The Effect of Microorganisms on the Surface Properties of Chalcopyrite

by

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Declaration

I declare that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university. To the best of my knowledge this thesis does not contain materials previously published or written by another person except where due reference is made in the text.

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Yi Yang

List of Publications

The following publications or manuscripts have arisen from work completed by the candidate for the present thesis.

Yang, Y., Liu, W., Chen, M., 2013. A copper and iron K-edge XANES study on chalcopyrite leached by mesophiles and moderate thermophiles. Minerals Engineering 48, 31-35.

Yang, Y., Harmer, S., Chen, M., 2014. Synchrotron X-ray photoelectron spectroscopic study of the chalcopyrite leached by moderate thermophiles and mesophiles. Minerals Engineering, 69, 185-195.

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Abstract

To understand the chalcopyrite dissolution and passivation mechanism during bioleaching, the leaching kinetics, surface species, mineralogy and bacteria-mineral interaction under different conditions (temperature, Eh, pyrite, Ag^+ and bacteria species) have been investigated. X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), Powder X-ray diffraction (XRD), Raman spectroscopy, X-ray fluorescence microscopy (XFM) and Electron backscatter diffraction (EBSD) have been applied in this study.

The results indicate thermophiles significantly enhanced the leaching efficiency, which was mostly caused by the increased abiotic reaction rate. Cu K-edge XANES analysis indicated the formation of CuS_n-like species in the early stages of leaching. XPS results show a sulfur-rich layer developed with time which is likely to be the rate limiting factor of the surface reaction. There is no significant difference on surface sulfur speciation between the chalcopyrite bioleached at 48 or 30 ^{o}C.

The electrochemical studies show that there was an activated region in the middle of two passive regions for chalcopyrite dissolution. In the active region, between 550 to 630 mV (vs. Ag/AgCl), S_n^{2-}/S^0, S_2^{2-} species and covellite were found by XPS and Raman. XPS study suggested a thin sulfur rich layer formed in the first passive region (530 mV). At 650 mV, S_2^{2-} species and covellite started to dissolve, leaving a highly metal deficient polysulfide layer.

Bacterial concentration at the mineral surfaces increased to about 5-7% coverage in 24 hrs. Raman spectroscopy showed the presence of organic species in the colourful film covered areas, which confirmed the formation of biofilm. From EBSD and optical images analysis, no significant difference in selectivity of bacterial attachment was found on crystal orientation of chalcopyrite.

Low Eh (350-480 mV vs. Ag/AgCl) significantly promoted the chalcopyrite (bio)leaching. The leaching results and quantitative XRD and XANES analysis show jarosite and elemental sulfur did not primarily account for the passivation of chalcopyrite. Secondary mineral covellite was detected in chalcopyrite dissolution.

Chalcopyrite leaching was significantly enhanced by pyrite addition. Chalcopyrite was selctively leached in chemical leaching as a result of galvanic effect. The favourable influence of galvanic effect and to chalcopyrite leaching is at least partially because of its function on Eh control. However, in bioleaching pyrite dissolution was significant which decreased the chalcopyrite leaching efficiency. μ-XRF and Raman studies suggest a sulfur-rich layer developed inhomogenously on mineral. The galvanic effect was also verified in column leaching of low grade chalcopyrite, which increased the yield of copper by a factor of about 3 in bioleaching.

The bioleaching effeciency of chalcopyrite was enhanced at low concentration of Ag^+ but decreased at high concentration of Ag^+. AgCuS species was found in the leaching residue. The solution pH of the case with high concentration of Ag^+ increased significantly in bioleaching but not in chemical leaching, which caused the formation of hematite.

Introduction

As high grade copper resources are depleted, the exploitation of low grade, complex copper ores becomes increasingly important. In many cases, those ores are not economically profitable to be processed by conventional pyrometallurgy technologies, while biohydrometallurgy provides an alternative (Brierley, 2010; Brierley, 2008). Biohydrometallurgy possesses several advantages over pyrometallurgy technology, for instance, it consumes less energy and is more environmental-friendly. Biohydrometallurgy has been successfully applied into commercial use for secondary copper sulfide recovery. However, for chalcopyrite, the most abundant copper sulfide mineral in terms of availability, its leaching rate in application is still not economically feasible. The dissolution mechanism of chalcopyrite in bioleaching process needs to be better understood in order to enhance the chalcopyrite leaching rate, in order to apply it in commercial scale.

So far, the dissolution mechanism of chalcopyrite is generally considered via polysulfide pathway as indirect mechanism, in which chalcopyrite is attacked and dissolved by the Fe^{3+} and H^+ generated by bacteria (Sand et al., 2001). In this process, various species containing Fe, Cu, and S are generated at the mineral surface (Rodríguez et al., 2003; Sandström et al., 2005; Sasaki et al, 2009). These surface chemical products carry information about the chalcopyrite decomposition mechanism, which is not clear in the presence of bacteria. Besides the oxidative decomposition described above, an alternative mechanism has been proposed by Hiroyoshi et al (2000), which considers the reduction of chalcopyrite to secondary minerals at low Eh values, and needs to be further understood.

The surface chemistry and the mineralogy changes during chalcopyrite bioleaching also prominently affect the kinetics of chalcopyrite bioleaching. Passivation is one of the major issues that retards the application of chalcopyrite bioleaching, and this is apparently related some of the leaching products. Unfortunately, the nature of the passivation layer is still in debate (Klauber, 2008; Liang et al., 2010; Rodríguez et al., 2003; Sandström et al., 2005; Sasaki et al, 2009). The surface chemical species are influenced by various conditions such as pH, Eh, temperature, impurities and bacteria species, and related to the kinetics variation

(Rodríguez et al., 2003; Vilcaez et al., 2008, 2009; Liang et al., 2010). Those connections are of vital importance in establishing an improved model of chalcopyrite leaching.

Although it is generally accepted there is no direct enzymatic attack from microorganisms to chalcopyrite, studies indicate the cell attachment and biofilm is important for mineral dissolution (Sand and Gehrke, 2006). The physical attachment of bacteria to mineral surfaces has also been proposed to accelerate leaching. The biofilm formation at mineral surfaces upon bacteria-mineral attachment provides a reaction space enriched in ferric ions. It is worthy to study the behaviour of the bacteria attachment and biofilm formation to determine how the microorganisms interact with chalcopyrite.

Therefore, this thesis aims to understand the surface species and properties changes in chalcopyrite bioleaching in response to the different environment conditions (temperature, Eh, pyrite, catalyst and bacteria species) as well as the interaction between bacteria and chalcopyrite, by which a deeper understanding to chalcopyrite dissolution mechanism and facilitates the establishment of a connection among the surface change, leaching kinetics, and environmental conditions, which further helps to establish a better control for chalcopyrite bioleaching. To achieve this purpose, the combination of solution and surface properties will be carried out. The surface characterization will be endeavoured to be carried out in inert atmosphere. With the combination of leaching study and electrochemical study, a range of state-of-art methods such as XPS, XAS, XRD and Raman and the morphologic techniques such as AFM, XFM played a key role in this project.