Minerals Engineering 23 (2010) 928–936

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Synchrotron XPS, NEXAFS, and ToF-SIMS studies of solution exposed chalcopyrite and heterogeneous chalcopyrite with pyrite

Robert G. Acres, Sarah L. Harmer, David A. Beattie *

Ian Wark Research Institute, University of South Australia, ARC Special Research Centre for Particle and Material Interfaces, Mawson Lakes Campus, Mawson Lakes 5095, Australia

ARTICLE INFO

Article history:
Received 30 November 2009
Accepted 6 March 2010
Available online 1 April 2010

Keywords:
Sulfide ores
Leaching
Oxidation

ABSTRACT

The surface species present on two pure chalcopyrite samples (one with a smooth fracture surface; one with a rough fracture surface) and one heterogeneous sample containing both chalcopyrite and pyrite have been studied using synchrotron X-ray photoelectron spectroscopy (SXPS), near-edge X-ray Absorption Fluorescence Spectroscopy (NEXAFS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The measurements were performed for samples fractured in N_2 and for samples subsequently exposed to pH 1 HCl solution for 2 h. The comparison of freshly fractured and solution exposed mineral surfaces has allowed for the investigation of the role of other mineral phases on the development of chalcopyrite surface species, and the role of chalcopyrite grain size on surface species development. Analysis of the chalcopyrite region of each sample indicates that increased surface roughness and the presence of pyrite in intimate contact with chalcopyrite increases the formation of surface sulfur species that are implicated in the formation of passivating layers on leached chalcopyrite surfaces. ToF-SIMS analysis of the chalcopyrite and pyrite regions of the heterogeneous sample support the conclusions obtained from the synchrotron surface analysis experiments.

1. Introduction

Chalcopyrite ($CuFeS_2$) is a widely occurring copper sulfide mineral and a major source of industrial copper. In order to separate chalcopyrite from gangue minerals it is typically processed by froth flotation at alkaline pH, followed by pyrometallurgical treatment to extract copper from the mineral. Oxidative acid leaching to extract copper from chalcopyrite is being increasingly studied as a viable alternative to pyrometallurgy for low grade copper ores, but the dissolution rate of copper using this method is inhibited by the formation of a passivating layer at the surface of chalcopyrite which retards ion and electron transport (Parker et al., 1981). Chalcopyrite oxidation involves diffusion and dissolution of metal ions, preferentially iron, from the bulk resulting in metal deficient, polysulfide surface and near surface layer as observed in air, alkaline and acidic conditions in an X-ray photoelectron spectroscopy (XPS) study by Buckley and Woods (1984). A metal deficient sulfide (i.e. polysulfide) has been proposed as the passivating layer responsible for inhibiting copper recovery in chalcopyrite leaching (Hackl et al., 1995; Mikhlin et al., 2004; Parker et al., 1981) and a three step pathway has been proposed by which the dissolution of metal ions from chalcopyrite results in polysulfide formation in the surface and near surface region (Harmer et al., 2006).

How a chalcopyrite surface changes during processing is critical to the outcome of that processing and many factors may influence the evolution of surface layers. The majority of studies into chalcopyrite surface evolution look at either pure minerals or samples of real ore. Such studies have shown that impurity phases influence chalcopyrite oxidation and processing. Despite the importance of impurity phases to surface layer evolution, and by extension to mineral processing, there are few studies dealing with different mineral phases that are locked in intimate contact and how such composite particles alter surface behaviour when subjected to processing related conditions. Galvanic interaction is one process by which one mineral phase may alter another. Since metal sulfide minerals are semiconductors to varying degrees a galvanic cell is created when two sulfides are in intimate contact in solution, the magnitude of this interaction being determined by each mineral's rest potential (Holmes and Crundwell, 1995; Yelloji Rao and Natarajan, 1989). As a result of galvanic interactions the oxidation rates of both minerals in the galvanic cell can be significantly altered (Al-Harahsheh et al., 2006; Ekmekçi and Demirel, 1997; Qing You et al., 2007; Yelloji Rao and Natarajan, 1989).

Pyrite (FeS_2) is the most common sulfide mineral and is often associated with chalcopyrite. The presence of pyrite locked with chalcopyrite has been shown to increase the oxidation and leach rates of chalcopyrite due to galvanic interactions (Al-Harahsheh et al., 2006; Liu et al., 2008) due to the higher rest potential of pyrite (Ralston, 1991). In fact, chalcopyrite is preferentially oxidised

---

* Corresponding author. Tel.: +61 8 83023676; fax: +61 8 83023683.
E-mail address: David.Beattie@unisa.edu.au (D.A. Beattie).

0892-6875/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.mineng.2010.03.007

while pyrite is protected from oxidation (Qing You et al., 2007) and pyrite has even been used as an additive to increase chalcopyrite leaching (Dixon et al., 2008). Ekmekçi and Demirel (1997) studied mixtures of chalcopyrite and pyrite using cyclic voltammetry and microflotation to study the effect galvanic interactions between the two minerals had on their flotation response. It was found that when the two minerals were present together the flotation of both minerals was affected and the relative magnitude of each mineral in the mixture determined the extent of the galvanic influence. Dutrizac and MacDonald (1989) leached sintered discs of synthetic chalcopyrite in binary mixture with other sulfide minerals to study how the second phase affected the dissolution rate of chalcopyrite. When the second phase was pyrite there was an acceleration of chalcopyrite's dissolution rate which was attributed to galvanic corrosion. Galvanic interactions have also been shown to occur between minerals and grinding media with implications for flotation response (Huang et al., 2006; Peng et al., 2003).

The work presented in this manuscript attempts to underpin these bulk scale observations of galvanic interactions between chalcopyrite and pyrite during acid leaching with detailed surface spectroscopy and mass spectrometry measurements. Importantly, these experiments are performed using N_2 atmosphere fractured mineral samples of chalcopyrite and chalcopyrite with pyrite, analysed freshly fractured and then immediately after exposure to solution (solution exposure carried out in a N_2 atmosphere). This ensured that the relative concentrations of the surface species detected are as close as possible to those that will be present on these mineral surfaces under processing conditions. The data indicates that the presence of pyrite acted to enhance the formation of disulfides and polysulfides at the chalcopyrite surface under the leaching conditions investigated, indicating an enhanced leach rate.

2. Experimental

2.1. Materials

Pure chalcopyrite samples originated from Huanzala Mine, Huallanca District, Huanuco Department, Peru and were provided by the South Australian Museum, Adelaide (no catalogue number). Heterogeneous samples of chalcopyrite with pyrite were also provided by the South Australian Museum, Adelaide and originated from Geko Mine, Northern Territory, Australia (museum catalogue number G14939). A second pure chalcopyrite sample was obtained from Ward's Natural Sciences, originating from Durango, Mexico (Ward's catalogue number 46 E 0068). Ultrapure water was produced using a Barnstead NanoPure Diamond at 18.0 MΩ cm^{-1}. The leach solution was prepared using ultrapure water adjusted to pH 1 using 37% HCl.

2.2. Surface modification

Mineral surfaces were freshly fractured in a nitrogen atmosphere in a glove box attached to the introduction chamber of the vacuum system. Three representative fracture surfaces are pictured in Fig. 1. Fig. 1D shows a backscattered scanning electron micrograph from a polished cross section of the mixed region in the heterogeneous sample. After fracture the samples leached in pH 1 HCl for 2 h. The samples were rinsed in a clean solution of the same pH to stop solution species from drying down on the sample surface and contributing to surface chemical analysis. Excess rinse solution was removed from the samples using lint free laboratory tissues without touching the surface to be analysed. The samples were then introduced to the vacuum system without leaving the nitrogen atmosphere. Roughness values of fractured Durango, Peru and heterogeneous chalcopyrite were determined using a Handysurf E-35A profilometer (Accretech): Durango RMS = 5 ± 2 µm; Peru RMS = 1 ± 0.5 µm; Geko Mine CpPy RMS = 2 ± 0.5 µm.

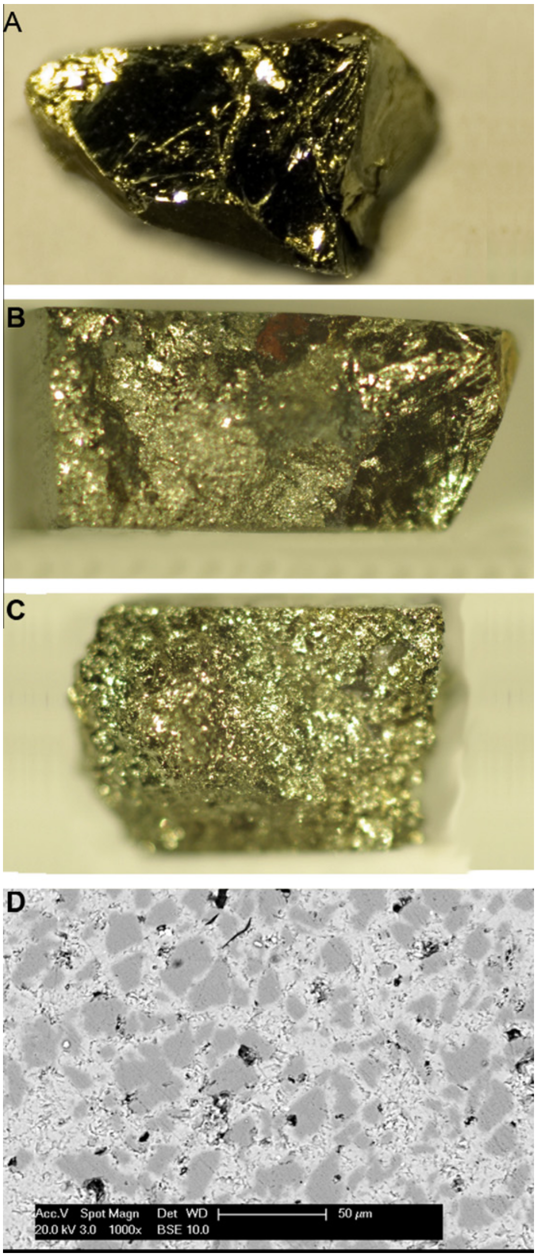

Fig. 1. (A) Homogeneous Peru chalcopyrite, (B) heterogeneous chalcopyrite/pyrite, (C) homogeneous Durango chalcopyrite and (D) backscattered scanning electron micrograph of a polished cross section from the mixed region on the heterogeneous sample. Lighter region is chalcopyrite and the darker grey is pyrite. Collected at 20 kV accelerating voltage.

2.3. Synchrotron analysis

The major advantages of synchrotrons over conventional (laboratory based) sources are the brilliance of the light and the ability to provide a continuous spectrum of radiation from infrared up to hard X-rays. For XPS analysis the ability to tune energy allows surface sensitivity to be maximised because the inelastic mean free path (IMFP) of an electron is a function of its kinetic energy, with a minimum around ~50 eV (Seah, 1990). Synchrotron XPS (SXPS) was conducted using the Soft X-ray Spectroscopy beamline