LEACHING OF CHALCOPYRITE CONCENTRATE IN HYDROGEN PEROXIDE SOLUTION

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Abstract: The leaching conditions of chalcopyrite (CuFeS$_2$) concentrate in a hydrogen peroxide medium were investigated by studying the effects of its leaching parameters, such as stirring speed, temperature, hydrogen peroxide concentration and the particle size of the concentrate on Cu extraction. It was found that stirring speed has no effect on the leaching. Copper extraction from chalcopyrite is directly proportional to hydrogen peroxide concentration, but the extraction decreases at temperatures above 60°C. The maximum copper extraction was obtained with the following conditions without stirring: 240 min of leaching time, 3.0 M hydrogen peroxide concentration, 40°C leaching temperature and 53-75 μm particle size fraction.

Keywords: chalcopyrite, dissolution, hydrogen peroxide, leaching, extraction

Introduction

Chalcopyrite (CuFeS$_2$) is the most important commercial copper sulphide mineral and is the principal source of commercially produced copper. It is generally associated with other sulphide minerals such as galena (PbS), sphalerite (ZnS) and pyrite (FeS$_2$). In conventional technology Cu is recovered from CuFeS$_2$ concentrates by crushing, beneficiation concentration, roasting and smelting techniques, followed by electrorefining and electrowinning operations (Habashi, 1978). Approximately 80-85% of the total world copper production is carried out through pyrometallurgical processes that produce SO$_2$ gas (Antonijević et al., 2004). Hydrometallurgical methods were developed opposed to the classic pyrometallurgical routes due to stringent regulations on SO$_2$ emission (Habashi, 1999; Antonijević et al., 2004). Although SO$_2$ gas is used in the production of sulphuric acid, it causes storage and transportation problems.

Chalcopyrite is the most abundant copper mineral and the most refractory and difficult to leach (Plumlee, 1999; Vanhanen, 1999). For that reason, numerous
leaching studies have been performed by many researchers using various oxidants in acidic media, such as cupric ion (Liddicoat and Dreisinger, 2007; Al-Harahsheh et al., 2008; Yevenes et al., 2010; Skrobian et al., 2005; Lundstrom et al., 2005; Tchoumou and Roynette, 2007), ferric ion (Al-Harahsheh et al., 2008; Akcil and Ciftci, 2002; Dutrizac, 1990; Hirato et al., 1987; Yoo et al., 2010; Cordoba et al., 2008; Nazari and Asselin, 2009), dichromate ion (Antonijevic et al., 1994; Aydogan et al., 2006; Altundogan et al., 2004), nitrate ion (Antonijevic et al., 2004; Aydogan et al., 2006; Altundogan et al., 2004), nitrate ion (Antonijevic et al., 2004), hydrogen peroxide (Balaz and Briancin, 1990; Antonijevic et al., 2004; Mahajan et al., 2007; Turan and Altundogan, 2013), hypochlorite (Ikiz et al., 2006) and oxygen (Padilla et al., 2007; Puvvada and Murthy, 2000). Among these agents, hydrogen peroxide is a strong and environmentally safe oxidizing agent. It is reported that hydrogen peroxide produces no reaction products apart from water during the oxidation of sulphide minerals (Antonijevic et al., 2004). Oxidative dissolution of chalcopyrite in hydrogen peroxide solutions can be summarised as follows (Dold, 2005):

\[
2\text{CuFeS}_2 + 17/2\text{O}_2 + 5\text{H}_2\text{O} \leftrightarrow 2\text{Cu}^{2+} + 2\text{Fe(OH)}_3 + 4\text{SO}_4^{2-} + 4\text{H}^+. \quad (1)
\]

The reactions that take place in Cu extraction from chalcopyrite concentrate are (Habashi, 1999):

\[
2\text{CuFeS}_2 \leftrightarrow 2\text{Cu}^{2+} + 2\text{Fe}^{2+} + 4\text{S}^2- \quad (2)
\]

\[
\text{H}_2\text{O}_2 \leftrightarrow \text{H}_2\text{O} + 1/2\text{O}_2 \quad (3)
\]

\[
2\text{Fe}^{2+} + 1/2\text{O}_2 + 5\text{H}_2\text{O} \leftrightarrow 2\text{Fe(OH)}_3 + 4\text{H}^+ \quad (4)
\]

\[
4\text{S}^2- + 8\text{O}_2 \leftrightarrow 4\text{SO}_4^{2-}. \quad (5)
\]

Elemental sulphur is stable in an acid medium, but it oxidizes slowly in water at high temperatures (above 150°C) with oxygen pressure to form sulphuric acid (Habashi, 1999):

\[
\text{S} + 3/2\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4. \quad (6)
\]

The present paper, aims to investigate the effects of leaching parameters such as stirring speed, temperature, hydrogen peroxide concentration and particle size, on the dissolution of chalcopyrite in an oxidative medium (only with hydrogen peroxide solution). Copper ions were extracted selectively from chalcopyrite concentrate at atmospheric pressure and lower temperature with a high recovery. Generally, chalcopyrite leaching studies were carried out using a combination of different media. Mahajan et al. (2007) and Antonijevic et al. (2004) obtained copper extraction in a mixture of \text{H}_2\text{O}_2–\text{H}_2\text{SO}_4–\text{ethylene glycol} and a \text{H}_2\text{SO}_4–\text{H}_2\text{O}_2 medium, respectively.
Leaching of chalcopyrite concentrate in hydrogen peroxide solution

Material and methods

Material

Samples of the chalcopyrite concentrate were taken from the Menka Flotation Plant (Sivas, Turkey), where the CuFeS$_2$–PbS–ZnS complex ore is enriched. The particle size of the concentrate was ~212 μm. The concentrate was wet sieved to obtain 212×106, 106×75 and 75×53 particle size fractions. The chemical analysis of each size fraction is given in Table 1.

Table 1. Chemical analysis of chalcopyrite concentrate (wt.%)

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Zn (%)</th>
<th>Pb (%)</th>
<th>S (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>212×106</td>
<td>23.52</td>
<td>23.17</td>
<td>1.01</td>
<td>1.13</td>
<td>27.27</td>
<td>23.9</td>
</tr>
<tr>
<td>106×75</td>
<td>26.91</td>
<td>26.56</td>
<td>1.46</td>
<td>1.70</td>
<td>31.48</td>
<td>11.89</td>
</tr>
<tr>
<td>75×53</td>
<td>24.90</td>
<td>25.16</td>
<td>2.42</td>
<td>3.08</td>
<td>30.57</td>
<td>13.87</td>
</tr>
</tbody>
</table>

Experimental procedure

A Pyrex beaker of 1 dm$^3$ was used as a leaching reactor placed in a temperature-controlled water bath and closed with a rubber cover. Stirring was carried out by a Heidolph RZR 2021 model mechanic stirrer equipped with a Teflon-covered propeller. A 2 g/dm$^3$ chalcopyrite sample with a fraction size of 75×53 μm was used for all experiments. Then, the stirring speed was raised to 600 rpm, the temperature was varied in the range of 30–70 °C, the hydrogen peroxide concentration was in the range of 0.5–3.0 M and the particle size range was 212×106, 106×75 and 75×53 μm. The amount of Cu in the leaching solution was determined using a GBC SensAA model flame atomic absorption spectrometer (AAS). For this purpose, 1 cm$^3$ of leaching solution was withdrawn from the reactor at various time intervals and diluted with water to 100 cm$^3$ in a volumetric flask. Distilled water and reagent grade chemicals were used for all required solutions.

Results

Effect of stirring speed

The effect of stirring speed on the dissolution of chalcopyrite was investigated at different stirring speeds that ranged from 0 to 600 rpm in a 2.0 M H$_2$O$_2$ solution at 50 °C (Fig. 1). It can be seen from Fig. 1 that the Cu extraction was independent of the stirring speed. Thus, all subsequent experiments were carried out without stirring except for homogenizing the solution prior to the sampling for the Cu analysis.
Effect of temperature

The experiments were carried out in the 30–70°C temperature range in the solutions containing 2.0 M H₂O₂ (Fig. 2). It can be seen in Fig. 2 that the Cu extraction obtained in 90 min of leaching time reached above 80% at 40 °C. However, in the 90–240 min leaching time interval, Cu extraction reached almost stable values. In addition, it decreased with increasing temperature in the range of 50–70 °C compared to lower
temperatures. These findings suggest that the decomposition of hydrogen peroxide happens more readily at higher temperatures (Antonijevic et al., 1997; Mahajan et al., 2007). Antonijevic et al. (1997) reported that the accelerated decomposition of hydrogen peroxide was above 60 °C.

**Effect of H\textsubscript{2}O\textsubscript{2} concentration**

The experiments were carried out in solutions containing various H\textsubscript{2}O\textsubscript{2} concentrations at 40°C. The results are given in Fig. 3. Cu extraction increased with increasing H\textsubscript{2}O\textsubscript{2} concentration within a 240 min leaching time. However, in the 90-240 min leaching time interval, Cu extraction almost reached stable values for the solutions containing 2.0 and 3.0 M H\textsubscript{2}O\textsubscript{2}. In addition, the Cu extraction rate decreased for the solutions containing 0.5 and 1.0 M H\textsubscript{2}O\textsubscript{2}.

![Fig. 3. Effect of H\textsubscript{2}O\textsubscript{2} concentration on chalcopyrite dissolution. Conditions: 40 °C, 2 g/dm\textsuperscript{3} (75×53 µm) chalcopyrite concentrate, no stirring](image)

**Effect of particle size**

The experiments were carried out using three different particle size fractions in the solutions containing 3.0 M H\textsubscript{2}O\textsubscript{2} at 40°C. The results are given in Fig. 4. Cu extraction increased with decreasing particle size because of the increase in surface area at unit weight.

**Discussion**

According to the XRD analysis (Fig. 5), the chalcopyrite concentrate used in the leaching experiments contained mainly chalcopyrite and pyrite. After leaching, the
major mineral determined in the residue was chalcopyrite. Pyrite was almost absent. In addition, no elemental sulphur was detected, at least in its crystal form. In addition, elemental sulphur production was not observed during the leaching experiments. However, amorphous iron compounds were observed with an optical microscope (Fig. 6). In the leaching solutions, approximately 5% Fe extraction was achieved. Therefore, it was concluded that rather than the iron existing in the chalcopyrite, the iron in the pyrite is extracted. In order to confirm this, pyrite leaching experiments were performed under conditions identical to those of the chalcopyrite leaching experiment, and this phenomenon was supported by the XRD results (Fig. 7).

Fig. 4. Effect of particle size on chalcopyrite dissolution.
Conditions: 3.0 M H₂O₂, 40 °C, 2 g/dm³ (75×53 µm) chalcopyrite concentrate, no stirring

Fig. 5. XRD patterns for the chalcopyrite concentrate (SA1) and the residue obtained after the leaching (SA2)
Leaching of chalcopyrite concentrate in hydrogen peroxide solution

Fig. 6. Microscopic photograph of chalcopyrite concentrate after hydrogen peroxide leaching Conditions: 3.0 M H$_2$O$_2$, 40°C, 2 g/cm$^3$ (75x53 μm) chalcopyrite concentrate, no stirring

Fig. 7. XRD patterns for a pyrite concentrate before (SA3) and after (SA4) the leaching

During the leaching, a clear pH decrease was observed (Fig. 8) from the beginning of the experiment. Hence, it was concluded that the reaction produces acid in the solution. The dissolution of pyrite in hydrogen peroxide occurred in the reaction as follows:

$$\text{FeS}_2 + 7.5\text{H}_2\text{O}_2 \leftrightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{H}^{+} + 7\text{H}_2\text{O}. \quad (7)$$

The potential-pH diagram for sulphur is given in Fig. 9 (Habashi, 1999). Figure 9 shows that sulphate ions occurred in the oxidizing conditions achieved in this study. Besides, by adding BaCl$_2$ to the centrifuged leach solution, it was proved that sulphate ions existed in the leach solution, and white barium sulphate precipitate was observed.
Conclusions

In this study, the extraction of Cu from chalcopyrite concentrate in hydrogen peroxide solutions was studied. It was determined that the dissolution process was independent of the stirring. In general, the Cu extraction rate increased with increasing temperatures during the early times of the leaching period. However, it decreased prolonged periods of times, due to the decomposition of hydrogen peroxide at higher temperatures. Cu extraction increased with increasing H₂O₂ concentration in the 240 min leaching time. However, in the 90–240 min leaching time interval, it reached
stable values for the solutions containing 2.0 and 3.0 M H₂O₂, respectively. Cu extraction increased with decreasing particle size because of the increase in surface area at unit weight. Optimum leaching conditions of chalcopyrite concentrate in H₂O₂ solution were found as: H₂O₂ concentration: 3.0 M, leaching temperature: 40 °C, stirring speed: 0 rpm; particle size: 75×53 µm. Under these conditions, copper recovery may be as high as 99%. In the studied conditions, it was determined that Cu extraction from chalcopyrite concentrate is possible and iron ions dissolved from chalcopyrite and precipitated. In addition, the pyrite mineral that was present in the concentrate dissolved; thus, the XRD analyses supported these results.

References


