



Interfacial reactions of chalcopyrite in ammonia–ammonium chloride solution



Xiao-ming HUA¹, Yong-fei ZHENG², Qian XU², Xiong-gang LU²,
Hong-wei CHENG², Xing-li ZOU², Qiu-shi SONG¹, Zhi-qiang NING¹

1. School of Metallurgy, Northeastern University, Shenyang 110004, China;

2. State Key Laboratory of Advanced Special Steel, Shanghai Key Laboratory of Advanced Ferrometallurgy,
School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

Received 20 November 2016; accepted 23 May 2017

Abstract: The interfacial reactions of chalcopyrite in ammonia–ammonium chloride solution were investigated. The chalcopyrite surface was examined by scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) techniques. It was found that interfacial passivation layers of chalcopyrite were formed from an iron oxide layer on top of a copper sulfide layer overlaying the bulk chalcopyrite, whereas $\text{CuFe}_{1-x}\text{S}_2$ or copper sulfides were formed via the preferential dissolution of Fe. The copper sulfide layer formed a new passivation layer, whereas the iron oxide layer peeled off spontaneously and partially from the chalcopyrite surface. The state of the copper sulfide layer was discussed after being deduced from the appearance of S^{2-} , S_2^{2-} , S_n^{2-} , S^0 and SO_4^{2-} . A mechanism for the oxidation and passivation of chalcopyrite under different pH values and redox potentials was proposed. Accordingly, a model of the interfacial reaction on the chalcopyrite surface was constructed using a three-step reaction pathway, which demonstrated the formation and transformation of passivation layers under the present experimental conditions.

Key words: chalcopyrite; interfacial reaction; ammonia; passivation layer; oxidation mechanisms

1 Introduction

Chalcopyrite is the most refractory and abundant source of copper [1]. Oxidation of chalcopyrite is an important research topic in environmental geochemistry, since it is one of the main copper minerals and significant accessory minerals in many igneous and sedimentary rocks [2,3]. A decline in copper grades has occurred in recent times, which is a future challenge to the copper industry [4]. An efficient hydrometallurgical process has thus far not been widely applied to the industry; neither has significant research been conducted for gaining a deeper understanding of the reaction mechanisms of low-grade and/or complex ores. However, hydrometallurgy provides numerous advantages for mineral processing. For example, a hydrometallurgical refining pathway enables selective dissolution and precipitation of elements in a desired form at a preferred stage of the process [5]. To ensure further industrial applications of chalcopyrite, a full understanding of the mechanism of its leaching process is necessary.

In a previous study on interfacial reactions, Fe

hydroxide/oxyhydroxide was detected in the first few atomic layers when fresh chalcopyrite was exposed to water [6]. Iron was leached out of the chalcopyrite structure, preferentially forming a layer of a metal-deficient phase [7]. An intermediate phase of $\text{Cu}_{n-1}\text{Fe}_{n-1}\text{S}_{2n}$ was considered to be the product [8]. The products Cu_5FeS_4 and Cu_2S were formed between the outer iron oxide layer and bulk chalcopyrite [9]. Furthermore, a passivation film of CuS_2 was formed on the surface at a low potential in alkaline solution by atmospheric and electrochemical methods [10]. Sulfur remained unoxidized as CuS_2 , with $\text{Fe}(\text{OH})_3$ and Fe_2O_3 , forming a film that retarded the oxidation. Furthermore, ferrous-promoted chalcopyrite leaching was assumed to be due to the formation of intermediate CuS_2 , which is more amenable to oxidation than chalcopyrite. It was proposed that some copper was leached into the solution, forming an altered layer of $\text{Cu}_{0.8}\text{S}_2$ in air-saturated ammonia solution [9]. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) observations revealed that in addition to Cu-rich sulfides and iron hydroxides, a CuS_n layer approximately 1 μm in thickness existed on a polished chalcopyrite surface [11].

A previously developed model [12] predicted that the formation of Cu_2S and chalcopyrite leaching occurred when the redox potential of the solution was below a critical potential, due to the function of the ferrous and cupric ion concentrations. CuS_2 first converted to CuS , after which it formed a group of secondary covellite phases with stoichiometries between $\text{Cu}_{1.6}\text{S}$ and $\text{Cu}_{1.1}\text{S}$ [13]. CuS and CuS_2 appeared to be the two main Cu sulfides, owing to iron depletion from the subsurface area [14]. In another study, the absolute energies of calculated and experimental Cu L-edge spectra were closely aligned for both Cu/Fe sulfides and CuS_2 , but not for Cu_2S and CuS . Moreover, a solid product with a stoichiometry of $\text{Cu}_{0.75}\text{S}_2$ was formed after Fe^{2+} and Cu^{2+} were dissolved from the chalcopyrite structure at a mass ratio of 4:1 [15]. The thickness of the formed layer was about 3 nm, and it was composed of CuS and other S compounds.

Other analytical studies of oxidized or leached chalcopyrite suggest that a formed S^0 layer may also act as a diffusion barrier to the transport of ions and electrons in the absence of either bacteria or electrochemical inducement, thereby dismissing the possibility of S_n^{2-} formation and claiming that only the sulfur species S^{2-} , S_2^{2-} , S^0 and S_4^{2-} were detectable on the leached CuFeS_2 surface [16]. Evidence of the formation of a copper-rich sulfide with a composition of either Cu_5FeS_4 or Cu_2S was found [17]. When the chalcopyrite surface was exposed to air, Cu and S components could not be examined because of the formation of an Fe oxide layer having a thickness of between 20 and 40 nm.

The passivation layer and intermediate compounds vary with the physicochemical conditions, so does the dissolution process [18]. As a result, there is no real consensus from the results of previous studies regarding the intermediary products during the oxidation process of chalcopyrite. This paper presents optical microscopy (OM) images, XPS investigation results, and scanning electron microscopy (SEM) images of the leaching-product layer of chalcopyrite, which demonstrate the occurrence of a mild interfacial reaction in ammonia–ammonium chloride solution. The aim of this study is to provide a deeper understanding of alkaline leaching theory in terms of the formation of layers and the interfacial reactions on the chalcopyrite surface, especially the complex Cu sulfide under-layer, and to provide a model of the interfacial reaction by using a three-step reaction pathway.

2 Experimental

2.1 Materials and methods

The raw ore was extracted from a mine in Sinkiang,

China. The composition determined by X-ray fluorescence (XRF, Shimadzu, XRF–1800) spectrometry analysis was as follows: 3.6524% Cu, 2.5450% Ni, 39.5300% Fe, 26.1787% S, 6.2071% Si, and 2.3080% Mg (mass fraction). No concentrate was used in the XRF or X-ray diffraction (XRD, Rigaku, D/Max–2550) analyses. Samples for OM measurements were chosen carefully so as to be devoid of gangue, and those for leaching experiments were carefully selected such that the chalcopyrite content was at least 80% (mass fraction). To focus on the mechanism of the leaching process of one phase, samples with high purity of chalcopyrite were selected because this would ensure reduced interference from other ores during the leaching experiments. All samples were mounted in epoxy resin and polished with 2.5 μm diamond abrasive and finally dispersed in deionized water. The mounted and polished samples were rinsed with deionized water/ethanol and dried after being leached in ammonia–ammonium chloride solution (1 mol/L $\text{NH}_3\cdot\text{H}_2\text{O}$ with 2 mol/L NH_4Cl) at 25 °C.

2.2 Characterization

The interfacial reaction surface of the leached sample was observed by OM (Leica, DM4000M). The surface of each sample was rinsed with deionized water/ethanol and dried after being leached for the scheduled time (0–100 h). The leaching layer was examined by SEM (JEOL, JSM–6700F) and energy-dispersive X-ray spectrometry (EDS, Oxford INCA EDS system), which were used to distinguish the different mineral phases and to analyze the surface changes. The surface of the sample was coated with platinum before the measurements. An XPS measurement (Fisher Scientific, ESCALAB) was performed on the interfacial reaction surface of chalcopyrite on the cubic sample by adopting a monochromatic Al K_α X-ray source. All core-level spectra were referenced to the C 1s neutral carbon peak at 284.8 eV. The spot size was 400–600 μm , which almost entirely covered the area of the chalcopyrite surface.

3 Results and discussion

3.1 Mineral composition

The crude ore belonged to a low-grade copper–nickel mineral whose chemical analysis data are discussed in Section 2. According to the XRD pattern of the ore shown in Fig. 1, chalcopyrite, pentlandite, and pyrrhotite were the main sulfidic mineral phases associated with magnetite and other gangue.

Figure 2(a) shows an optical microscope photograph of the surface of the polished cubic ore that was carefully chosen so as to be devoid of gangue. The

Download English Version:

<https://daneshyari.com/en/article/8011699>

Download Persian Version:

<https://daneshyari.com/article/8011699>

[Daneshyari.com](https://daneshyari.com)