hydrophilic substance and thus hydrophilic membrane layer comes into being; -SH group renders mineral surface hydrophilic when contacted due to its property of reducibility and combination with mineral. Thereout, hydrophilic property of the mineral is enhanced and impurities are prevented from getting involved in froth concentration and sulfide concentration. However, the exact mechanism is still not clear. Aimed at verifying the effect of surface absorption on flotation, we try to make a

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combination of flotation process and crystal structure, surface electronic properties.

Simulation is widely considered as a useful complement to experimental techniques, because it allows direct observation of atomic-scale phenomena in complete isolation, which cannot be achieved in current experimental studies. To ascertain the difference of the minerals surface, the first-principle calculation is used and the results can provide important insight into the mechanism. Many other minerals such as chalcopyrite, sphalerite, marmatite and their adsorption properties, oxygen adsorption on galena, have been studied with the first-principle theory to understand the mechanisms and flotation behaviors, and the effects of crystal structure on flotation [12–15]. In order to better understand chalcocite, molybdenite and the action principle between minerals and reagent, The Materials Studio Software was employed to study the electronic structure of chalcocite and molybdenite.

2. Experiment

2.1. Materials

Chalcocite and molybdenite used in the experiment as single mineral samples were derived from Yuanyang copper-molybdenum deposit in Yunnan province. After hand-picked, the relative high-purity minerals were crushed to -3 mm to meet the feed size requirement of porcelain ball mill. The mineral grindings were sieved to obtain -0.074 mm product as flotation specimen. The sample was stored in nitrogen atmosphere to avoid oxidation. Chemical analysis of the chalcocite sample, using X Ray Fluorescence (XRF), showed Cu 60.32%, S 29.45%, and the molybdenite sample contains Mo 27.21%, S 58.82%. The reagents used in this study are all of chemical pure grade. Distilled water was used throughout the experiment.

2.2. Techniques and methodology

2.2.1. Micro flotation test

The micro flotation test was executed in a Plexiglas cell (40 mL). 2 g single mineral sample was used in every single test, then it was ultrasonically cleaned for 5 min with 20 mL distilled water to remove the oxidation layer covered on the surface. In determining the influence of collectors on selective flotation of chalcocite and molybdenite, addition order of reagents went as follows: pH regulator (NaOH or HCl), collector and frother. Further tests were carried out to verify the influence of dereagent and depressant on flotation of the two minerals. Orders of reagents addition, condi-

tion time and operation procedures were shown in Fig. 1. After flotation test, the sunken and flotated products were collected, filtered, dried and weighted separately to calculate the recoveries. All experiments were done in duplicate.

2.2.2. Computational method

The calculations were performed using the Materials Studio program Cambridge Serial Total Energy Package (CASTEP) developed by Payne, which is a first-principle pseudo potential method based on density-functional theory (DFT) [16]. DFT calculations within the generalized gradient approximation (GGA) using the Perdew, Burke and Ernzerhof (PBE) functional were carried out to realize geometry optimization and property calculation. The interaction between valence electron and ionic core was presented by Ultra-soft Pseudopotential.

The space group of chalcocite is P63/MMC, and the crystal parameters are $a = b = 0.4033$ nm, $c = 0.6739$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. Molybdenite belongs to the hexagonal crystal system, its space group is P63/MMC, the crystal parameters are $a = b = 0.315$ nm, $c = 1.230$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. Crystal structures of chalcocite and molybdenite display in Fig. 2. Surfaces (110) and (001) are the main cleavage surfaces of the two minerals [17].

Valence electron configurations of chalcocite involved in the calculation include Cu $3d^{10}4s^1$ and S $3s^23p^4$. The kinetic energy cut-off of 320 eV for the plane wave basis was used throughout the study, and the Brillouin zone was sampled using Monkhorst and Pack's special k -points of a $5 \times 5 \times 4$ grid for all structure calculations, which shows that the energy cut-off and the k -point mesh are sufficient for the system [18]. For self-consistent electronic minimization, the Pulay Density Mixing method was employed with a convergence tolerance of 1.0×10^{-5} eV/atom. The convergence criteria for structure optimization and energy calculation were set to: an energy tolerance of 1.0×10^{-5} eV/atom; a maximum force tolerance of 0.03 eV/Å; a maximum displacement tolerance of 0.001 Å and a maximum internal force tolerance of 0.06 GPa.

Structure and geometry optimization and quality calculation of molybdenite are basically the same with chalcocite. Valence electrons configurations of molybdenite considered in the study include Mo $4d^55s^1$ and S $3s^23p^4$. Energy cut-off is 250 eV, k -points is $9 \times 9 \times 2$ after convergence test. The kinetic energy cut-off of 300 eV for the plane wave basis was used throughout the study, and the Brillouin zone was sampled using Monkhorst and Pack's special k -points of a $9 \times 9 \times 2$ grid for all structure calculations. For self-consistent electronic minimization, the Pulay Density Mix-

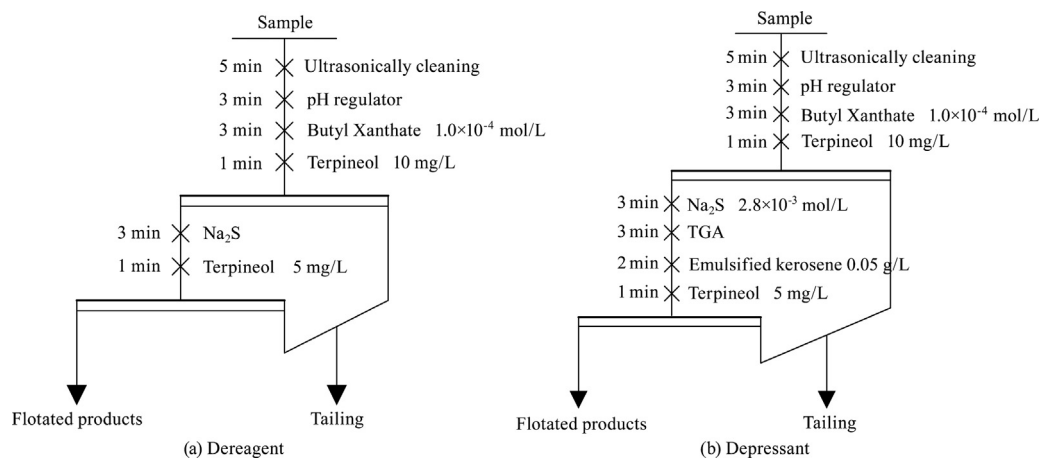


Fig. 1. Flowsheets of flotation test in testing effect of dereagent and depressant.

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