



# Understanding the interactions of thiophosphorus collectors with chalcopyrite through DFT simulation



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## ABSTRACT

Density functional theory simulations were performed to study the adsorption mechanism of four different thiophosphorus collectors including diethyl dithiophosphate (DEDTPA), diethyl dithiophosphinate (DEDTPI), diethyl monothiophosphate (DEMTPA) and diethyl monothiophosphinate (DEMTPI) on chalcopyrite (100) and (110) surfaces. DFT revealed a major reconstruction of sulfur and metal exposed chalcopyrite (100) surfaces after cleavage. This results into formation of disulfide dimers on the surface and migration of copper and iron inwards with respect to bulk with formation of new Fe–Fe, Cu–Fe and Cu–Cu bonds in the latter after relaxation. Thiophosphorus collectors chemisorb on the sulfur-exposed chalcopyrite (100) surface through formation of a monodentate covalent bond between sulfur atom from the collector polar head and surface-unsaturated sulfur atom. However, the interaction of the collectors with the metal exposed chalcopyrite (100) is through physisorption. The interaction of chalcopyrite (110) surface with thiophosphorus collectors involves bidentate chemical bonding between surface copper and iron atoms and sulfur and/or oxygen atoms of the collector polar-head.

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## 1. Introduction

Chalcopyrite is the main and most wide-spread mineral source of copper in the world [1–4]. Chalcopyrite in its natural form is associated with a variety of sulfide ores such as sphalerite, galena and pyrite [1,5]. Separation of chalcopyrite from gangue minerals is performed in practice through froth flotation which is a complex process for selective separation of hydrophobic minerals from the hydrophilic ones [6,7]. In froth flotation, the mineral surface hydrophobicity is commonly induced by the attachment of collectors to promote flotation. A variety of traditional collectors has been already tested in froth flotation to separate chalcopyrite from other metal sulfide ores [8–10]. Among these, xanthates are recognised as powerful traditional collectors used widely in industrial practice for chalcopyrite flotation [3,7,10–12]. However, their low selectivity towards chalcopyrite, especially in its mixture with pyrite, presents an important disadvantage for this family of collectors [13]. The presence of pyrite impurities in copper concentrates not only reduces their quality but also increases the economic and environmental costs in the downstream smelting process [14]. Consequently, considerable efforts have been vested for increasing selectivity of the collectors towards chalcopyrite through synthesis

of non-traditional chelate-forming collectors whose structure possesses donor atoms and show higher selective chemical affinity towards copper metal ions than iron [15].

Thiophosphorus-based chelating agents are a family of non-traditional collectors widely tested for their higher selectivity towards chalcopyrite and galena in their mixture with pyrite [3]. Dialkyl dithiophosphate and dialkyl dithiophosphinate are among the most widely studied thiophosphorus collectors used for the separation of metal sulfide ores. Dialkyl dithiophosphinate collectors have shown stronger interaction and better selectivity towards chalcopyrite than dialkyl dithiophosphates [3,4,15]. Zhong et al. [14] benchmarked the collecting performance of diisobutyl dithiophosphinate collector for flotation of chalcopyrite and galena against that of traditional butyl xanthate collector. Higher floatability of chalcopyrite and galena as well as higher depression of pyrite and sphalerite was observed with diisobutyl dithiophosphinate as compared to butyl xanthate at pHs varying from 2 to 13.

Although the collecting performance and selectivity of dithiophosphate and dithiophosphinate based collectors towards chalcopyrite and galena have been studied widely through experiments and spectroscopic techniques, very few studies directly addressed the interaction mechanism of chalcopyrite/galena–thiophosphorus collectors to explain the macroscopic behavior observed in the flotation tests. Guler et al. [3] studied the adsorption mechanism of diethyl dithiophosphate and diisobutyl

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dithiophosphinate on chalcopyrite through diffuse reflectance Fourier transformation (DRIFT) spectroscopy. The DRIFT spectra evidenced chemical interactions between adsorbed dithiophosphate (and dithiophosphinate) collectors with chalcopyrite in the form of Cu–S bond signatures. Zeta potential and FTIR analyses performed by Pecina-Trevino et al. [15] also confirmed chemical interactions between diisobutyl dithiophosphinate collector and galena and pyrite that resulted in the formation of Pb–S and Fe–S bonds between surface lead and iron atoms with dithiophosphinate-bearing sulfur atoms. Strength of the chemical interactions between several thiophosphorus collectors including diisobutyl dithiophosphate, diisobutyl dithiophosphinate, diisobutyl monothiophosphate and diisobutyl monothiophosphinate and several metal sulfide minerals such as chalcopyrite, galena and pyrite was also studied by Liu et al. [16] through quantum mechanical simulations. Electron donating and accepting strength of the collectors and the electronic orbital configuration of isolated metal ions such as  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were computed. Among the investigated thiophosphorus collectors, the simulations highlighted the highest collecting affinity of diisobutyl dithiophosphinate towards chalcopyrite and galena.

Contrary to above simplified assumptions [16], the goal of the present study is to investigate through density functional theory simulations (DFT) directly the interaction mechanism with chalcopyrite surface of several thiophosphorus collectors such as diethyl dithiophosphate (DEDTPA), diethyl dithiophosphinate (DEDTPI), diethyl monothiophosphate (DEMTPA) and diethyl monothiophosphinate (DEMTPI). Quantum mechanical simulations based on density functional theory (DFT) have been advocated over the past decades as a powerful tool to study the electronic interactions between collectors and the surface of minerals [17,18]. DFT simulations have been also recently performed by a few groups to study the relaxation of chalcopyrite surface after breakage as well as its interaction with water solvent and dissolved iodine anions [19–23]. An important reconstruction of chalcopyrite surface which results in the oxidation of surface migrated  $\text{S}^{2-}$  ions has been reported by de Oliveira et al. [21]. Furthermore, these authors also reported the downward movement of surface metal atoms which results into the formation of metallic like two-dimensional alloys underneath the surface. The interaction of water solvent molecules with relaxed (001) chalcopyrite surface has been also studied through DFT simulations by the same group which has revealed the preferred interaction of water molecules with iron atoms on the chalcopyrite surface along with the formation of surface hydrogen bonds [19]. Surface iron and copper atoms have been also reported to be the most favorable adsorption sites for iodate and iodide, respectively [23]. To the best of our knowledge, the potential of DFT simulations to generate an understanding on the interaction mechanism of thiophosphorus collectors with the surface of chalcopyrite is not yet explored and therefore this study constitutes an opportunity for generating new understanding on this crucial issue.

## 2. Computational methodology and assumptions

Spin unrestricted DFT calculations were carried out for the total energy calculations and corresponding structure optimization to find the most stable adsorption configurations using DMol3 package implemented in Materials Studio 2016. DMol3 applies numerical functions on an atom-centered grid as its atomic basis and atomic basis functions are attained by solving the DFT equations for every individual atom leading to rather accurate calculations. The revised Perdew–Burke–Ernzerhof generalized-gradient approximation (RPBE) was used to approximate the exchange–correlation energy. The core electrons were treated using DFT semi-core Pseu-

dopots and the double numerical plus d-function (DND) basis set was used to develop the electronic eigenstates with an orbital cut-off radius of 4.3 Å. The self-consistent field (SCF) convergence was fixed to  $10^{-5}$  and the convergence criteria set for the energy, maximum force and maximum displacement were  $2 \cdot 10^{-5}$  Ha,  $4 \cdot 10^{-3}$  Ha/Å and  $5 \cdot 10^{-3}$  Å, respectively.

Prior to surface adsorption simulations, the chalcopyrite unit cell was optimized using DFT (Fig. 1a). Chalcopyrite is a covalent copper iron sulfide which belongs to the I–III–VI<sub>2</sub> type semiconductor groups [1]. Ideally the optimized unit cell of chalcopyrite  $\text{CuFeS}_2$  is composed of eight sulfur, four iron and four copper atoms forming a tetragonal unit cell structure in which the cell dimension in *c* direction is almost twice larger than in *a* and *b* directions ( $c = 10.05$  Å,  $a = b = 5.11$  Å). Each iron/copper atom in the chalcopyrite unit cell is tetrahedrally bonded with four sulfur atoms. As a result, the chalcopyrite unit cell can also be represented as a complex of iron-centered and copper-centered tetrahedra with four-vertex sulfur atoms (Fig. 1b). Both iron- and copper-centered tetrahedra retain a disphenoid structure where the four faces are congruent acute-angled triangles. The S–Cu bond length (2.288 Å) in the chalcopyrite unit cell is larger than that of S–Fe (2.121 Å) resulting into a larger volume of copper-centered disphenoid (6.125 cubic Å) than iron-centered disphenoid (4.791 cubic Å).

The optimized chalcopyrite unit cell was subsequently used to construct selected slabs to investigate the interaction of thiophosphorus collectors with chalcopyrite. Chalcopyrite has a conchoidal fracture pattern resulting in particles with plenty of exposed surfaces after cleavage [1]. As a result, in this study we choose slabs cleaved along (100) and (110) planes as representative of polar–metal cations and sulfur anions in separate layers– and nonpolar–equal number of metal cations and sulfur anions in each layer–chalcopyrite surfaces. The different chalcopyrite slabs were then constructed using  $(1 \times 2)$   $\text{CuFeS}_2$  (110) and (100) surface supercells with 40 Å vacuum spacing to prevent interactions between image slabs. Due to the polarity of chalcopyrite (100), ideally cleaved chalcopyrite along (100) direction could expose sulfur-exposed (100) or metal-exposed (100) layers to the collector solution. However, the chalcopyrite cleavage along (110) plane only presents one possibility for the exposed surface atoms. It is known that chalcopyrite surfaces undergo considerable relaxation and reconstruction from the bulk termination [20,21]. Consequently, in all the simulations, except for the last atomic layer which was fixed to represent the bulk atoms of chalcopyrite, the rest of atomic layers were allowed to relax. The pre-optimized slabs were then used to obtain their most stable interaction configuration with thiophosphorus collectors while taking into account the water solvent effect by means of the conductor-like screening model for real solvents (COSMO-RS). The adsorption energy of collector on chalcopyrite was calculated as  $E_{\text{ads}} = E_{[\text{slab}+\text{collector}]} - E_{[\text{slab}]} - E_{[\text{collector}]}$  where  $E_{[\text{slab}+\text{collector}]}$  represents the total energy after collector adsorption on the surface,  $E_{[\text{slab}]}$  is the energy of relaxed bare slab and  $E_{[\text{collector}]}$  is the energy of reagent molecule/ion. Negative adsorption energy is indicative of exothermic adsorption and strong interaction of the collector/activator on the chalcopyrite surface [18]. Finally, formation of a bond between the adsorbed collectors and the chalcopyrite surface was assessed by evaluating the distance between the collector–surface atoms and its comparison with the ideal sum of the covalent radius of the two atoms.

## 3. Results and discussion

### 3.1. Optimized structure of solvated thiophosphorus collectors

The collector molecular structure could play an important role in its interaction with the surface of chalcopyrite. Thus, the struc-

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