Adsorption of Water and Oxygen on Arsenopyrite (001) Surface

Silva, J. C. M,[a] (PG), Heine, T.[b](PQ), De Abreu, H. A.[a] (PQ) and Duarte, H. A.[a](PQ)

[a] *Universidade Federal de Minas Gerais, Department of Chemistry, Av. Antônio Carlos 6627, 31.270-901, Belo Horizonte – BRAZIL*
[b] *Jacobs University, Physics and Earth Sciences, Campus Ring 1, 28759, Bremen – GERMANY*
e-mail: julianacmsilvaq@gmail.com

Keywords: Density Functional Theory (DFT), Arsenopyrite, Surface, Adsorption, Oxidation.

INTRODUCTION

Arsenopyrite is a mineral present in gold mining tailings and, as the other mineral sulfides, it is responsible for Acid Rock Drainage (ARD) – a process in which the sulfide mineral in contact with water and oxygen oxidizes, yielding sulfuric acid – contaminating soils and waters. Therefore understanding the reaction process involved in ARD is very important and not yet completely understood. The reactions involved are much complex, leading to a lack of consensus in the literature[1]. Therefore, theoretical calculations can contribute to the understanding of the reaction mechanism at a molecular level. In this work the adsorption of water and oxygen on the most stable arsenopyrite surface[2] was investigated in order to understand the first step of the oxidation mechanism of this mineral.

METHODS

Density Functional Theory (DFT) with plane waves approximation implemented in Quantum Espresso package was used for investigating the adsorption of water and oxygen on the (001) surface of arsenopyrite. The spin-polarized calculations were performed using PW91 XC functional, with an energy cutoff of 30 Ry, a **K**-point mesh of 2×2×1 and a vacuum layer of 15Å.

The Density of States (DOS) analysis of the surface indicate that the adsorption of a Lewis base is preferred at the Fe site[2]. This is probably the site where the oxidation reaction starts.

RESULTS AND DISCUSSION

The results show that the molecular adsorption of one water molecule to a Fe atom on the surface is favorable, with adsorption energy of -11.04 kcal mol^{-1}, unlike the dissociative adsorption, which has an adsorption energy of 4.50 kcal mol^{-1}. Due to two different types of Fe sites on the surface model, the most stable configuration for a full coverage of water molecules on the surface is when 4 water molecules bond to the iron atoms on the surface and other 4 molecules make hydrogen bonds with the adsorbed molecules. In this case the adsorption energy per water molecule is similar to the energy of a single molecule (-11.45 kcal mol^{-1}).

The adsorption of one oxygen molecule is also favorable with high energy, especially when it is dissociative (-59.41 kcal mol^{-1}). In the last case the oxygen atoms bond to Fe and As atoms of the surface in a 3 member ring. The effect of the co-adsorption of water and oxygen on the surface has been investigated and will be discussed in detail.

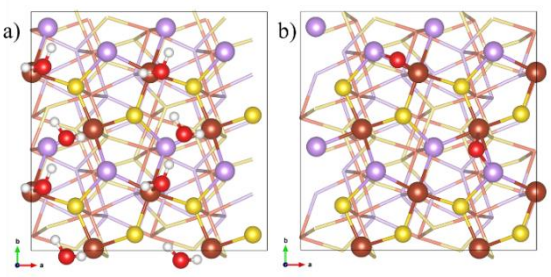

Figure 1. Adsorption on arsenopyrite (001) surface: a) water molecules, b) one dissociated oxygen molecule.

CONCLUSIONS

The adsorption of water and oxygen molecules on arsenopyrite surface was investigated using DFT/plane waves method. Water adsorbs molecularly up to 4 molecules to the surface and oxygen is strongly adsorbed.

ACKNOWLEDGMENTS

The authors are grateful for the support given from the CNPq, CAPES, FAPEMIG, INCT-Acqua, and the European Commission FP7-PEOPLE-2011-IRSES TEMM1P, GA 295172.

[1] C. L. Corkhill and D. J. Vaughan, Applied Geochemistry, 24, 2342, (2009).
[2] J. C. M. Silva, H. A. De Abreu, and H. A. Duarte, RSC Adv., 5, 2013, (2015).