INFLUENCE OF PYRITE CONTENT ON THE FLOTATION OF CHALCOPYRITE AFTER REGRINDING WITH ISAMILL

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ABSTRACT

In the flotation of copper ores several processing plants report that copper recovery is affected by the proportion and type of pyrite in the ore, with the effect becoming more intense when the feed ore particles are fine, i.e. in fine regrinding. In this work, a model mix mineral system consisting of chalcopyrite and pyrite with varying pyrite content (in the range 20-80 wt. %) was used to investigate the effect of pyrite content on the pulp chemistry and chalcopyrite recovery. Surface species responsible for the flotation performance of the various blends were quantified with X-ray photoelectron spectroscopy (XPS). Flotation tests showed that the flotation chemistry and recovery of chalcopyrite are affected by the proportion of pyrite present. Both chalcopyrite flotation recovery and grade decreased with increasing pyrite content. XPS results confirm that copper activation of pyrite increases with increasing pyrite content, reflecting the attenuation in chalcopyrite recovery.

INTRODUCTION

Copper exists in the earth crust as copper iron sulphide or copper sulphide minerals. Examples of such minerals include chalcopyrite (CuFeS₂), bornite (Cu₅Fe₄S₉), chalcocite (Cu₂S) and covellite (CuS). In recent time, it is very rare to find large copper mineral deposits with head grade averaging about 2% Cu (Davenport et al., 2002) due to the presence of other metal sulphides and non-sulphide gangue minerals such as pyrite (FeS₂), sphalerite, quartz, etc (Aplan and Chander, 1988; Kydros et al., 1994). Chalcopyrite, a major mineral for copper production, is not exceptional. It is often in association with iron sulphide minerals, particularly pyrite and minor amounts of sphalerite and molybdenite (Habashi, 1987; Wang, 2005). Recent studies indicate that the selective separation of chalcopyrite from pyrite is very difficult due to several interactions that occur at the mineral surfaces during the processes of grinding and conditioning (Fuerstenau, 1982; Finkelstein, 1997). Galvanic interactions occurring between pyrite and chalcopyrite surfaces during grinding and conditioning, prior to flotation, lead to chalcopyrite oxidation and copper activation of the former. This also results in the formation of hydrophilic surface coatings of iron hydroxide species that inhibit chalcopyrite flotation. Copper activation of pyrite increases collector adsorption onto pyrite surface, promoting its flotation which subsequently lowers the overall chalcopyrite recovery and grade (Xu et al., 1995; Peng et al., 2003). For improved mineral liberation due to changes in ore mineralogy in order to increase flotation recovery and grade of the final concentrate (Gaudin, 1939; Sutherland 1989), regrinding to very fine particle size is performed. However, Ye et al. (2010) showed that the surface chemistry of minerals which impacts on the optimum
mineral separation may change significantly after regrinding depending upon the type of mill and grinding media used. Similarly, reports from various processing plants show that chalcopyrite recovery after regrinding is affected by the proportion and type of pyrite in the ore, the effect becoming more intense when the feed ore particles are fine (Yong, personal communication).

In this study, a model mineral system comprising different proportions pyrite and chalcopyrite was studied to investigate the effect of pyrite content in chalcopyrite recovery, grade and selectivity after ore regrinding with an IsaMill. Surface species formed on the mineral surfaces before and after regrinding were determined using XPS spectroscopy.

**EXPERIMENTAL**

**Materials**

Chalcopyrite (Cp) and pyrite (Py) minerals of size fractions 2-400 µm and 2-600 µm obtained from Mannum minerals and a Peruvian mine, respectively, were used for this study. The chemical compositions of the two samples are reported in Table 1. Sodium isopropyl xanthate (SIPX) and Dowfroth 250 (polypropylene glycol, AR grade) were used as a collector and a frother, respectively. Analytical reagent grade lime was used throughout the whole experiment for pH regulation, unless otherwise stated.

Tab. 1: Chemical composition of chalcopyrite and pyrite samples used for the studies

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Zn</th>
<th>Fe</th>
<th>S</th>
<th>Ca</th>
<th>Cu</th>
<th>Si</th>
<th>Pb</th>
<th>Mn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>0.012</td>
<td>28.9</td>
<td>29.0</td>
<td>1.76</td>
<td>26.4</td>
<td>4.20</td>
<td>0.34</td>
<td>0.02</td>
<td>0.68</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.180</td>
<td>44.9</td>
<td>53.5</td>
<td>0.44</td>
<td>0.13</td>
<td>0.69</td>
<td>0.02</td>
<td>0.02</td>
<td>0.08</td>
</tr>
</tbody>
</table>

**Experimental procedures**

**Flotation**

A 200 g ore sample comprising different proportions of pyrite and chalcopyrite (20%, 50% and 80% Py) together with demineralised water and lime was milled in a Galigher Mill to \(d_{80}\) of 105 µm at pH 10 using stainless steel rods. The mill product was conditioned in a 1.5 L flotation cell (Agitair Model LA-500R) with xanthate collector (200 g/t SIPX) for 2 min and pH adjusted to 10.5 with lime. The conditioned pulp was reground to \(d_{80}\) of 20 µm in a 1 L IsaMill for 15 min. The mill discharge was then transferred back into the 1.5 L Agitair flotation cell and conditioned with 50 g/t of SIPX and frother (25 g/t Dowfroth 250) for 2 and 1 min, respectively, before flotation. A summary of the flotation procedure is shown in Figure 1. Pulp agitation speed, pH and aeration during conditioning and flotation in the cell were maintained at 1000 rpm, 10.5 and 2 L/m respectively for all experiments. Pulp oxidation potential (Eh) and dissolved oxygen level (DO) were measured at the start of conditioning, before and after collector addition, at the start of 1st concentrate collection and in the tailings at the end of flotation. Four concentrates were collected at time intervals of 1, 2, 3 and 4 min. These
concentrates were filtered and dried overnight in an oven at 50°C. The dry weights of the four concentrates and tailings were determined and chemical assays undertaken for their elemental compositions using X-Ray Fluorescence Spectroscopy (XRF). In some tests the amount of collector added was kept constant through all experiments whilst in others it was scaled to the amount of Cu in the mixture (200 g/t after primary grinding and 50 g/t after regrinding, referred to the mass of chalcopyrite in the mixture). Recovery versus time data were fitted to a first order rate equation $R = R_{\text{max}} (1 - e^{-kt})$, where $R$ is the recovery at time $t$, $R_{\text{max}}$ is the maximum recovery at infinite time and $k$ is flotation rate constant. From this equation, $R_{\text{max}}$ and $(k)$ were calculated for both chalcopyrite and pyrite.

![Fig. 1: Flowsheet of the experimental flotation.](image)

After chemical analysis, the elemental compositions (i.e. %Cu and %Fe) of each sample were converted into mineral composition using the following mathematical relations for each of the elements based on stoichiometric compositions of chalcopyrite (Cp) and pyrite (Py) (i.e. under ideal conditions).

$\%\text{Cp} = \%\text{Cu} \times \left(\frac{183.3}{63.5}\right)$  \hspace{1cm} \text{(Chalcopyrite)} \hspace{1cm} (1)

$\%\text{Fe}^+ = \%\text{Fe} - \%\text{Cu} \times \left(\frac{55.8}{63.5}\right)$  \hspace{1cm} \text{(Iron present as pyrite)} \hspace{1cm} (2)

$\%\text{Py} = \%\text{Fe}^+ \times \left(\frac{119.8}{55.8}\right)$  \hspace{1cm} \text{(Pyrite in sample)} \hspace{1cm} (3)

**Surface analysis (XPS)**

To understand the surface species responsible for the flotation behaviour of both minerals, samples were collected after regrinding with the IsaMill. These samples after collection were purged with nitrogen gas for 2 min before placing them in liquid nitrogen and stored in a refrigerator at 4 °C prior to XPS analysis. This was done to prevent further surface oxidation.

**Dissolved oxygen demand test**

Dissolved oxygen demand (DO) was measured to investigate if the reduction in oxygen content in the pulp during conditioning was due to the presence of pyrite. The oxygen demand test was conducted in an airtight container vessel equipped with a stirrer to keep the mineral particles in suspension (Figure 2). Eh, DO and pH were recorded to determine the changes in the pulp as a function oxygen addition with time.
The rougher concentrate obtained after IsaMilling (1 L IsaMill) was used for the DO demand tests. Mill discharge (d80 = 10 to 30 µm) obtained after IsaMilling for 15 min was transferred into an airtight container and stirred for 2 min to obtain a homogeneous pulp after which the initial readings for Eh, DO, and pH were recorded. The pulp was purged with oxygen at a pressure of 200 KPa for 2 min, at 5 L/min. After 2 min, the oxygen tap was closed and the decay in oxygen content monitored for 10 min. This procedure was repeated several times until oxygen concentration reached equilibrium. During the oxygen demand experiment, the pulp pH, DO and Eh values were monitored at time 10 sec intervals.

RESULTS AND DISCUSSION

Reproducibility of flotation results

The flotation experiments for the various blends were repeated several times in order to assess reproducibility of the results. As an example, values of chalcopyrite (Cp) and pyrite (Py) recovery after 10 min of flotation, and the first order flotation rate constant (k) for three tests with 20% pyrite content are summarised in Table 2.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Cp</th>
<th>Py</th>
<th>Cp</th>
<th>Py</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98</td>
<td>48</td>
<td>0.945</td>
<td>0.473</td>
</tr>
<tr>
<td>2</td>
<td>99</td>
<td>43</td>
<td>0.950</td>
<td>0.477</td>
</tr>
<tr>
<td>3</td>
<td>97</td>
<td>49</td>
<td>0.925</td>
<td>0.490</td>
</tr>
<tr>
<td>Average</td>
<td>98</td>
<td>47</td>
<td>0.940</td>
<td>0.480</td>
</tr>
</tbody>
</table>

Effect of pyrite content on flotation

The effect of pyrite content on the flotation recovery and grade of chalcopyrite after IsaMilling is shown in Figures 3 and 4. The initial experiments (Figure 3) were carried out at a constant collector addition of 250 g/t, irrespective of the proportion of chalcopyrite in the mixture, whilst in subsequent experiments (Figure 4), the amount of collector added was scaled to the amount of chalcopryite present. This was done to deconvolute the effects of two mechanisms:

- Surface modifications on chalcopyrite (oxidation) and reduced floatability,
- Copper activation of pyrite and subtraction of collector available for chalcopyrite.

For tests with constant collector addition (Figure 3), an increase in pyrite content from 0% to 80% resulted in a decrease in chalcopyrite recovery from 98% to 80% and a concomitant decrease in the flotation rate constant from 0.94 to 0.42 min⁻¹ (Table 3).

In the tests at scaled collector addition (Figure 4), chalcopyrite recovery and flotation rate constant decreased from 98% to 60% and from 0.94 to 0.39 min⁻¹, respectively.
In contrast to chalcopyrite, the recovery of pyrite gradually increased as the amount of chalcopyrite present in the mixture increased (Figures 3b and 4b). For example, in the scaled collector addition test at 20% chalcopyrite addition (80% pyrite), the maximum pyrite recovery was 15%. However with an increase in chalcopyrite content to 80% (20% pyrite), 30% of pyrite was recovered.

A comparative study of results in Figures 3 and 4 reveals consistent trends, where the pulp containing the lowest pyrite proportion (20%) attained the highest chalcopyrite recovery followed by intermediate (50%) and (80%) pyrite addition resulting in the lowest chalcopyrite recovery. Similar trend was also observed for the flotation rate constant. The only difference between the results in Figures 3 and 4 is the fact that, in the former, chalcopyrite flotation recovery and flotation rate constant are generally
higher, and the detrimental effect of pyrite is less pronounced. Furthermore, pyrite recovery in the tests at constant collector addition (Figure 3b) was much higher, suggesting that pyrite competes with chalcopyrite for collector adsorption, with the collector dosage being critical.

These results correlate well with those obtained by Young (2010), where the recovery of copper after regrinding was affected by the proportion of pyrite in the ore. There is also good agreement with the results reported by Ekmekci and Demirel (1997), where the flotation behaviour of chalcopyrite and pyrite was controlled by their proportions in the mixture.

It is clearly shown in Table 3 that an increase in pyrite content or proportion leads to a decrease of the pulp Eh. For example, at 20% pyrite addition the Eh was 203 mV whilst at 80% pyrite addition the Eh dropped to 176 mV (Table 2). Similar trend was also observed for the dissolved oxygen level in the pulp at the start of the flotation experiment. This effect may be attributed to the fact that pyrite is more cathodic and hence consumes oxygen thereby resulting in a significant deleterious impact on flotation recovery.

Table 3: Summary of results

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Equal amount of Collector addition after IsaMilling (250 g/t SIPX)</th>
<th>Collector addition after IsaMilling scaled to copper (250 g SIPX / t of Cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mixtures (Cp-Py)</strong></td>
<td><strong>pH =10.5</strong></td>
<td><strong>Eh</strong></td>
</tr>
<tr>
<td></td>
<td>mV</td>
<td>Cp</td>
</tr>
<tr>
<td>20% Py</td>
<td>240</td>
<td>0.94</td>
</tr>
<tr>
<td>50% Py</td>
<td>195</td>
<td>0.77</td>
</tr>
<tr>
<td>80% Py</td>
<td>190</td>
<td>0.42</td>
</tr>
</tbody>
</table>

**Dissolved oxygen demand**

The exact role of oxygen in sulphide mineral flotation is complicated. Various studies (Gaudin and Finkelstine 1965; Gaudin 1974; Woods 1984; Laajalehto et al., 1993) clearly indicate its strong influence when it comes to collector adsorption onto sulphide mineral surfaces. The presence of oxygen in a flotation pulp changes the oxidation state of sulphide minerals, which consequently results in the formation of surface species that can either promote or inhibit mineral floatability.

In theory, pyrite is more cathodic than chalcopyrite, hence it is expected that its oxygen consumption rate will be higher than that of chalcopyrite. Figure 5 actually confirms that theory. At 0%, 50% and 100% pyrite addition, the rate constant for the decrease in oxygen concentration in the pulp \( k_{O_2} \) was 0.023, 0.045 and 0.26 mg dm\(^{-3}\) min\(^{-1}\), respectively.
Figure 5: Oxygen concentration decay for different proportions of pyrite

Figure 6 shows the results of tests at intermittent oxygenation of the slurry (2 min on and 5 min off). In this type of test, the progressive oxidation of mineral surfaces and reduced activity were monitored with time. For example, in Figure 6 (100% Py), after an initial oxygenation of 2 min and monitoring for 5 min, the end point of dissolved oxygen concentration in the pulp decreased from 20 to 5.2 mg/dm$^3$. However, when the pulp was oxygenated for six cycles, the end point of dissolved oxygen concentration was $\approx$ 22 mg/dm$^3$. This is because an increase in oxygenation time increases the oxidative reaction occurring on the mineral surface. This reaction continues until the total surface of the mineral is oxidized and further oxygenation results in no consumption. Figure 7 displays the end point dissolved oxygen content for the individual minerals.

![Graph showing oxygen concentration decay](image)

**Fig 6: Effect of increased oxygenation on DO levels –pyrite**

**Fig 7: End point oxygen content vs. conditioning time (Cp and Py)**

It is observed that pyrite is much more oxygen consuming than chalcopyrite, and that it continues to adsorb oxygen from the system even after 30 min of continuous $O_2$ purging of the pulp (the end point DO concentration in Fig. 7 is 22 ppm, well below the saturation level of XX, indicating that oxygen is still consumed at the mineral
surface). This presupposes that the required amount of oxygen for maximum flotation selectivity in a chalcopyrite/pyrite blend will definitely vary according to the relative abundance of the two minerals.

**Surface analysis**

The atomic and weight percent (%) of elements on the mineral surface for different blends of chalcopyrite and pyrite mixtures as measured by XPS are shown in Table 4. Table 5 is the bulk weight percent (Bulk wt %) of elements in the feed material. From Tables 4 and 5, surface to bulk ratio of elements (wt %) was calculated (Table 6). Both Tables 4 and 5 indicate that the surface and bulk concentration of Cu in the mixed phase pulp decreased with increasing pyrite content as expected.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Atomic (%)</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Fe</td>
</tr>
<tr>
<td>20% Py</td>
<td>13.4</td>
<td>12.3</td>
</tr>
<tr>
<td>50% Py</td>
<td>9.50</td>
<td>11.5</td>
</tr>
<tr>
<td>80% Py</td>
<td>6.60</td>
<td>11.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Bulk weight (%)</th>
<th>Surface to bulk ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Fe</td>
</tr>
<tr>
<td>20% Py</td>
<td>21.9</td>
<td>34.8</td>
</tr>
<tr>
<td>50% Py</td>
<td>13.1</td>
<td>38.6</td>
</tr>
<tr>
<td>80% Py</td>
<td>5.3</td>
<td>42.4</td>
</tr>
</tbody>
</table>

The data in Table 6 show that the concentration of Cu at mineral surface increases with respect to the bulk concentration, as the pyrite content in the blend increases. The abundance of Cu on the surface is possibly the result of the transfer of Cu species onto pyrite particle surface. Also, it can be observed that the surface to bulk ratio of Fe and S in all samples is <1 and ≈ 1 respectively (Table 6). This could be attributed to the oxidation of the sulphide mineral surfaces with formation of oxide/hydroxide species, with O replacing S on the surface (Table 4). This also implies that an increase in pyrite content promotes the formation of Fe and Cu oxidation species.

The XPS results show that the decrease in chalcopyrite recovery can be attributed to the formation of stable hydrophilic metal oxide/hydroxides coatings on the chalcopyrite surface, thereby minimizing or preventing the adsorption of collector onto the chalcopyrite surface (Majima and Takeda, 1968; Peng et al., 2003). Such surface oxide/hydroxide species decrease the chalcopyrite hydrophobicity and collector adsorption, thereby impacting on the flotation response of the mineral. In contrast, the
relative increase in pyrite recovery at pH 10.5 can be attributed to copper activation of pyrite (Fuerstenau, 1982; Finkelstein, 1997). Pyrite in contact with chalcopyrite during grinding and conditioning generates galvanic coupling that leads to anodic dissolution of chalcopyrite with the release of Cu\(^{2+}\) ions into solution which adsorbs onto and activates pyrite for enhanced collector adsorption. These increase pyrite surface hydrophobicity and subsequently promote flotation in alkaline conditions (Xe et al., 1995; Ekmekçi and Demirel, 1997).

CONCLUSIONS

- After IsaMilling, chalcopyrite flotation kinetics and final recovery decrease with increasing the pyrite content in the mixture. The chalcopyrite grade also decreases as a result of higher pyrite recoveries.
- Pulp dissolved oxygen content (DO) and pulp oxidation potential also decrease with increasing pyrite content in the mixture. Surface analysis (XPS) suggests that oxidation of chalcopyrite and copper activation of pyrite occurs.
- Decrease in chalcopyrite flotation recovery is possibly a result of the formation of hydrophilic metal oxide/hydroxide species on the surface of chalcopyrite and the consumption of collector by copper activated pyrite.
- During processing of chalcopyrite-pyrite mixtures, it is likely that different dissolved oxygen levels in the pulp are required for optimum mineral separation, depending on the relative abundance of the two minerals in the feed.

ACKNOWLEDGEMENTS

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REFERENCES


**BIOGRAPHY**

Clement Owusu is currently at the first year of his 3-year PhD degree program in the Ian Wark Research Institute (IWRI), University of South Australia. This work forms part of his research project entitled “Effect of pulp oxidation potential in the separation of chalcopyrite from pyrite after regrinding with an IsaMill. Clement obtained his Bachelor of Science degree in Minerals Engineering (2009) from University of Mines and Technology (UMaT), Tarkwa, Ghana.