Copper Recovery from Silicate-Containing Low-Grade Copper Ore Using Flotation Followed by High-Pressure Oxidative Leaching

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Abstract
In this paper, we present the results for recovery of copper from silicate-containing low-grade copper ore using flotation followed by atmospheric and high-pressure oxidative leaching. The effects of various flotation parameters, such as flotation time, PAX dosage, slurry pH and air injection rate on beneficiation of copper from the low-grade copper ore were studied. The recovery of copper reached 93.1% and the grade of copper improved to 18.2 mass% from 0.4 mass% under collector-less optimum flotation conditions. The enrichment ratio of copper in the concentrate was 45. The copper concentrate obtained from flotation of the low-grade copper ore was treated by atmospheric leaching and high-pressure oxidative leaching processes. A maximum recovery (>93.0%) of copper was obtained by high-pressure oxidative leaching in the water, whereas the copper recovery was lower than 12% in the sulfuric acid solution under atmospheric leaching conditions. The copper concentration in a pregnant leach solution enriched up to 15.0 g/L under the optimized leaching conditions. The effect of impurity such as iron in the sample on the froth flotation and both leaching processes is also considered. A process flow for the recovery of copper from silicate-containing low-grade copper ores is proposed as a result of these studies.

Key words: Low-grade copper ore, Chalcopyrite, Flotation, High-pressure oxidative leaching

1. Introduction
Copper is one of the important non-ferrous metals which has a lot of commercial applications in a wide range of industries such as medicine, construction, machinery, electrical and electronics and telecommunication1. Chalcopyrite (CuFeS2) is the most abundant and the most refractory copper sulfide mineral which accounts for about 70% of the copper reserves in the world2. At present, a large portion of the copper is produced from chalcopyrite ore via flotation followed by the pyrometallurgical method3–5. Due to the long-term mining activity and economic growth of countries in the world, the reduction of copper grade and deple-
metallurgical route, particularly acid leaching, which suggests a viable alternative approach to extract copper from low-grade sulfide ores, complex ores and tailings\textsuperscript{11-14}. There are many studies related to the development of hydrometallurgical routes to extract copper from low-grade sulfide ores by atmospheric leaching and biological leaching processes\textsuperscript{15-18}. Authors have concluded that both direct atmospheric and biological leaching of copper from its ore are extremely slow due to the formation of an elemental sulfur passivating layer on the surface of unreacted particles\textsuperscript{3}. On the other hand, huge amounts of acid are required in the copper leaching from the low-grade copper ore, especially it contains large amounts of carbonates or siliceous gangue minerals as impurities which make difficulty on the separation process and produce many residues. Additionally, copper concentration in the leach liquor/pregnant leach solution (PLS) is much lower when acid leaching is applied for copper extraction from low-grade ores and it causes difficulty in subsequent processes such as solvent extraction (SX) and electrowinning (EW). Hence, it is essential to develop the hydrometallurgical processes for the extraction of copper from low-grade copper ores in combination with flotation which is widely used to beneficiate and selectively separate copper ores as a pre-treatment process for upgrading the copper grade and reducing the impurity content. However, low-grade copper ores cannot be economically beneficiated by the conventional flotation process due to the fine particle size distribution of the ores. Therefore, an efficient approach, which could give reasonably high copper recovery, low impurity content and low reagent consumption, has been attracting much attention from researchers in this field. For these reasons, this study aims to develop an efficient method for the recovery of copper from low-grade copper ore by flotation followed by high-pressure oxidative leaching processes, respectively. As a result of this study, an efficient method has been proposed to recover copper from a silicate-containing low-grade copper ore by flotation followed by high-pressure oxidative leaching.

2. Experimental

2.1 Sample

A silicate-containing low-grade copper ore from Chile was used in this study. The sample was firstly prepared by a jaw crusher (P-1, Fritsch Japan Co., Ltd) and a disc mill (P-13, Fritsch Japan Co., Ltd) followed by a Sieve Shaker (AS200 digit, Retsch Japan Co., Ltd) to a size fraction of under 160 μm. The average particle size of the sample was 27 μm (D\textsubscript{50}) which estimated by a wet type size distribution analyzer (Microtrac MT3300II). The chemical composition of the silicate-containing low-grade copper ore was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, SPS5510 SII Hitachi High-Tech Science Corporation, Chiba, Japan) and X-Ray Fluorescence Spectrometer (XRF, ZSX Primus II Rigaku). As shown in Table 1, the sample consists of 0.4 mass% copper (Cu), 4.6 mass% iron (Fe) and 38.3 mass% silicon (Si), and small amounts of a number of other elements, including aluminium (Al), calcium (Ca), potassium (K), magnesium (Mg) and sulfur (S). The mineral composition of the ore was identified by X-Ray Diffractometer (XRD, RINT-2200V Rigaku) and XRD pattern of the sample is shown in Fig. 1. The main mineralogical constituents of the sample are gypsum (CaSO\textsubscript{4}·2H\textsubscript{2}O), chlorite ((Mg, Fe)\textsubscript{6}Si\textsubscript{4}O\textsubscript{10}(OH)\textsubscript{8}) and quartz (SiO\textsubscript{2}).

2.2 Procedure

2.2.1 Flotation of silicate-containing low-grade copper ore sample

All the flotation tests were carried out using a laboratory mechanical flotation machine (237FL, Mekhanobr-teknika Corp.) equipped with a plastic flotation cell (500 mL) as shown in Fig. 2. The most common reagents for traditional copper flotation such as collector of potassium amyl xanthate (PAX, C\textsubscript{5}H\textsubscript{11}OCSSK), frother of methyl isobutyl carbinol (MIBC, C\textsubscript{6}H\textsubscript{14}OCSSK) and pH regulator of calcium hydroxide (Ca(OH)\textsubscript{2}) and sulfuric

<table>
<thead>
<tr>
<th>Al</th>
<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>K</th>
<th>Mg</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>1.4</td>
<td>0.4</td>
<td>4.6</td>
<td>1.3</td>
<td>2.7</td>
<td>38.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>

RESOURCES PROCESSING
acid (H$_2$SO$_4$) were used in this study. The silicate-containing low-grade copper ore samples were first introduced into the flotation cell with 500 mL water under constant stripping (1000 rpm) to prepare a slurry of 10% pulp density. pH of the slurry was then adjusted to target pH ranging from pH 4 to pH 10 using 1 M H$_2$SO$_4$ and 1 M Ca(OH)$_2$ solutions and conditioning continued for 5 min. After adjusted the pH of the slurry, appropriate amounts of PAX as a collector and MIBC as frother were added to the cell and stirring continued for 5 min. Then, a certain amount (0.8–1.7 L/min) of air was injected into the cell throughout the flotation. Froth layer at the top of the cell during the flotation was gathered in the collection chamber by an auto-scraper. The collected froth concentrate and tailing of flotation were dried at 70°C into an electric drying oven for 1 day and analyzed by ICP-OES, XRF and XRD. The yield (Y), enrichment ratio (I) and recovery (R) of each metal from the low-grade copper ore were evaluated by Eqs. (1)–(3).

\[
\text{Yield : } Y(\%) = \frac{C}{F} \times 100
\]  

(1)

\[
\text{Enrichment ratio : } I = \frac{c}{f}
\]  

(2)

\[
\text{Recovery : } R(\%) = \frac{c(f-t)}{f(c-t)} \times 100
\]  

(3)

Where Y is the yield, I is an enrichment ratio, and R is the recovery of each metal. F and C are the weight of the feed and concentrate, f, c, and t are the metals grade in feed, concentrate and tailing, respectively.

2.2.2 Atmospheric acid leaching of froth concentrate

Froth concentrate from the flotation of silicate-containing low-grade copper ore sample was dissolved in sulfuric acid (H$_2$SO$_4$) solution placed in a beaker. All experiments were carried out using various acid concentrations (0–10 M (mol/L)) at a fixed temperature (90°C), fixed leaching time (60 min) and adjusted stirring speed (700 rpm). After experiment, solid residue and pregnant leach solution (PLS) were separated by filtration. Concentrations of metals in PLS were measured by ICP-OES and the leaching rate of metals from the froth concentrate into the sulfuric acid solution was calculated by Eq. (4) as shown bellow.

\[
\text{Metal leaching rate : } R_M(\%) = \frac{C_L \cdot V_L}{C_F \cdot m_F} \times 100
\]  

(4)

Where $C_L$ and $C_F$ is the concentration of metal in PLS (mg/L) and feed (mg/kg), respectively. $V_L$ is the volume of PLS (L) and $m_F$ is the dry mass of the feed (kg).

2.2.3 High-pressure oxidative leaching of froth concentrate

High-pressure oxidative leaching experiments were conducted in an autoclave (Nitto Koastu, Japan) using the froth concentrate obtained from the flotation of the silicate-containing low-grade copper ore. The autoclave is equipped with 0.2 L of a Teflon vessel, inlet/discharge lines for oxygen and excess gasses, pressure and temperature sensors as well as an electrical heating system. A schematic illustration of the autoclave is shown in
Fig. 3 A 5 g sample of the froth concentrate was transferred into a vessel with 50 mL distilled water or sulfuric acid solution with concentration ranging from 0.5 to 1.0 M. The vessel containing slurry was placed into the autoclave and experimental parameters were set to their nominal values throughout the leaching experiments as follows: when temperature reached at desired value (100°C, 160°C, 170°C and 180°C), oxygen gas was injected to the slurry into the vessel with controlling the total pressure (0.8 MPa, 1.5 MPa, 2.0 MPa and 2.5 MPa), and allowed the oxidation reaction at varying times from 60 to 180 min. After the oxidation reaction is completed, turn off the oxygen gas supply followed by cooling down the slurry to below 50°C and purge the autoclave with excess oxygen gas and vapor through the discharge line. The oxidized slurry was filtrated to separate solid residue and pregnant leach solution and both phases were analyzed by using ICP-OES, XRF and XRD. The dissolution rate of each metal from the froth concentrate in distilled water and in H₂SO₄ solution under high-pressure oxidative leaching condition was calculated using Eq. (4).

3. Results and Discussion

3.1 Flotation of silicate-containing low-grade copper ore

3.1.1 Effect of flotation time

The effect of flotation time on the copper beneficiation and recovery from a silicate-containing low-grade copper ore was investigated by varying times from 5 to 20 min. Other conditions, namely pulp density, slurry pH, collector (PAX) dosage, frother (MIBC) dosage and air injection rate, were kept constant at 10%, pH of 8, 50 g/t-ore, 200 g/t-ore and 0.8 L/min. The experimental results presented in Fig. 4 and Table 2 showed that the grade, recovery and enrichment ratio of copper are increased with increasing of flotation time from 5 to 10 min. The maximum grade, recovery and enrichment ratio of copper from the low-grade copper ore were 7.1 mass%, 87.8% and 22.6 after 10 min of flotation. An increase in the flotation time further up to 20 min resulted in a 3.2% and 10.4 decreases in the copper grade and enrichment ratio, while the copper recovery did not change obviously. The yield of the low-grade ore sample is increased with increasing the flotation time while there is no change like other flotation results (Table 2). The increment of the yield may be related to the flotation of impurity minerals such as clay minerals and silicates present in a silicate-containing low-grade copper ore. As a result, flotation time was selected to be 10 min as an optimum condition for further flotation experiments.
3.1.2 Effect of PAX and its dosage

The flotation experiments were conducted under the fixed conditions as follows: pulp density of 10%, frother (MIBC) dosage of 200 g/t-ore, air injection rate of 0.8 L/min at natural pH (pH 8) and flotation time of 10 min when collector (PAX) dosage varied from 0 to 50 g/t-ore. The results of the flotation experiments shown in Fig. 5 indicated the maximum copper grade of 11.1 mass%, maximum copper enrichment ratio of 24.7 and copper recovery of 78.6% when performed the flotation without PAX. These findings are in good agreement with other published result\(^\text{19}\): low-grade ore i.e. chalcopyrite is floatable without a collector due to its self-induced/ collector-less flotation ability in the pulp potential ranges. Self-induced/collector-less flotation is an influential property of this type ore to promote the copper recovery and reduce the reagent consumption. With the increase of PAX dosage to a 50 g/t-ore, copper grade in the froth concentrate decreased to 6.4 mass% and copper recovery and yield increased to 90.5% and 5.5% (Fig. 5 and Table 3). It is expected that the availability of extra collector molecules in the feed enhances the hydrophobicity of particles promoting the bubble-particle attachment that represents an increase of yield\(^\text{20}\). The tendency of the grade of iron in concentrate and the recovery of iron from the low-grade copper ore were quite similar to the both of grade and recovery of copper.

3.1.3 Effect of slurry pH

The flotation tests were performed under varying slurry pH ranging from pH 4 to pH 10 when other fixed parameters were: pulp density of 10%, collector (PAX) dosage of 0 g/t-ore, frother (MIBC) dosage of 200 g/t-ore, air injecting rate of 0.8 L/min and flotation time of 10 min. 1 M \(\text{H}_2\text{SO}_4\) and 1 M \(\text{Ca(OH)}_2\) were used as a pH regulator. The results obtained were presented in Fig. 6 and Table 4, respectively. When the slurry pH increased from pH 4 to pH 10, the grade of copper reached to 16.7 mass% from 9.4 mass%, whereas the recovery of copper and yield were decreased to 74.7% and 2.3, from 83.1% and 3.9, respectively. The grade of iron decreased with increasing the pH of slurry from pH 4 to pH 6 and increased further with increasing the pH of the slurry. The results obtained are verified that high pH value of the slurry has a positive effect on copper beneficiation due to the depression effect of pyrite (FeS\(_2\)) and gangue minerals including...
silicate ($\text{SiO}_2$)$^{21-23}$. Result showed that collectorless flotation is possible to recover copper from the low-grade copper ore containing silicate.

### 3.1.4 Effect of air injection rate

The flotation experiments were carried out at air injection rates varied from 0.8 to 1.7 L/min, slurry pH: 10, PAX: 0 g/t-ore, flotation time: 10 min, pulp density: 10% and MIBC: 200 g/t-ore. The results of these flotation experiments were summarized in Fig. 7 and Table 5. The copper grade and enrichment ratio of copper decreased to 12.6 mass% from 16.7 mass% and to 31 from 42, whereas its recovery increased up to 91.0% from 74.7%, respectively, when the air injection rate is increased from 0.8 to 1.0 L/min. This result revealed that the formation of froth and its relatively faster flow as well as lightly loaded stabilized hydrophobic particles$^{24}$. However, the air injection rate increased further until 1.7 L/min, the copper grade and its enrichment ratio increased to 18.2 mass% and 45.5, while the recovery of copper did not change much (>93%) than that value with air injection of 1.0 L/min. It seems that this observation may be related to the greater froth depth and stability of bubbles formed through sufficient particle attachment.

### 3.1.5 The beneficiation of copper from the high-silicate containing low-copper grade ore under optimum flotation conditions

As a result of a batch flotation experiments described in Chapter 3.1.1–3.1.4, the optimum flotation conditions were determined and results are summarized in Table 6. Under the optimum flotation conditions, flotation experiments were performed and the results obtained are presented in Table 7. It was revealed that the grade of copper achieved 18.2% with enrichment ratio of 45.5 when the recovery of copper was 93.1%. The XRD patterns of silicate-containing low-grade copper ore and its froth concentrate obtained from flotation under the optimum condition are shown in Fig. 8. Main mineral constituents in the froth concentrate are chalcopyrite ($\text{CuFeS}_2$), quartz ($\text{SiO}_2$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), chlorite ($\text{Mg}_x\text{Fe}_{y}$(\text{Si, Al})$_z$(OH)$_{10}$), and pyrite ($\text{FeS}_2$). The peak of chalcopyrite ($\text{CuFeS}_2$) and pyrite ($\text{FeS}_2$) were not detected by XRD of silicate-containing low-grade copper ore because of their low-grade and detection limitation of the equipment.

The froth concentrate containing 18.2 mass% 

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**Table 5** Effect of air injection rate on copper enrichment ratio and yield

<table>
<thead>
<tr>
<th>Air injection rate, L/min</th>
<th>Cu enrichment ratio</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>41.79</td>
<td>2.04</td>
</tr>
<tr>
<td>1.0</td>
<td>31.38</td>
<td>2.13</td>
</tr>
<tr>
<td>1.3</td>
<td>34.63</td>
<td>2.33</td>
</tr>
<tr>
<td>1.7</td>
<td>45.51</td>
<td>1.52</td>
</tr>
</tbody>
</table>

**Table 6** The optimum conditions for recovery of copper from a silicate-containing low-grade copper ore

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
<th>Cu recovery, %</th>
<th>Cu grade, mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp density</td>
<td>10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAX dosage</td>
<td>0 g/t-ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIBC dosage</td>
<td>200 g/t-ore</td>
<td>93.1</td>
<td>18.2</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air injection rate</td>
<td>1.7 L/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flotation time</td>
<td>10 min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 7** Chemical compositions of silicate-containing low-grade copper ore and froth concentrate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grade, mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Initial sample grade</td>
<td>1.8</td>
</tr>
<tr>
<td>Froth concentrate</td>
<td>2.2</td>
</tr>
</tbody>
</table>

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**Fig. 7** The grade and recovery of copper and iron as a function of air injection. (Air injection rate: 0.8–1.7 L/min, slurry pH: 10, PAX: 0 g/t-ore, flotation time: 10 min, pulp density: 10% and MIBC: 200 g/t-ore)
Cu and 19.6 mass% Fe was further used for extraction of copper with distilled water and sulfuric acid solutions using atmospheric and high-pressure acid/oxidative leaching.

3.2 Atmospheric and high-pressure oxidative leaching of copper from the froth concentrate

3.2.1 Atmospheric acid leaching

Under the atmospheric oxidative condition, a sample of the froth concentrate was dissolved in various concentrations (0–12 M) of sulfuric acid (H₂SO₄) solutions at the temperature of 90°C, and agitation speed of 700 rpm for 1 hour. As shown in Fig. 9, the leaching efficiencies of copper and iron dissolution from the copper concentrate did not exceed 12% and 18% respectively with sulfuric acid solutions. The solid residue obtained from the atmospheric leaching with sulfuric acid was analyzed by SEM-EDS. It can be seen from Fig. 10 that the surface of minerals in the froth concentrate was coated by sulfur-passivating layer. For that reason, it could be concluded that some of the chalcopyrite (CuFeS₂) dissolved into the pregnant leach solution at an early stage and after that the formation of passivation layers of elemental sulfur (S⁰) on the chalcopyrite may impede the leaching kinetics of copper from its concentrate.

3.2.2 High-pressure oxidative leaching

3.2.2.1 Effect of total pressure

The effect of total pressure (oxygen and vapor pressure) on the copper and iron dissolution were conducted in the range of 0.8 (without oxygen supply)–2.5 MPa. The other conditions were fixed at a pulp density of 10%, leaching temperature of 170°C, leaching time of 60 min, agitation speed of 700 rpm and sulfuric acid concentration of 1 M. It can be seen from the results shown in Fig. 11 that both copper and iron dissolution depend significantly on the total pressure. The copper and iron leaching rate reached 52.2% and 40.7%, respectively at the total pressure of 1.5 MPa, whereas their rates were 7.8% and 5.5%, which is similar to that rates under atmospheric leaching condition (Fig. 9), when the total pressure was 0.8 MPa (without oxygen gas addition in
It was observed that as a result of oxygen gas supply, sulfide minerals entirely oxidized to sulfate under the high-pressure oxidation condition at 170°C promoting the dissolution of copper and resulted in the higher copper leaching rate. However, a further increase in the total pressure from 1.5 to 2.5 MPa does not produce a substantial increase in the dissolution rate of copper and iron. These results are in agreement with the observation made by some researchers they concluded that due to surface saturation by oxygen, leaching is not affected by oxygen partial pressure after a certain pressure. When the total pressure was 2.0 MPa, a maximum copper dissolution rate of 59.7% was achieved within 60 min leaching. Thus total pressure of 2.0 MPa was selected in subsequent experiments.

3.2.2.3 Effect of temperature

The influence of the temperature ranging between 100–180°C on the copper and iron leaching rate was studied under certain conditions while the sulfuric acid concentration of 1 M, pulp density of 10%, leaching time of 60 min, agitation speed of 700 rpm and a total pressure of 2.0 MPa. As shown in Fig. 12, the temperature has a large effect on the leaching of copper and iron. A linear relationship between temperature and copper leaching rate was found. With increasing the temperature from 100°C to 180°C, the copper leaching rate was raised from 17.7% to 61.1%. It suggested that the dissolution of copper from chalcopyrite (CuFeS₂) is a highly temperature-dependent process.

3.2.2.4 Effect of sulfuric acid concentration

To determine the efficiency of copper dissolution, the copper concentrate was leached with distilled water and different concentrations of sulfuric acid solutions ranging from 0.5 to 1.0 M. The leaching experiments were conducted under different leaching times from 0 to 180 min while other parameters like pulp density, total pressure in an autoclave, agitation speed and temperature were fixed at 10%, 2.0 MPa, 700 rpm and 180°C. The results of copper dissolution with distilled water and with different concentrations of sulfuric acid solutions at varying leaching times are shown in Fig. 13 (a). It is interesting that an excellent copper leaching rate (93.4%) achieved after 120 min and the maximum (98.3%) copper dissolution obtained after 180 min leaching with distilled water, while the iron dissolution did not exceed 5.4% (Fig. 13 (b)). The efficiency of copper dissolution decreased with increasing the sulfuric acid concentration and reached the minimum dissolution of 70.8% with 1.0 M H₂SO₄ solution under the leaching condition. It was observed that the sulfuric acid concentration gave an opposite effect on the dissolution of copper from the copper concentrate. On the contrary, the efficiency of iron dissolution from the concentrate increased with increasing the sulfuric acid concentration and the iron dissolution rate reached 67.7% and 70.0%

Fig. 11 The leaching efficiency of copper and iron as a function of total pressure. (Total pressure: 0.8 (without oxygen supply)–2.0 MPa, H₂SO₄ concentration: 1.0 M, leaching time: 60 min, pulp density: 10%, temperature: 170°C and agitation speed: 700 rpm)

Fig. 12 The leaching efficiency of copper and iron as a function of temperature. (Temperature: 100–180°C, H₂SO₄ concentration: 1.0 M, leaching time: 60 min, total pressure: 2.0 MPa, pulp density: 10%, and agitation speed: 700 rpm)
after 120 min and 180 min leaching, respectively, when sulfuric acid concentration was 1.0 M (Fig. 13 (b)). The reduction of copper dissolution from the concentrate in the sulfuric acid solution may be induced by the solubility of oxygen in sulfuric acid solution containing copper and iron sulfates and the salting-out effect of the sulfuric acid solution.26

It was observed that after high-pressure oxidative leaching with distilled water under the optimum condition, pH of slurry decreased up to pH of 1.47 while an initial slurry pH was 6.1. The major mineral phase in the solid residue is hematite (Fe₂O₃) as identified by XRD analysis (Fig. 14). When using 0.5 M and 1.0 M sulfuric acid solutions in the leaching, the initial pH values of slurries of pH 0.72 and pH 0.49 were increased to pH 0.9 and pH 0.8, respectively. The XRD patterns of solid residues from 0.5 M and 1.0 M sulfuric acid leaching showed the quartz, chalcopyrite and hydromion jarosite ((H₂O)Fe₃(SO₄)₂(OH)₆) peaks (Fig. 14). This result is consistent with previous data reported in the literature.27,28 It was seen that hematite is the favorite phase around pH 1.5 at 180°C and the major iron phase of the solid residue is transported to jarosite when decreasing the pH to 1 from 1.5. On the other hand, the complete copper dissolution (>98%) was obtained with water (0 M H₂SO₄), about 70% copper leaching rate was achieved with 0.5 and 1.0 M sulfuric acid conditions due to the stability areas of copper in an aqueous solution under the conditions was favorited as cupric ions (Cu²⁺).29 However, it is evident from the Figs. 13–14 that chalcopyrite was remained in the solid residues of the sulfuric acid leaching and confirmed the decrease of the efficiency of copper dissolution in the acid solution under the high-pressure oxidative conditions. As a result, it is concluded that the higher extraction (98.4%) of copper from the froth concentrate of a silicate-containing low-grade copper ore with water (without sulfuric acid) can be achieved by using high pressure oxidative leaching process.

3.2.2.4 Application of optimum high-pressure oxidative leaching for copper extraction

The results of numerical experiments as described above sections suggested that the optimum high-pressure oxidative leaching conditions...
for copper extraction from the froth concentrate were found to be as shown in Table 8. Under the optimum high-pressure oxidation conditions, 98.4% of copper was leached with distilled water and the obtained pregnant leach solution contained 15.0 g/L copper (Table 8).

The mechanism of copper dissolution from the froth concentrate, which contains chalcopyrite, can be described by Eq. (5). It means that sulfur in chalcopyrite entirely oxidized to sulfate under the high-pressure (2.0 MPa) oxidation condition at 180°C in the presence of oxygen gas, resulting an excellent copper dissolution (>90%).

$$2\text{CuFeS}_2 + 8.5\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{CuSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \quad (5)$$

It can be seen from Eq. (5) that the oxidation of chalcopyrite is an acid consuming reaction, and complete dissolution (>98%) of copper from the froth concentrate in distilled water was achieved under the high-pressure oxidative condition. It is obvious that pyrite in the froth concentrate can be a source of sulfuric acid as presented below:

$$2\text{FeS}_2 + 7.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 \quad (6)$$

Oxygen gas (O\text{3}) supply in the slurry promotes the oxidation of minerals such as pyrite and chalcopyrite and the generation of sulfuric acid which can dissolve copper efficiently from the concentrate under the high-pressure and high-temperature condition. Hence, it can be said that the presence of pyrite in the sample has a significant for the production of sulfuric acid and dissolution of copper from the sample.

Furthermore, XRD measurement confirmed the formation of hematite ($\text{Fe}_3\text{O}_4$) and hydronium jarosite ($((\text{H}_2\text{O})\text{Fe}_2(\text{SO}_4)_3(\text{OH})_6)$) in the solid residues after the high-pressure oxidative leaching with distilled water and with sulfuric acid solution due to undergo hydrolysis of ferric ions ($\text{Fe}^{3+}$) in aqueous solution (Fig. 14) by the following reactions (Eqs. 7 & 8).

$$\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \quad (7)$$

$$3\text{Fe}_2(\text{SO}_4)_3 + 14\text{H}_2\text{O} \rightarrow 2(\text{H}_2\text{O})\text{Fe}_2(\text{SO}_4)_3(\text{OH})_6 + 5\text{H}_2\text{SO}_4 \quad (8)$$

It is observed that the formation of hematite and jarosite by high-pressure oxidative leaching of the chalcopyrite with distilled water and sulfuric acid solution depends not only on the leaching medium, but also on the pH value of slurry.

Based on the experimental results, a flowchart is proposed for the recovery of copper from silica-containing low-grade copper ore, as seen in Fig. 15. The copper grade in the froth concentrate reached 18.1 mass% from 0.4 mass% under the optimum flotation conditions, when the recovery of copper was 93.1%. The vast majority of copper (>98.4% Cu) was leached from the froth concentrate in distilled water under the high-pressure oxidation leaching conditions after flotation of the silicate-containing low-grade copper ore. The concentration of copper in the pregnant leach solution from high-pressure oxidative leaching reached to 15.0 g/L. On the other hand, more than 98% of iron was removed from the copper concentrate by the high-pressure oxidation leaching process, and it precipitated as hematite in the solid residue. As a result, a selective and the highest copper recovery (>91%) was achieved by the combined process with flotation and high-pressure oxidation leaching.

### 4. Conclusions

This study focused on the development of a hydrometallurgical process for recovering copper from a silicate-containing low-grade copper ore by combined process of flotation and leaching. Experimental results obtained can be concluded as bellow.

(1) Flotation process: A collector-less flotation was suggested for beneficiation of copper from the silicate-containing low-grade copper ore due to its high self-induced ability under the flotation condition. The copper grade in the froth concentrate reached 18.1 mass% from 0.4 mass% with an enrichment ratio of 45 under the optimum flotation conditions, while the recovery of copper was 93.1%.

(2) Leaching process: Experimental results revealed that the copper dissolution from the froth concentrate did not exceed 11.9% under atmospheric leaching with sulfuric acid solution. However, about 98.4% of copper could be dissolved from the froth concentrate in dis-

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
<th>Cu leaching rate, %</th>
<th>Cu concentrate, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\text{2SO}_4 \text{4} concentration</td>
<td>0 M (Water)</td>
<td>98.4</td>
<td>15.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>180°C</td>
<td>98.4</td>
<td>15.0</td>
</tr>
<tr>
<td>Total pressure</td>
<td>2.0 MPa</td>
<td>98.4</td>
<td>15.0</td>
</tr>
<tr>
<td>Pulp density</td>
<td>10%</td>
<td>98.4</td>
<td>15.0</td>
</tr>
<tr>
<td>Leaching time</td>
<td>180 min</td>
<td>98.4</td>
<td>15.0</td>
</tr>
</tbody>
</table>
Copper Recovery from Silicate-Containing Low-Grade Copper Ore Using Flotation Followed by High-Pressure Oxidative Leaching

Puddled water by high-pressure oxidation leaching. The copper concentration in the pregnant leach solution reached to 15.0 g/L. Moreover, over 98% of iron in copper concentrate was removed and precipitated as hematite in the residue under the optimum conditions.

(3) The presence of pyrite (FeS₂) in the sample has a positive effect on copper leaching process, and it can be a source of sulfuric acid (H₂SO₄) production under the high-pressure oxidative leaching condition promoting the copper dissolution.

(4) It can be concluded that the leaching media, pressure (oxygen supply), temperature and acidity of the slurry are the important variables for the dissolution of copper, and the formation of hematite and jarosite throughout the copper leaching from chalcopyrite (silicate-containing low-grade copper ore) in the presence of aqueous solutions under high-pressure oxidative leaching conditions.

A selective (iron removal rate >98%) and efficient copper extraction (Cu leaching rate >98%) method is proposed for the recovery of copper (total Cu recovery >91%) from the silicate-containing low-grade copper ore using flotation followed by high-pressure oxidative leaching.

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References