

# Chalcopyrite leaching at moderate temperature and ambient pressure in the presence of nanosize silica

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## Abstract

Leaching of chalcopyrite occurs at modest temperature (less than 100 °C) and atmospheric pressure when nanosize silica is added to the system. Important parameters in the system are chalcopyrite particle size, oxidant type and concentration, nanosilica concentration, pulp density and temperature. Electron micrographs and EDX spectra are presented showing the chalcopyrite surface covered with sulfur after leaching in the absence of nanosilica whereas the chalcopyrite surface is covered with nanosilica (with little sulfur) after leaching in the presence of nanosize silica.

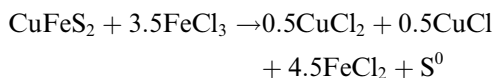
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*Keywords:* Chalcopyrite; Leaching; Nanosize silica; Ferric chloride; Ferric sulphate; Hydrogen peroxide

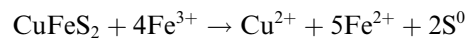
## 1. Introduction

Chalcopyrite (CuFeS<sub>2</sub>) is the most abundant and important source of copper metal available in the earth's crust. Over the years considerable research has been devoted to developing hydrometallurgical processes for leaching copper sulfide concentrates, especially chalcopyrite, at moderate temperature and pressure. Impetus for this research has been the desire for an economical alternative to smelting with its attendant generation of sulfur dioxide.

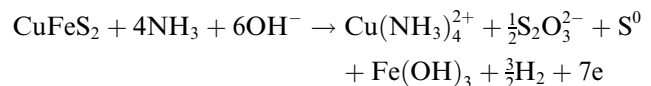
Commonly-used oxidants for the leaching of chalcopyrite are ferric chloride and ferric sulfate in an acidic medium. The ferric chloride leaching reaction can be written as (Dutrizac, 1978)



In sulfuric acid solutions containing ferric sulfate, the reaction is (Mateos et al., 1987)



In ammoniacal solution the reaction is seen to produce thiosulfate and elemental sulfur (Reilly and Scott, 1984)



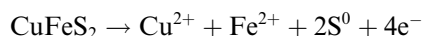
The sulfur layer that forms on the surface of the chalcopyrite in the case of ferric sulfate and ammonia leaching is passivating and highly protective. Hackl et al. (1995) suggest that this layer is comprised of copper polysulfide, CuS<sub>n</sub>. XPS analysis conducted by Balaz et al. (1996) revealed the existence of sulfur in three chemical forms, S<sup>2-</sup>, S<sup>0</sup> and S<sup>6+</sup>, when experiments were performed under combined bacterial and chemical leaching. Other investigators, such as Antonijevic et al. (1994), suggest the sulfur to be elemental in nature. Biegler and Swift (1979) observed the properties of sulfur to vary with experimental conditions. When

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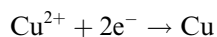
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standing over a period of days, sulfur lightened in color due to the transformation to the yellow rhombic form. As can be noted, there is no real consensus among investigators as to the nature of the sulfur associated with the passive layer that is formed during chalcopyrite leaching. Nevertheless, it has been established that the decreased leaching of chalcopyrite is due to the passive sulfur/polysulfide layer formation.

Use of high oxidation potential offers a possibility of dissolving chalcopyrite. Chalcopyrite can be made the anode in an aqueous electrolyte in conjunction with a counter electrode. The anodic dissolution reaction can be written as (Ilingovan et al., 1975)



and the corresponding cathodic reaction is



To increase recovery, investigators have tried a number of methods to obviate the formation of the layer of elemental sulfur/polysulfide. One of the most successful techniques was developed by Miller and Portillo (1979) using silver catalysis. Recovery was almost 100%, but the economics of using silver to extract copper has precluded its use. Ozone oxidation was tried by Havlik and Skrobjan (1990). This approach, too, has not progressed beyond laboratory investigation.

Munoz et al. (1979) reduced the chalcopyrite particle size to 4  $\mu\text{m}$  and achieved about 60% recovery at 90 °C, 1200 rpm and 1.0 M sulfuric acid in 20 h of leaching. When the particle size was increased to 12  $\mu\text{m}$ , leaching had to be conducted for 100 h to achieve about the same recovery.

(King et al., 1993) have shown that pressure oxidation of chalcopyrite concentrate is a potentially viable process for the dissolution of copper. Personnel at Phelps Dodge Mining Company have recently developed commercially-viable autoclaving techniques at high temperature and pressure for dissolving finely-divided chalcopyrite (Marsden, 2003).

The development of a technique to leach chalcopyrite under modest temperature and pressure has been a goal of the copper industry for decades. It is the objective of this investigation to establish conditions under which chalcopyrite can be leached effectively at moderate temperature and pressure.

## 2. Experimental materials and procedures

Chalcopyrite ordered from Wards Earth Science and a chalcopyrite flotation concentrate were used in the study. Copper content of the mineral was 30.2% and that of the chalcopyrite concentrate was 28.0%.

With the exception of nanosize silica which was a commercial product, reagent-grade chemicals were used

in the study. The ferric chloride was anhydrous; the ferric sulfate was hydrated (average iron content, 22%). The hydrogen peroxide was added as a solution (30 wt%). De-ionized water was used.

Chalcopyrite samples were prepared by dry grinding with a mortar and pestle and sized by screening ( $-37 \mu$ ).

### 2.1. Leaching of chalcopyrite

Leaching experiments were conducted with 1.25 and 5.0 g/L chalcopyrite samples in acidic medium in the presence of specific additions of leaching reagents for various lengths of time in a constant temperature bath. After leaching, solid/liquid separation was effected with an ultracentrifuge, and the solution was analyzed for copper content by atomic absorption spectroscopy.

## 3. Experimental results

### 3.1. Leaching

In the early part of this work, the electrochemistry of chalcopyrite leaching was investigated. Three electrodes of chalcopyrite were prepared, and the impedance of each electrode was measured in an open circuit potential. With two of the chalcopyrite samples, the impedance was noted to increase with time, while the third showed no change in impedance. In examining the third sample of chalcopyrite with an optical microscope, the sample was observed to contain veinlets of microcrystalline silica. In adding silicic acid and fluosilicic acid to the other two anodes, significant dissolution was noted. Nanosize silica was also added, and similar results were obtained.

The first series of experiments involved leaching of chalcopyrite in acidic medium with no added oxidant. Experimental conditions were: 5 g/L chalcopyrite concentrate ( $-37 \mu$ ), 200 ml 0.5 N  $\text{H}_2\text{SO}_4$ , 75 °C, and 24 h leaching time. As anticipated, only nominal dissolution of chalcopyrite (8.8%) was obtained under these conditions.

The effect of nanosize silica addition to these systems with ferric chloride as oxidant is given in Fig. 1. It can be noted that the extent of dissolution was increased with increased additions of nanosilica (50 nm in size). After 24 h of leaching in the absence of nanosilica, about 35% of the chalcopyrite concentrate was dissolved. In the presence of 17.5 g/L nanosilica, about 60% of the concentrate was dissolved.

Experiments were also conducted for longer leaching times. As shown in Fig. 2, after 72 h of leaching, about 70% of the chalcopyrite concentrate was dissolved in the presence of 40 g/L  $\text{FeCl}_3$ , while about 85% of the concentrate was dissolved in the presence of nanosize silica and the same oxidant concentration.

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