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Adsorption mechanism of 2-mercaptobenzothiazole on chalcopyrite and sphalerite surfaces: *Ab initio* and spectroscopy studies

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Abstract: Interaction mechanism of the collector, 2-mercaptobenzothiazole (MBT), with chalcopyrite and sphalerite surfaces were investigated by Fourier transform infrared (FTIR) and density functional theory. Results of FTIR showed that some characteristic peaks of MBT were observed on the chalcopyrite surface, including C═N, C═N—S and C—S stretching vibration peaks, and the adsorption product was CuMBT. But there were no characteristic peaks of MBT on the sphalerite surface. The thione molecular form of MBT was the most efficient and stable, N and exocyclic S were the more favourable reactive sites for nucleophilic attacked by metal atoms. Compared with ZnS (110), MBT is more readily adsorbed on $CuFeS_2$ (112). Attachment of MBT occurs due to strong bonding through exocyclic S p and s orbits with Cu d orbit on $CuFeS_2$ (112) and electron transfer from Cu atom to S atom. Under the vacuum condition, MBT in the form of thione molecular cannot be adsorbed on ZnS (110) spontaneously.

Key words: chalcopyrite; sphalerite; 2-mercaptobenzothiazole; adsorption mechanism; density functional theory

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1 Introduction

With the mineral resources rapidly becoming depleted, fine-grained and complex, the flotation becomes more and more difficult. Unintentional (accidental) activation of minerals by contaminant metal ions is one source of mineral misplacements in separation by flotation reported by RASHCHI and FINCH [1]. Recently, much attention has been paid on searching for new chemical reagents which have a stronger affinity and better selectivity for certain metal ions [2−8], because the choice of collector type is crucial in the flotation performance of minerals.

2-mercaptobenzothiazole (MBT), was found to be alternatives to conventional xanthate collectors, and it has a lower dosage required to obtain high recoveries in sulfide-mineral flotation [9]. It has been suggested as a new collector in the flotation of metal sulfide ores, precious metal ores, gold-bearing pyrite, tarnished and secondary Cu, Pb and Zn minerals [2,10]. In our previous work [11], we found that in the presence of isopropyl ethylthionocarbamate, butyl xanthate, and ammonium dibutyl dithiophosphate, the separation between chalcopyrite and marmatite could not be achieved at neutral pH. MBT is as powerful as the other three collectors for the chalcopyrite, but it is a more selective collector against copper-activated marmatite at neutral pH and even better at alkaline pH. SZARGAN et al [12] investigated the adsorption of MBT on galena and pyrite surfaces by X-ray photo-electronic spectroscopy (XPS). They concluded that in 1×10^{-5} mol/L aqueous solution, MBT chemisorbed on the mineral surfaces via the thiolate group in monolayers. It was proposed that MBT adsorption on PbS occurred according to the mechanism that MBT−Pb formed on the PbS surface confirmed by FTIR investigations [3], and MBT bonded to Pb atom on the PbS surface through the exocyclic sulfur atom. Besides, MBT is used as the collectors in mineral processing. It is also used as effective corrosion inhibitors because MBT can form hydrophobic complexes with many metals such as Fe, Cu, Co and Ni [13−15]. Therefore, thorough studies on the electronic structure and reactivity between MBT and surfaces are necessary.

Many modeling studies have been carried out on the

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collectors [16−18] and minerals [19−25]. STEELE et al [26] performed calculations of possible modes of interaction of Pb^{2+} ions with the (110) surface of sphalerite by using DFT to treat electron correlation. BLANCHARD et al [27] investigated the influence of incorporation of arsenic in FeS_2 pyrite, and they predicted that the formation of AsS dianion groups on FeS_2 surface is the most energetically favorable mechanism [28]. In order to probe the adsorption of Cu on pyrite (100), theoretical calculations were performed by OERTZEN et al [29] by using *ab initio* density functional theory, which supported the interpretation of the spectroscopy. In order to better understand the surface passivation in the leaching of chalcopyrite, OLIVEIRA et al [30,31] studied the reconstruction of (001), (100), (111), (112), (101) and (110) chalcopyrite surfaces by DFT calculations within the plane wave framework. Three different mechanisms were proposed: S^{2-} ions migrated to the surface tended to oxidize to form disulfides $S_2{}^{2-}$, while the superficial Fe^{3+} was concomitantly reduced to Fe^{2+}; metal atom moved downward to the surface and metallic-like bidimensional alloys formed underneath the surface, which were in good agreement with the results of XPS [32]. As stated previously, it was well established that DFT calculations were used in studying the electronic and molecular properties of collectors and minerals, and the adsorption mechanisms have been well recognized.

As MBT is more selective towards copper−zinc sulfide minerals than conventional collectors, to obtain further insights into the MBT−mineral surfaces interactions, the present communication presents the studies of the interactions of 2-mercaptobenzothiazole (MBT) with chalcopyrite and sphalerite surfaces by using FTIR and density-functional theory (DFT). The flotation process of sulfide minerals involves many factors that are beyond the scope of this study, such as pH, pulp potential [33−35], water, surface defects [19,37,38] and reconstruction [30,31,38]. Even a full description of solid−liquid interface is still a difficult task for the present quantum-chemical methods, hence it is important to start with a simple model for this theoretical investigation. Therefore, in this work, we only considered the adsorptions of MBT on perfect chalcopyrite (112) and sphalerite (110) surfaces.

All of the results aimed to contribute to the knowledge of the chemical reactivity of the chalcopyrite and sphalerite surfaces at a molecular level. Although the results calculated in this work show a good agreement with experimental observations, future investigation will have to be focused on the effects of different exposure atoms and surface reconstructions in order to better understand the adsorption mechanisms of reagents on mineral surface in flotation.

2 Experimental

2.1 Fourier transform infrared test

High-purity chalcopyrite, sphalerite and marmatite samples used in the test were obtained from Dachang concentrator, Guangxi, China. The chemical analysis of the chalcopyrite sample showed 35.90% Cu, 33.99% S and 29.17% Fe. The sphalerite sample contained 66.63% Zn, 32.13% S and 0.16% Fe. The samples were dry ground using a porcelain ball mill at a speed of 80 r/min. Then, the ground samples were dry screened and <37 μm sized fraction was used. The infrared spectra were recorded by NEXUS−470 spectrometer operating in the range of 4000−400 cm^{-1}. A mass of mineral sample (1 g) was mixed with 20 mL of reagent solution at pH 6.86 and then ground in an agate mortar for 30 min, filtrated, and rinsed twice or three times using the corresponding pH buffer solution. Subsequently, the sample was dried in a vacuum desiccator at 25 °C, and then used for FTIR reflection spectra measurement. The KBr pellet technique was adopted for recording the spectra.

2.2 Computational details

The quantum chemical calculations were performed using the Materials Studio 5.5 program CASTEP within the framework of nonlocal density functional theory using the generalized gradient approximation (GGA) of PERDEW et al [39]. The Perdew, Burke and Ernzerhof (PBE) functional models were carried out to study MBT adsorption on chalcopyrite and sphalerite surfaces [39]. Valence electron configurations in this work included Zn $3d^{10}4s^2$, S $3s^23p^4$, Cu $3d^{10}4s^1$, and Fe $3d^64s^2$. To model bulk properties using the super cell formalism, a suitable model system was constructed, and then repeated periodically. The size of the super cell must be sufficiently large to avoid spurious effects caused by interaction of the model system with its images.

Chalcopyrite crystallizes in tetragonal group with four formulas per unit cell; the space group is *I*-42*d*. The lattice parameters were determined by KNIGHT et al [40] to be $a=b=5.29$ Å and $c=10.4217$ Å. When the mineral cleavage plane was constructed, the vacuum thickness was fixed at 10 Å, and then the surface free energies were calculated under the corresponding atomic layer number. The convergence test results of surface free energy of $CuFeS_2$ (112) and (101) slices are shown in Fig. 1. The formula is shown as follows:

$$E_{\text{surf}} = \frac{1}{2}\lim_{M\to\infty}\frac{E_{\text{latt}} - E_{\text{slice}}}{A_{\text{hkl}}} \tag{1}$$

where E_{latt} is the energy of body model with the same atomic number; E_{slice} is the energy of crystal surface model; A_{hkl} is the crystal surface area; 1/2 is the two