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MECHANOCHEMICAL LEACHING OF CHALCOPYRITE IN LOW MOISTURE CONDITIONS

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ABSTRACT - Copper concentrates represent 80% of the world's copper production. The main processing routes for copper extraction are pyrometallurgical via smelting or hydrometallurgical using moderate to high temperatures and/or high-pressure conditions, which affects the processing costs. An alternative presented in this work is the mechanochemical processing of concentrates, where the combined use of grinding and oxidizing reagents accelerates the leaching kinetics. Several mechanochemical tests were run in a laboratory mill using chalcopyrite in conjunction with various oxidants in low moisture conditions. The oxidants were ferric chloride ($FeCl_3$), ferric sulfate $Fe_2(SO_4)_3$, and ferric sulfate with silver added as a catalyst. The best results were for ferric chloride with 56% copper recovery after grinding for 15 min and ferric sulfate with added silver with 63% copper recovery after grinding for 25min.

Keywords: Mechanochemical Leaching, Mineral Processing, Grinding, Copper Extraction.

INTRODUCTION

Over the past decades, mechanochemical reactions have captured the attention of many researchers due to their versatility and simplicity in synthesizing new materials and processing raw materials [1]. This allows the synthesis and production of chemical compounds and materials that are difficult under normal conditions with respect to reaction time, reactivity, and consumption of reagents such as water, which is critical in the chemical and mining industry.

Copper concentrates represent approximately 80% of the world's copper production. Smelting, used to produce metallic copper and by-products such as industrial gases and sulfuric acid [2] generates significant amounts of pollution. For this reason, studies are focusing on the hydrometallurgical processing of copper concentrates. These processes typically use oxidants based on ferric ions which results in the formation of elemental sulfur and the release of (oxidized) copper into the

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solution for further extraction. This process is illustrated in equation (1) [3]:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \quad (1)$$

Equation (1) highlights that copper leaching is proportional to the concentration of ferric ion in the solution, though additional aspects need to be considered such as redox potential and temperature, both of which critically influence leaching kinetics. Redox potential, i.e. the electrochemical couple $[Fe^{3+}]/[Fe^{2+}]$, given by the anodic reaction (2):

$$4Fe^{3+} + 4e^- \rightarrow 4Fe^{2+} \quad (2)$$

controls the oxidative potential of solution, which impacts the leaching kinetics [4].

Chalcopyrite is a mixed n-p semiconductor with a low electrical conductivity (29 S/cm) [5]; this results in inefficient electron transfer between chalcopyrite and ferric ions. Additionally, during leaching at atmospheric pressure and low to medium temperatures a passivating layer of elemental sulfur is formed. This coating is detrimental to the leaching process as it blocks ferric ions accessing the chalcopyrite and minimises the mass transfer of copper [6].

Grinding, while leaching, aids in removing the sulfur passivating layer on the surface of the chalcopyrite, allowing ferric ions to continue to interact with the mineral. This has been demonstrated by the ROL (rapid oxidative leach) process developed by FLSmith™, with the oxidative leaching of chalcopyrite and other copper sulfides using a stirred reactor with grinding media [3]. In this process, by reducing the passive layer and particle size during the mechano-oxidative process, it is possible to recover up to 95% copper in 6 h processing time.

In this study, the mechanochemical leaching of chalcopyrite at room temperature is tested by grinding in a low moisture media. This enables a high concentration of oxidant to be present on the surface of the mineral, increasing the oxidation potential, while simultaneously cleaning the passivating layer. Overall, this accelerates the leaching process.

EXPERIMENTAL PART

Materials and characterisation methods

Chalcopyrite from Wallaroo (courtesy of the South Australian Museum) with a particle size D_{50} = 45 µm was used in this study. This mineral is composed of 34.24% Cu, 30.05% Fe and 30.74% S (measured by portable-XRF).

Chemicals used in the experiments were: ferric chloride hexahydrate $FeCl_3 \cdot 6H_2O$ (Sigma Aldrich, reagent grade), ferric sulfate hydrate, $Fe_2(SO_4)_3 \cdot xH_2O$ (Sigma Aldrich, reagent grade), ferrous sulfate heptahydrate $FeSO_4 \cdot 7H_2O$, (Sigma Aldrich, reagent grade), silver nitrate $AgNO_3$ (Sigma Aldrich, reagent grade), cupric chloride dihydrate, $CuCl_2 \cdot 2H_2O$, (Sigma Aldrich, reagent grade), cupric sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$ (CSA Scientific, Australia, reagent grade) and sulfuric acid (96%, Merck, analytical grade).

A ring mill 0.2 L (Rock labs, New Zealand) was used for the grinding tests (Figure 1). Tables 1-2 detail the grinding conditions and chemical mixtures that were used.

Table 1 Processing Conditions Used in Grinding Experiments

Processing Condition	Units	Value
Mill Volume	L	0.20
Grinding Material	--	WC/SiN_3
Grinding Speed	rpm	1000
Mill Power	kW	1.1
Moisture Content (Dry basis)	wt%	8 - 21

Table 2 Moisture Solutions Composition Used in Grinding Experiments

Experiment	Chalc., g	Ox., g	H_2SO_4, g	Moist. Sol., g	Added Liquid Composition, g/L				
					Cu^{2+}	Fe^{2+}	Fe^{3+}	H_2SO_4	Ag^+
$FeCl_3$	3	13	0.17	1.29	2	1	3	5	---
$Fe_2(SO_4)_3$	3	6.5	0.11	2.02	2	1	3	5	---
$Fe_2(SO_4)_3$ & Ag^+	3	6.5	0.11	2.02	2	1	3	5	10

Figure 1 Grinding Equipment Used During the Experiments

The feed materials and leaching products were characterized by: (i) a laser diffraction particle sizer, Malvern Panalytical, model Mastersizer 2000, UK, was used to measure the particle size distribution. (ii) Elemental analysis of leaching solutions was carried out using ICP-OES analyser, model: iCAPTM 7400 duo ICP–OES, Thermo Fisher, USA, using reference standards for different elements in a concentration between 0-100 mg/L respectively. (iii) The elemental composition of the feed material and leaching products were quantified using an Olympus portable X-ray fluorescence analyzer (model Vanta, USA). (iv) X-ray diffraction (XRD) was carried out using a Rigaku benchtop powder XRD, model Miniflex600, Japan, using 40 kV and 15 mA with a copper cathode as the radiation source.

Experimental procedure of mechanochemical trials

All the experiments were carried out at room temperature (15-20°C). For each grinding experiment, 3 g of chalcopyrite was used and variable compositions of oxidant (either $FeCl_3 \cdot 6H_2O$ (13 g) and $Fe_2(SO_4)_3 \cdot xH_2O$ (6.5 g)). The moisture content in the mill (between 8 wt% - 21 wt% water) was controlled using acidic solutions containing oxidizing reagents, with compositions specified in Table 2 for each experiment.

The materials were placed in the ring mill and were ground for 5, 15 and 25 min at 1000 rpm. After the experiment the solid was collected from the mill and washed with an acid solution containing 50 g/L H_2SO_4, for 15min and the slurry was filtered and solids were dried for 18h at 50°C in an oven (Qualtex, Thermstat, Australia). Then all samples were weighed using a scale (Mettler Toledo, model MS204S/02, Switzerland) and analysed. The washing solution products were collected, filtered using a 0.45µm pore size syringe filter (Pall corp., USA) and analysed with ICP-OES.

Leaching data processing methodology

The amount of copper extracted during each test was calculated based on the mass and grades of materials in the head, solutions, and residues collected at the specified time intervals. The leaching kinetics is defined by parameters such as the kinetic rate constant (k) and the ultimate recovery (RI). They were calculated using a first-order leaching kinetic model.

$$R = RI\,[1 - exp\,(-k\,(t)] \quad (4)$$

These parameters are obtained from the logarithmic-linear correlation given in equation (5).

$$\ln\left(\frac{RI - R}{RI}\right) = -kt \quad (5)$$

The slope of the linear regression gives the kinetic rate constant in equation (5).

RESULTS AND DISCUSSION

The amount of copper extracted was relatively similar for experiments using ferric chloride and ferric sulfate + silver (Figure 2a). However, in Figure 2b, kinetic analysis indicated a faster copper extraction for experiments using ferric chloride compared to ferric sulfate + silver. Experiments using only ferric sulfate had the slowest leaching kinetics with a low copper extraction of ~10% after 25 min grinding time. The standard deviation (σ_{Exp}) shown in the table inset is moderate, indicating a good reliability for these experiments based on ICP-OES analysis of solutions after leaching. Note that copper extraction and kinetics were based on ICP-OES analysis as pXRF results for solids had a high standard deviation.

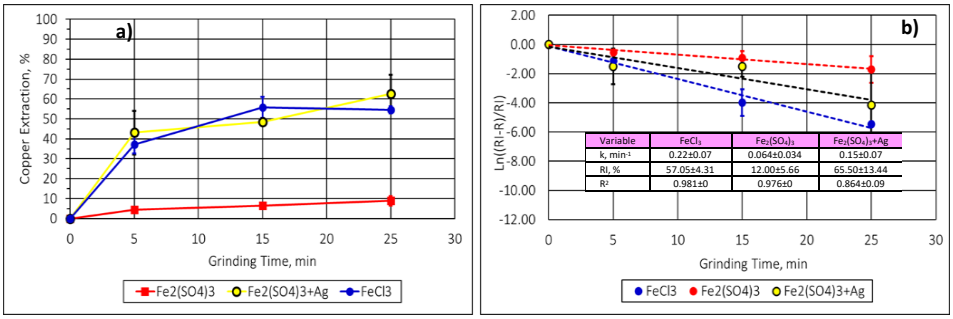

Figure 2 Copper Ext. versus Time (a) and Kinetic Plot (b) for All Experiments Tested.

The effect of the oxidant type and grinding time on the chalcopyrite leaching is shown by the intensity of XRD chalcopyrite peaks found for feed and leaching products. This is shown in Figure 3 (a to c).

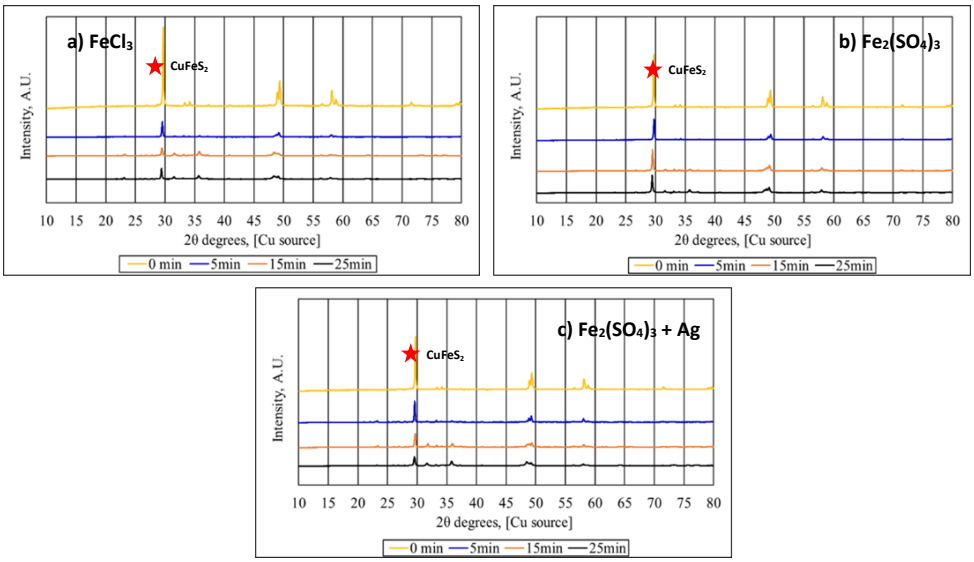

Figure 3 XRD Patterns versus Time for All Experiments Tested

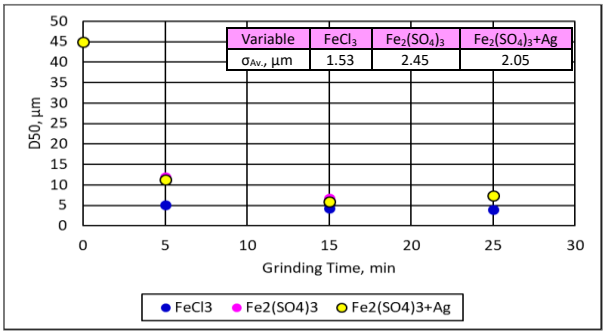

Figure 4 Particle Size D_{50} versus Grinding Time.

It is difficult to extract quantitative kinetics from XRD data due to the appearance of variable amounts of other phases (e.g. WC from the mill). However, the area of the dominant chalcopyrite peak at 2θ ~ 29° can be correlated with the reaction extent. These peak decreases rapidly for experiments using $FeCl_3$, and slowly for $Fe_2(SO_4)_3$. However, when silver is added into the solution, the copper extraction kinetics increases substantially, showing similar results to $FeCl_3$. This could be related with the generation of more soluble and conductive copper species such as CuS and geerite (Cu_8S_5) [7,8]. The effect of the mechanochemical reaction on the particle size (D_{50}) is analysed in Figure 4. Grinding has the largest first order impact, thus the three oxidants have a similar particle

size after grinding for 25 mins. However, there is a noticeable difference in particle size between chloride and sulfate oxidants after grinding for only 5 mins; this can be explained by the highly oxidizing nature of ferric chloride, along with the added benefit that chloride complexes well with copper (I) ions, promoting more reaction and leading to smaller average chalcopyrite particles.

CONCLUSIONS

In this study, the mechanochemical processing of chalcopyrite in low moisture conditions and using common reagents were carried out using a ring mill. The main conclusions of this work are the following:

1. Experiments showed that a high copper extraction can be achieved in a relatively short grinding time (15-25 min), under low moisture conditions.
2. Grinding experiments using ferric chloride shows the fastest leaching kinetics, followed by ferric sulfate + silver and ferric sulfate without silver.
3. Silver used in a high concentration (10 g/L) in the moisture solution has a big impact on the leaching kinetics, improving the oxidation in sulfate media.
4. Grinding experiments using ferric sulfate showed the slowest leaching kinetics. This could be related to the low stability of Cu(I) ions in sulfate media.

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