**Oil Agglomeration-Flotation of Finely Ground Chalcopyrite**

**Vothy HORNN**
Candidate for the Degree of Master of Engineering
Supervisor: Assoc. Prof. Mayumi ITO
Division of Sustainable Resources Engineering

**Introduction**

Chalcopyrite is the main source of copper worldwide and flotation is often used to concentrate chalcopyrite and remove most of associated gangue minerals prior to smelting processes. In flotation, attachment of mineral particles to bubbles depends on the size of bubbles and particles relative to each other, their relative velocities, and the concentration of particles in the suspension [1]. In mechanical flotation cells, collisions between fine particles and rising bubbles become poor because of their small mass and low momentum. The probability of particles attachment to bubbles (P) in the flotation cell can be expressed by the following equations [2]:

\[ P = P_c \times P_a \times (1 - P_d) \]  
\[ P_c = A \left( \frac{d_p}{d_b} \right)^n \]

where \( P_c, P_a, \) and \( P_d \) are the probabilities of collision, attachment, and detachment, respectively, \( d_p \) and \( d_b \) are the particle and bubble diameters, respectively, and \( A \) and \( n \) are empirical constants that depend on the flow regime. \( P_a \) and \( P_d \) are mainly dependent on chemical aspects and in the case of hydrophobic mineral like chalcopyrite, their values could be assumed to be 1 and 0, respectively. This means that \( P \) is mainly dependent on \( P_c \). Based on equation 2, the probability of collision \( (P_c) \) is directly dependent on the ratio of the particle and bubble diameters (equation 2). In other words, when the size of particles becomes very small \((d_p<d_b)\) the probability of collision is substantially decreased, which could explain why very low recovery rates of fine particles are encountered in mechanical-type flotation cells.

There are two main approaches that could be used to improve fine particle recovery in mechanically agitated-type flotation machines: (i) decreasing the bubble size, and (ii) increasing the particle size.

Oil agglomeration is a potential method for increasing the size of fine particle before flotation. This method has been studied in coal flotation [3] and some sulfides mineral such as molybdenite [4], sphalerite and galena [5]. House and Veal [6] carried out oil agglomeration of chalcopyrite and they could improve the floatability of fine chalcopyrite. However, high amounts of oil was used. Utilization of emulsified oil for coal agglomeration-flotation could significantly reduce the amount of oil [7–9]. Recently, there was very limited studies (almost none) of oil agglomeration of fine chalcopyrite using emulsified oil.

In this study, oil agglomeration-flotation technique was applied on finely ground chalcopyrite using emulsified oil, surface modifier and high speed mixer. First, the effects of particle size on flotation were investigated. Then fine chalcopyrite \((D_{50} = 3 \mu m)\) was chosen for agglomeration-flotation. Finally, the effects of agglomeration conditions on flotation recovery are discussed.

**Materials**

Chalcopyrite from Copper Queen Mine, Arizona, USA was used. This sample was characterized using X-ray fluorescence (XRF) and X-ray powder diffraction (XRD). Results of XRF and XRD are shown in Table 1 and Fig. 1. According to norm calculation, where content of \( CuFeS_2 \) is calculated from \( Cu \), this sample contains 73\% of chalcopyrite.

Potassium amyl xanthate (KAX) (Tokyo Chemical Industry Co., Ltd.) was used as a collector to improve the hydrophobicity of chalcopyrite before agglomeration. Kerosene (Wako Pure Chemical Industries, Ltd.) was used as bridging liquid, and Methyl Isobutyl Carbinol (MIBC), (Tokyo Chemical Industry Co., Ltd.) was used as frother in flotation.

**Table 1. Elemental composition of chalcopyrite (wt%)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Zn</th>
<th>Si</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>30</td>
<td>34</td>
<td>22</td>
<td>0.9</td>
<td>8.2</td>
<td>3.7</td>
</tr>
</tbody>
</table>

**Figure 1. XRD pattern of chalcopyrite**
Methods

Flotation

Flotation was carried out in a mechanical flotation machine (FT-1000, Cosmic Mechanical Technology Co., Ltd.). Modified release analysis method [10] (Fig. 2) was used as flotation. The pulp density was 5% and the volume of suspension was 400 ml. After addition of Methyl Isobutyl Carbinol (MIBC) of 25 μL/L, the suspension was conditioned for 3 minutes at 1000 rpm. 10 g/t of KAX was added and then the suspension was conditioned again for 3 minutes. After conditioning, air was introduced into the flotation cell at a flow rate of 1 L/min and the froth was collected. The same procedure was repeated with different added amounts of KAX (10, 20, 50, 100, 150, 200 g/t). The froth and tailing were weighed after drying in the oven (105 °C) for 24 hours.

Agglomeration-flotation

Agglomeration-flotation was conducted on finely ground chalcopyrite sample (D₅₀= 3μm) using the experimental procedure illustrated in Fig. 3. Before agglomeration, the suspension was conditioned with KAX (50, 200 g/t) for 5 minutes in the flotation cell. After conditioning, the suspension was transferred to a high speed mixer (SPB-600J, Cuisinart) and emulsified kerosene (0, 0.1, 0.3, 0.5 ml) was added. Agglomeration was conducted for 10 or 30 minutes at a mixing speed of 15,000 rpm. Agglomeration products was treated by flotation (0-1, 1-3, 3-5, 5-7, 7-10 min).

Results and discussion

Effects of particle size on flotation

Disk mill was used to obtain 4 different size fractions of chalcopyrite (D₅₀= 3, 5, 10, 17 μm) and flotation of each size fraction was carried out. The particle size distributions of these four samples are shown in Fig. 4.

Fig. 5 illustrates the effects of size on flotation yield. The chalcopyrite yield for 3, 5, 10 and 17 μm were 48, 76, 82 and 87%, respectively, indicating that the smaller the particle size, the lower the flotation yield. The flotation yield of chalcopyrite having D₅₀ = 3 μm was considerably low compared with the other size fractions. This means that this small size range cannot collide with bubbles, so the flotation yield was very low. This particle size fraction was selected for the agglomeration-flotation experiments.

Figure 4. Particle size distribution of crushed samples.

Figure 5. Flotation results of chalcopyrite having four different size fractions (D₅₀ = 3, 4, 10, 17 μm).
Agglomeration-flotation

Fig. 6 shows the results of flotation with and without agglomeration. The highest yield of chalcopyrite (81%) was achieved with 200 g/t of KAX, 0.3 ml of kerosene and mixing time of 30 minutes. Agglomeration-flotation improved the flotation yield by up to 30% compared to that without agglomeration (Fig. 6). Microscopic observations showed that the particle size greatly increased after agglomeration (KAX: 200 g/t, kerosene: 0.3 ml, mixing time: 30 minutes), and this increased in particle size was the reason for the improved recovery of fine chalcopyrite in flotation.

Effects of agglomeration conditions on flotation

a. Effects of kerosene dosage

Fig. 9 shows the flotation yield after agglomeration for 30 minutes at fixed KAX dosage (200 g/t), but different amounts of kerosene (0, 0.1, 0.3, 0.5 ml). The flotation yield of chalcopyrite increased with increasing dosage of kerosene until 0.3 ml. More kerosene addition after this amount resulted in the slight decrease of flotation recovery that may be due to saturation. Saturation could lead to slight decrease in size of the agglomerated products due to the reduction of capillary pressure of bridging liquid between particles. Yield of agglomeration-flotation without kerosene addition (0 ml) was 63%, which improved by 15% compared with the flotation yield without agglomeration. This indicates that even if the bridging liquid was absent, the size of agglomerated products was slightly increased in the presence of KAX and high agitation speed. This agglomeration phenomena is often called shear flocculation[11], which is agglomeration due to hydrophobic interaction of KAX.

b. Effects of agglomeration time

Fig. 10 shows the effects of agglomeration time on flotation yields. By fixing the KAX dosage (200 g/t) and kerosene addition (0.3 ml), the mixing time was changed between 10 and 30 minutes. The results showed that longer mixing time enhanced the yield of chalcopyrite. 10 min of agglomeration time was not enough for particle to agglomerate that resulted in lower flotation yield than those of 30 min agglomeration time.

c. Effects of KAX dosage on agglomeration-flotation

The effects of KAX were evaluated by fixing the kerosene dosage (0.3 ml) and agglomeration time (30 minutes), but varied dosage of KAX (0, 50, 200 g/t) for agglomeration experiment. The flotation yield without KAX addition was 63% and the yield with KAX addition of 50, 200 g/t were 71%, 77% respectively (Fig. 11). This indicates that KAX play very important roles in agglomeration-flotation.
Conclusions

Floitation of chalcopyrite having four different size distributions showed that the particle size effects on flotation yield was very important. Oil agglomeration methods are effective for recovering fine chalcopyrite. Oil agglomeration of fine chalcopyrite (200g/t KAX and 15 L/t emulsified kerosene) improved the flotation yield by up to 30% compared with normal flotation without agglomeration. Without kerosene addition, chalcopyrite was slightly agglomerated due to hydrophobic interaction. KAX plays a significant role for enhancing hydrophobicity of chalcopyrite and thus improved the flotation yield.

References