



## Full Length Article

## Adsorption of water, sulfates and chloride on arsenopyrite surface



Juliana C.M. Silva<sup>a,b</sup>, Egon C. dos Santos<sup>a</sup>, Aline de Oliveira<sup>a</sup>, Thomas Heine<sup>b,c</sup>,  
Heitor A. De Abreu<sup>a</sup>, Hélio A. Duarte<sup>a,\*</sup>

<sup>a</sup> Grupo de Pesquisa em Química Inorgânica Teórica – GPQIT, Departamento de Química, ICEx, Universidade Federal de Minas Gerais (UFMG), Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte, MG, Brazil

<sup>b</sup> Physics & Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

<sup>c</sup> Wilhelm-Ostwald-Institute of Physical and Theoretical Chemistry, University of Leipzig, Linnéstr. 2, 04103 Leipzig, Germany

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## ABSTRACT

Arsenopyrite is one of the sulfide minerals responsible for acid rock drainage (ARD) and is one of the most hazardous in regions affected by mining activities. This phenomenon involves complex reaction mechanism. Although it is intensely investigated, there is a lack of consensus concerning the reaction mechanisms and more information is still necessary. In this work, the adsorption of water, hydrochloric acid, and sulfuric acid on arsenopyrite (001) surface was investigated by means of Density Functional calculations and the results compared to other sulfides aiming to understand the mineral/water interface. The interaction of the chemical species with the (001) FeAsS surface is the first step to understand the intricate oxidation mechanism of arsenopyrite. Molecular water adsorption on (001) FeAsS is more favored than the adsorption of sulfate favoring the dissolution of sulfates and enhancing its oxidation. The estimated adsorption energies of water, sulfates and chloride on other sulfide minerals are compared with the estimated values for arsenopyrite and the chemical reactivity differences discussed in detail.

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## 1. Introduction

Pyrites are an important class of minerals in the earth crust such as pyrite (cubic FeS<sub>2</sub>), marcasite (orthorhombic FeS<sub>2</sub>), arsenopyrite (FeAsS) and chalcopyrite (CuFeS<sub>2</sub>). Noble metals such as gold, platinum, silver, copper and other metals of economic importance are normally found incrustated in pyrite and arsenopyrite. However, they also host many toxic metals, such as lead and cadmium [1]. In the process of extraction, great amounts of mineral are handled exposing it to the atmosphere and humidity. In the presence of oxygen and water, pyrites are oxidized releasing sulfuric acid in the very end of the process and, thus, enhancing the mobilization of heavy metals to the environment and aquifers. This phenomenon is called acid rock drainage (ARD) and is one of the most hazardous in the mining industry related to noble metal extraction. In spite of the anthropogenic causes, natural processes can also happen whenever the pyrites are exposed to the environment.

Efforts have been made to understand the structure and chemical reactivity of pyrite [2–6], arsenopyrite [7–11], covellite [12,13] and chalcopyrite [14–19] surfaces. The adsorption of water on

pyrite has received much attention [20–23] due to the importance of this mineral in flotation techniques to separate it from valuable metals and also to ARD. The interaction of HCl and H<sub>2</sub>SO<sub>4</sub> on chalcopyrite surface [16] has been investigated aiming to understand the low kinetics of the leaching process for copper extraction.

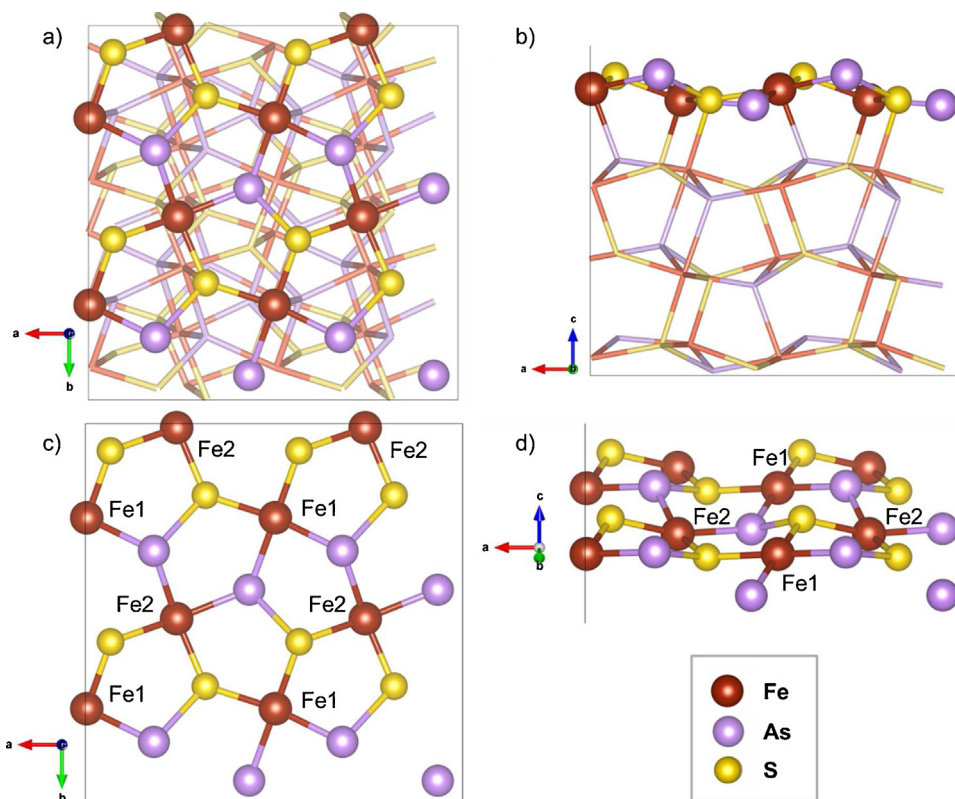
Investigating solid/liquid interface is the first step to understand the reactivity of the mineral surface and, consequently, the first steps of its oxidation mechanism. It has been shown that the water has an important role in this process and the leaching agents such as hydrochloric acid and sulfuric acid can bring new insights about the surface/liquid interface at the molecular level [16]. In this context, first-principle calculations can provide insights about the arsenopyrite surface reactivity and a molecular view of the surface/solution interface.

In natural environments, and especially in mining tailings, arsenopyrite surface is in contact with water, and the role of this molecule in the oxidation mechanism has not yet been investigated. The behavior of this mineral in aqueous medium is a step that must be investigated before any attempt to understand the mineral oxidation can be taken.

Arsenopyrite is a diamagnetic semiconductor [24]. Its unit cell has space group P2<sub>1</sub>/c [25] and contains 4 FeAsS formula units. The structure contains arsenic and sulfur dianions (As–S) coordinated to Fe atoms in a distorted octahedron. The Fe atoms are coordinated

\* Corresponding author.

E-mail address: [duarteh@ufmg.br](mailto:duarteh@ufmg.br) (H.A. Duarte).



**Fig. 1.** Arsenopyrite (001) surface: a) top view; b) side view; c) first layer of atoms in this surface showing the two different Fe sites: Fe1, more exposed, and Fe2, less exposed; d) first layer in side view.

to three As and three S atoms and each anion is coordinated in a tetrahedral arrangement to three iron atoms and another anion. Different cleavage planes were found in the literature as the most favorable: (100) [10], (001) [26], (101) [25,27] and (110) [7,28]. However, our previous study [8] indicated the planes (001), (010) or (100) as the most favorable ones for cleavage, especially the (001) plane, which has the lowest formation energy. This surface agrees with the observation of Schaufuss et al. [29] that the As atom is the closest one to the surface after cleavage of Fe–As bonds.

In the present work, the interaction of water,  $\text{Cl}^-$ ;  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  species with arsenopyrite surface is investigated aiming to contribute to the understanding of the arsenopyrite/water interface.

## 2. Methodology

Slab calculations have been performed based on the density functional theory (DFT)/plane waves methodology with periodic boundary conditions as implemented in the Quantum Espresso package [30]. The PW91 [31] exchange/correlation (XC) functional and ultrasoft pseudopotentials proposed by Vanderbilt [32] with the following valence configurations were used: Fe ( $3s^2 3p^6 3d^6 4s^1 4p^0$ ), As ( $4s^2 4p^3$ ) and S ( $3s^2 3p^4$ ). A cutoff energy of 30 Ry and a  $2 \times 2 \times 1$  K-point mesh sampling based on the Monkhorst-Pack scheme [33] were chosen, besides Marzari-Vanderbilt [34] 0.02 Ry smearing. The energy was converged to  $10^{-6}$  Ry.

All calculations were spin polarized. Geometry optimization was carried out using damped dynamics method [35] with Parrinello-Rahman extended Lagrangian [36], keeping a force tolerance criterion of  $10^{-3}$  Ry Bohr $^{-1}$ . The atomic positions were fully optimized with no symmetry constraint. The density of states (DOS) was calculated from the optimized geometries.

A ( $2 \times 2$ ) unit cell slab model, built from an optimized bulk structure, was chosen for the surface, in order to avoid lateral interaction between the adsorbed molecules in the neighbor cells. A 15 Å of vacuum was applied to avoid interaction between slab layers. The definition of appropriate thickness of this slab surface was investigated to ensure there are no edge effects. The number of 12 layers assures that the surface energy converges within  $0.01 \text{ J m}^{-2}$  as shown at Fig. S1. The slab was symmetric on top and bottom surfaces.

All adsorption energies were calculated using Eq. (1)

$$E_{ads} = E_{sur+mol} - E_{sur} - E_{mol} \quad (1)$$

where  $E_{ads}$  is the adsorption energy,  $E_{sur+mol}$  is the total energy of the surface with the molecule adsorbed,  $E_{sur}$  is the total energy of the relaxed surface and  $E_{mol}$  is the total energy of the isolated molecule calculated in a box identical to the one used for the surface calculation.

Bader analysis [37] of the surfaces and adsorbed molecules were performed using the software Critic2 [38,39] applying the Yu-Trinkle integration [40] in order to investigate the charges of the atoms involved in the adsorption, as well as the nature of its bond critical points. Charge density difference analysis was also employed to verify the influence of the chemical species in the adsorption process on the surface.

## 3. Results and discussion

Silva et al. [8] performed extensive DFT/plane waves slab calculations of Arsenopyrite and showed that the (001) surface is the most favorable cleavage plane. It is formed by breaking Fe–As and Fe–S axial bonds, exposing all three atoms, as shown in Fig. 1a and 1b. In this surface formation, a small relaxation changed the initial bulk atomic positions, in which the largest difference was 0.14 Å

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