

Article

# Agglomeration-Flotation of Finely Ground Chalcopyrite and Quartz: Effects of Agitation Strength during Agglomeration Using Emulsified Oil on Chalcopyrite

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Received: 27 March 2020; Accepted: 22 April 2020; Published: 23 April 2020



**Abstract:** In flotation, the size of mineral particles is one of the most important parameters: when the size becomes fine, collision efficiency of the particles and air bubbles becomes low, causing low flotation recovery. To improve the collision efficiency and flotation kinetics, agglomeration using the emulsified oil of finely ground chalcopyrite ( $D_{50} = 3.5 \mu\text{m}$ ) was carried out before flotation. In this study, the effects of agitation strength during agglomeration, kerosene dosage and potassium amyl xanthate (KAX) dosage on the flotation were investigated. Agglomeration using emulsified oil improved Cu recovery because the median diameter of agglomerate increased. With increasing agitation strength, KAX and kerosene dosages, Cu recovery was further increased. Agglomeration-flotation of a mixture containing chalcopyrite and quartz with 1:1 ratio (w/w, weight by weight) showed that Si recovery in froth was low and did not change with varying conditions (agitation strength, KAX and kerosene dosages); however, Cu recovery was significantly improved with increasing agitation strength, KAX and kerosene dosages, and thus the separation efficiency was improved.

**Keywords:** agglomeration; emulsified oil; agitation strength; flotation; chalcopyrite; fine particles; separation efficiency

## 1. Introduction

Sulfide ores, the main sources of base metals worldwide, are commonly processed by flotation to concentrate the valuable minerals and remove associated gangue minerals. One of the main challenges in flotation is the low recovery of fine particles (i.e., less than  $5 \mu\text{m}$ ), which are difficult to recover as froth by flotation because of their low mass causing low collision efficiency with bubbles [1].

There are two main approaches that could be used to improve the recovery of fine particles in flotation: (i) decreasing the bubble size and (ii) increasing the apparent size of particles (i.e., aggregation). Approaches aiming at reducing bubble size include column flotation [2,3], electro-flotation [4], microbubble flotation [5–9], and dissolved air flotation [10]. However, these techniques may result in entrainment of gangue minerals due to high water recovery [10,11]. Approach (ii)—increasing the apparent size of particles—includes shear flocculation [12], carrier flotation [13,14], polymer flocculation [15–17] and oil agglomeration [18–20].

All of these techniques have their own benefits and drawbacks, but from the perspective of economics, oil agglomeration—a method to increase particle size using oil as a bridging liquid under intense mixing—is the most promising because oil is relatively inexpensive, the process could be easily integrated into existing flotation circuits, and the technique could effectively improve the recovery of fine particles. Utilization of emulsified oil for agglomeration-flotation could reduce the amount of oil [20–22]. This method has been mainly studied in coal flotation [19] and some sulfide minerals such as molybdenite [23], sphalerite and galena [24]. House and Veal [25] carried out oil agglomeration of chalcopyrite with different types of oils followed by screening of agglomerated chalcopyrite. Although around 80% of Cu could be recovered by this method, it required the use of a significant amount of oil (around 85 L/t). To address this problem, Rubio et al. [26] investigated flotation of finely ground chalcopyrite using emulsified oil. In their study, the emulsified oil was used as an extra reagent and directly added into the flotation cell right before flotation, which is most likely not enough for agglomerating fine particles. In coal cleaning, a high-speed mixer and kitchen blender are used to selectively agglomerate coal and to remove gangue minerals trapped in agglomerates [27]. This paper investigates the two-step process, consisting of (1) potassium amyl xanthate (KAX) conditioning in the conditioning cell and (2) agglomeration with emulsified oil in the agglomeration vessel prior to flotation. The effects of agitation strength during agglomeration, the dosage of KAX as surface modifier and the dosage of oil as a bridging liquid are investigated. In addition, the separation efficiency of chalcopyrite and quartz by agglomeration-flotation using emulsified oil is evaluated.

## 2. Materials and Methods

### 2.1. Materials

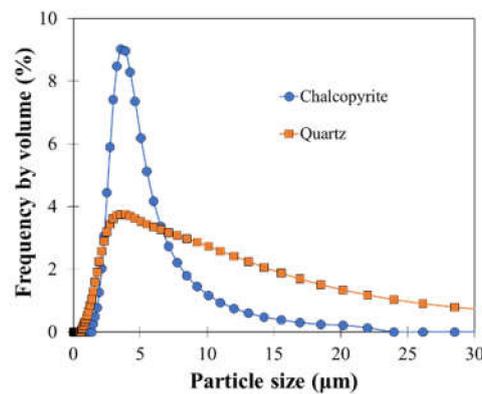
Two samples were used in this study: chalcopyrite and quartz. The chalcopyrite sample was obtained from Copper Queen Mine, Cochise County, AZ, USA, while the quartz sample (99% purity) was obtained from Wako Pure Chemical Industries Co., Ltd., Osaka, Japan. The chalcopyrite sample was characterized using X-ray fluorescence (XRF) (EDXL300, Rigaku Corporation, Tokyo, Japan) and X-ray powder diffraction (XRD, Multiplex, Rigaku Corporation, Tokyo, Japan). The elemental composition of the sample is shown in Table 1. XRD analysis indicated that chalcopyrite is the major mineral, while actinolite ( $\text{Ca}_2\text{Mg}_3\text{Fe}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ ), quartz and sphalerite are minor minerals.

**Table 1.** Chemical composition of the chalcopyrite sample.

Elements	Cu	Fe	S	Zn	Si	Ca
wt. %	26	27	26	0.8	6	2

The chalcopyrite specimen was crushed using a jaw crusher (1023-A, Yoshida Manufacturing co., Ltd, Sapporo, Japan) and ground by a vibratory disc mill (RS100, Retsch Inc., Haan, Germany), then screened to obtain a size fraction of less than 75  $\mu\text{m}$ . The ground sample (less than 75  $\mu\text{m}$ ) was ground again by the vibratory disc mill to obtain fine particles having a median particle diameter ( $D_{50}$ ) of 3.5  $\mu\text{m}$ . The quartz sample (primary particle diameter of less than 500  $\mu\text{m}$ ) was ground separately in the same manner as the chalcopyrite sample. The median particle diameter ( $D_{50}$ ) of the quartz sample was 6  $\mu\text{m}$ . The particle distribution of chalcopyrite and the quartz sample used in this study were measured in water after ultrasonication (Figure 1), using a laser diffraction machine (Microtrac<sup>®</sup> MT3300SX, Nikkiso Co., Ltd., Tokyo, Japan).

Potassium amyl xanthate (KAX) (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), Kerosene (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and Methyl Isobutyl Carbinol (MIBC), (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) were used in this study.



**Figure 1.** Particle size distribution of the crushed chalcopyrite and quartz.

## 2.2. Preparation of Emulsified Oil

Kerosene was mixed with distilled water in the concentration of 20 wt.%, then emulsification was carried out using an ultrasonic homogenizer (ULTRA-TURRAX, IKA, Königswinter, Germany) for 60 s. This emulsification was carried out immediately before agglomeration.

## 2.3. KAX Conditioning in the Conditioning Cell and Agglomeration in the Agglomeration Vessel

KAX conditioning and agglomeration were conducted on a finely ground chalcopyrite sample ( $D_{50} = 3.5 \mu\text{m}$ ) or a mixture of finely ground chalcopyrite and quartz ( $D_{50} = 6 \mu\text{m}$ ) at the ratio of 1:1 (w/w). Before agglomeration, 20 g of samples were suspended in 400 mL of distilled water, then the suspension was conditioned with the surface modifier, KAX (50, 200 or 1000 g/t) for 5 min at 1000 rpm in the flotation cell (FT-1000, Heiko, Tokyo, Japan). After conditioning, the suspension was transferred to an agglomeration vessel, and then emulsified oil (0, 15 or 25 L kerosene/t sample) was added, and agitation was carried out for 30 min with a predetermined stirring speed (1000, 4000, or 15,000 rpm). Two types of agglomeration machines were used: (machine A) a rotary stirrer (B.NR 301, Heidolph, Schwabach, Germany; rotation speed of 0–5000 rpm) with a two-bladed impeller and a cylinder vessel, and (machine B) a high-speed mixer with a s-shape impeller (SPB-600J, Cuisinart, Stamford, CT, USA; fix rotation speed of 15,000 rpm). Agglomeration was conducted for 30 min using agglomeration machine A at 1000 and 4000 rpm, and agglomeration machine B at 15,000 rpm. The suspension containing agglomerates was transferred to a flotation cell and the flotation experiments were carried out.

## 2.4. Flotation Tests

The suspension after agglomeration was transferred to a 500 mL flotation cell. Flotation was carried out using a mechanical flotation machine (FT-1000, Heiko, Tokyo, Japan). MIBC (25  $\mu\text{L/L}$ ) was added as a frother and the suspension was stirred for three minutes with an impeller speed of 1000 rpm. Air was then injected into the suspension at a flow rate of 1 L/min and flotation was carried out (total flotation time of 10 min). Froths were collected at predetermined time intervals, and both froth products and tailings were weighed after drying at 105 °C for 24 h and their elemental compositions were determined using an XRF.

## 3. Results and Discussion

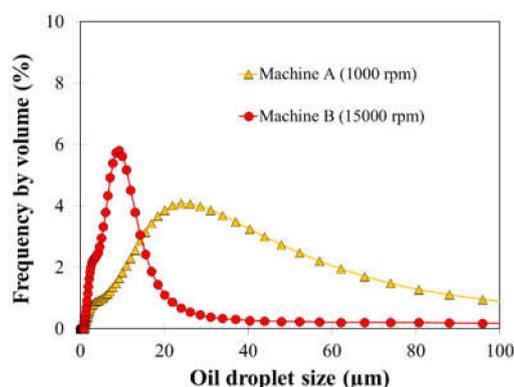
### 3.1. Effects of Agitation Strength

Agitation strength is an important factor for agglomeration of hydrophobic particles using oil as a bridging liquid [27]. Agglomeration kinetics and agglomerate size are mainly determined by (1) particle–particle collision, (2) particle–particle attraction, and (3) decomposition of agglomerate. Among them, the probabilities of particle–particle collision (1) and agglomerate decomposition (3)

are directly affected by agitation strength; that is, when agitation become strong, both collision and decomposition probabilities are increased.

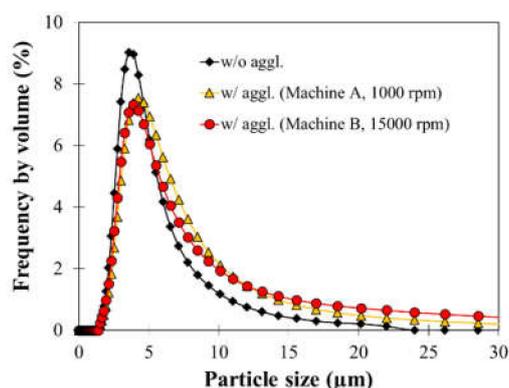
Particle–particle attraction (2) is also indirectly affected by agitation strength. The attraction force is determined by hydrophobic interaction between hydrophobic surfaces and the capillary force of the bridging liquid between particle and particle; that is, the former is improved by the addition of KAX while the latter is affected by the size of oil droplets attached to the surface of particles. In the case of capillary force, it is generated by the bridging liquid, which bridges particle and particle after the collision of particles occurs. However, when the size of oil droplets is too big, the capillary force becomes weak, and thus suitable conditions (e.g., funicular state and capillary state) [28] are desired to maximize capillary force. Moreover, the probability of attachment between particle and particle after collision is proportional to the number of oil droplets attached to the surface of particle. In short, particle–particle attraction (2) is affected by the size and number of oil droplets attached to the surface of particles, both of which are controlled by agitation strength; for instance, high agitation strength produces a small size and large number of oil droplets in suspension. Considering these things, the effects of agitation strength on oil droplet size, agglomerate size, and the flotation recovery of agglomerated chalcopyrite were investigated.

Figure 2 shows the size distribution of oil droplets. In this experiment, 20 mL of emulsified oil (20% kerosene, as explained in Section 2.2) was added to 380 mL distilled water and agitated for 30 min by the agglomeration machine. The size distribution of oil droplets generated by machine B (15,000 rpm) was shifted to smaller fractions compared to those generated by machine A (1000 rpm); that is, mode sizes (i.e., peak sizes) were about 10  $\mu\text{m}$  with machine B and 24  $\mu\text{m}$  with machine A. This is due to the stronger shear force of machine B: oil droplets were split by the shear force and the size became smaller.



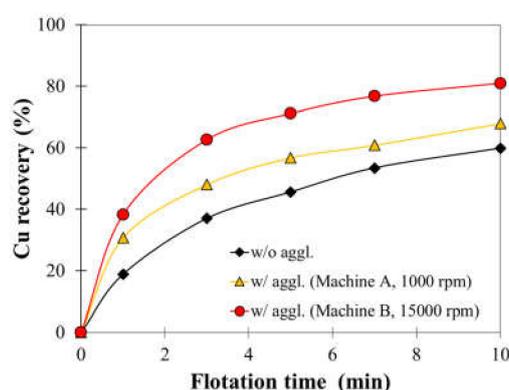
**Figure 2.** Size distribution of oil droplets in suspension (1 wt.% of kerosene and 99 wt.% of distilled water) prepared using machine A (1000 rpm) and B (15,000 rpm).

Figure 3 shows the size distribution with and without agglomeration. Before agglomeration, 20 g of samples were suspended in 400 mL of distilled water, before the suspension was conditioned with the surface modifier, KAX (200 g/t), for five minutes at 1000 rpm in the flotation cell. After KAX conditioning, the suspension was transferred to an agglomeration vessel. Emulsified oil (15 L kerosene/t sample) was then added and agitation was carried out for 30 min with a predetermined stirring speed (1000 or 15,000 rpm). The results showed that apparent particle sizes increased after agglomeration based on the increases in frequency of coarser fractions, indicating that agglomeration occurred. However, there is no significant difference in size distributions between machine A and machine B.



**Figure 3.** Size distribution of chalcopyrite without agglomeration and with agglomeration using machine A (1000 rpm) and machine B (15,000 rpm).

Figure 4 shows the flotation results with and without agglomeration. In the case of flotation without agglomeration (i.e., control), after conditioning with 200 g/t of KAX and 25 µL/L of frother, emulsified oil (15 L kerosene/t sample) was added and then immediately flotation was conducted. Even when emulsified oil was added after conditioning with KAX and frother (control), the result showed lower recovery than that with agglomeration. These results indicate that not only the addition of emulsified oil but also agglomeration treatment is essential for improving flotation recovery.



**Figure 4.** Cu recovery without agglomeration and with agglomeration using machine A (1000 rpm) and machine B (15,000 rpm).

When agglomeration was applied, higher Cu recovery was obtained. Cu recovery with agglomeration using machine B was higher than that with machine A. Flotation kinetics mainly depends on particle size and hydrophobicity [29–33], and the agglomeration technique can improve flotation kinetics due to an increase of apparent size resulting in high Cu recovery with agglomeration treatment (Figure 4). Based on these results, the detailed mechanisms of how agglomeration-flotation with emulsified oil improves Cu recovery can be proposed as follows.

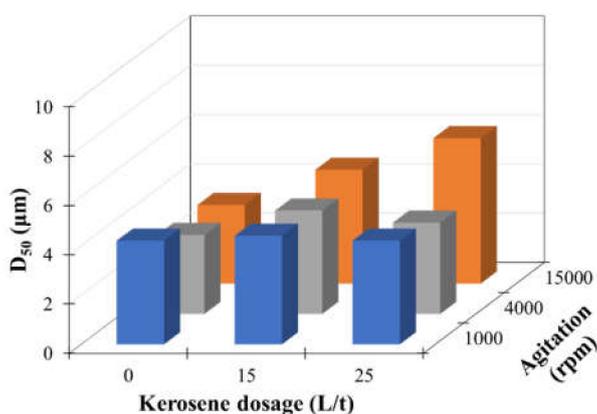
**Effects of agitation strength on oil droplets during agglomeration:** During agitation, oil droplets were split by the shear force and the size became smaller as shown in Figure 2. When the size of oil droplets becomes smaller, the number of droplets in the agitator increases, so stronger agitation energy can produce a large number of oil droplets. The frequency of collision of the oil droplets and particles in the agglomeration system is proportional to the number of oil droplets and the relative velocity of approach to each other, so it is reasonable to assume that the number of oil droplets attached to the particle surface, induced by the collision of oil droplet and particle, becomes larger when a stronger agitation condition is applied. This would affect the agglomeration process and the flotation of the agglomerate.

**Effects of agitation strength on agglomeration and flotation:** Flotation kinetics mainly depends on particle size and hydrophobicity [29–32], so the agglomeration technique can improve flotation kinetics due to the increase of apparent size resulting in high Cu recovery with agglomeration treatment (Figure 4). Agglomerate sizes were similar with agglomeration machines A and B (Figure 3), indicating that the difference in Cu recovery is not due to the difference in agglomerate size. As discussed previously, the number of oil droplets attached to the mineral surface may be larger when using the agitation machine B (15,000 rpm), which may increase the probability of attachment between mineral particles after collision, so the agglomeration could be enhanced. Under a stronger agitation condition in machine B (15,000 rpm), however, the decomposition of agglomerate would also be enhanced. This may be a reason why agglomerate size in machine B (15,000 rpm) is almost the same as that in machine A (1000 rpm). Even with the similar agglomerate size, the number of oil droplets attached to the mineral surface may be different: a larger number of oil droplets are attached to the mineral surface when machine B was used. This may cause a more hydrophobic surface and enhanced Cu recovery.

Agglomeration with both agglomeration machine A and B is effective to improve the recovery of finely ground chalcopyrite particles.

### 3.2. Effects of Kerosene Dosage

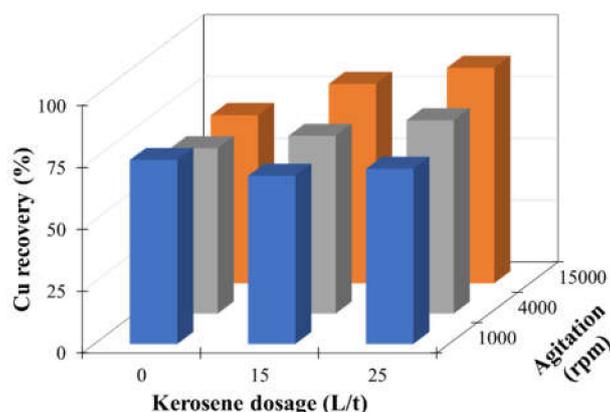
The effects of kerosene dosage on agglomerate size and the flotation of agglomerate were investigated. In the case of a kerosene dosage of 0 L kerosene/t sample, conditioning with KAX (200 g/t) was conducted for five minutes at 1000 rpm in the flotation cell, and then the suspension was transferred to an agglomeration vessel and agitated for 30 min without the addition of emulsified oil. Figure 5 shows the effects of kerosene dosage on the median diameter ( $D_{50}$ ) of agglomerates. As shown in Figure 5, at agitation speeds of 1000 rpm and 4000 rpm, the median diameter of agglomerate was less dependent on kerosene dosage, while the median diameter increased with increasing kerosene dosage when agitated at 15,000 rpm. As already discussed, when low-speed agitation is applied, the number of oil droplets attached to the mineral surface is limited, and this may be the reason why agglomerate size is less dependent on kerosene dosage. When a high agitation speed was applied, the number of oil droplets increased due to the decrease in the size of oil droplets, causing a high collision frequency between oil droplets and mineral particles. This causes an increase in the number of attached oil droplets on the mineral surface when kerosene dosage increases. As a result, the median size of agglomerate increased with increasing kerosene dosage when high-speed agitation was applied.



**Figure 5.** Effects of kerosene dosage and agitation speed on the median diameter ( $D_{50}$ ) of agglomerates (KAX 200 g/t). KAX—potassium amyl xanthate.

Figure 6 shows Cu recovery after 10 min flotation of agglomerate under varied agitation strengths. As shown in Figure 6, when emulsified oil was not added to the agglomeration process, Cu recovery was not affected by varying agitation strengths. Moreover, at low agitation strengths (i.e., 1000 rpm and 4000 rpm), Cu recovery showed a similar value even if kerosene dosage increased. Compared with the

result of the median diameter, Cu recovery was well correlated to the agglomerate size: at low-speed agitation (1000 rpm and 4000 rpm), the agglomerate size was relatively small regardless of the kerosene dosage, causing a low Cu recovery. When high-speed agitation (15,000 rpm) and larger kerosene dosage were applied, the agglomerate size became larger, resulting in high Cu recovery. This result agrees with the reported findings about flotation kinetics [32]: a faster flotation rate is achieved for larger particles due to a high collision probability between particle and air bubble.

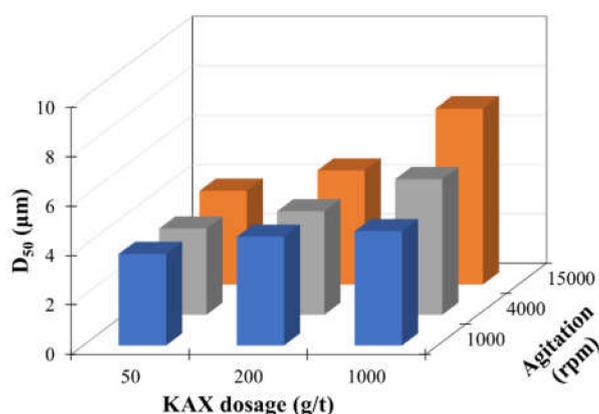


**Figure 6.** Effects of kerosene dosage and agitation speed on Cu recovery (KAX 200 g/t, flotation time 10 min).

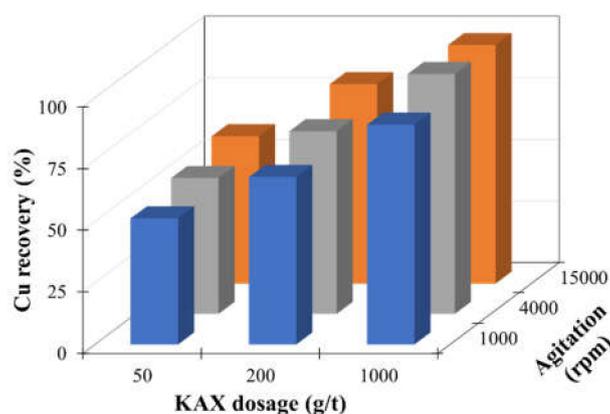
### 3.3. Effects of KAX Dosage

The effects of KAX dosage on agglomerate size and flotation of agglomerate were investigated under varied agitation conditions. Figure 7 shows the effects of KAX dosage on the median diameter ( $D_{50}$ ) of agglomerates. The dosage of kerosene was fixed to be 15 L kerosene/t sample. As shown in Figure 7, the median diameter of agglomerate slightly increased with increasing KAX dosage at agitation speeds of 1000 rpm and 4000 rpm, while the effect became significant at 15,000 rpm. There are two possible mechanisms of how KAX addition contributes to agglomeration: (1) increasing hydrophobic interaction between particles, and (2) an increasing attachment probability of particle and oil droplet. A chalcopyrite surface becomes hydrophobic when KAX is adsorbed on the mineral surface, and the increase in the adsorption amount of KAX may cause a strong hydrophobic interaction between particles, and thus the median size of agglomerates becomes bigger. In addition, when the mineral surface is rendered hydrophobic, the attachment probability after collision of oil droplet and mineral surface is increased, and thus the median size of agglomerates becomes bigger. These results indicate that the median diameter of agglomerate was affected not only by kerosene as a bridging liquid but also by the KAX amount as surface modifier.

Figure 8 shows Cu recovery after 10 min flotation of agglomerate under varied agitation strength. This result shows that Cu recovery increased with increasing both KAX dosage and agitation speed. High Cu recovery at high-speed agitation with a large KAX dosage can be interpreted as a result of the larger size of the agglomerate; for example, at 15,000 rpm with 1000 g/t KAX, both agglomerate size and Cu recovery become highest. At 1000 rpm, however, Cu recovery increased but agglomerate size was slightly increased with increasing KAX dosage. In addition, as described previously, the increase of KAX addition assists the attachment probability of oil droplet and mineral surface, resulting in the number of oil droplets attached to the mineral surface increasing, which improves the hydrophobicity of agglomerate even where the median diameter shows similar values. Thus, Cu recovery could be significantly increased, although the median diameter of agglomerate was slightly increased with increasing KAX dosage (Figures 7 and 8).



**Figure 7.** Effects of KAX dosage and agitation speed on the median diameter ( $D_{50}$ ) of agglomerates (Kerosene 15 L kerosene/t sample).



**Figure 8.** Effects of KAX dosage and agitation speed on Cu recovery (Kerosene dosage 15 L kerosene/t sample, flotation time 10 min).

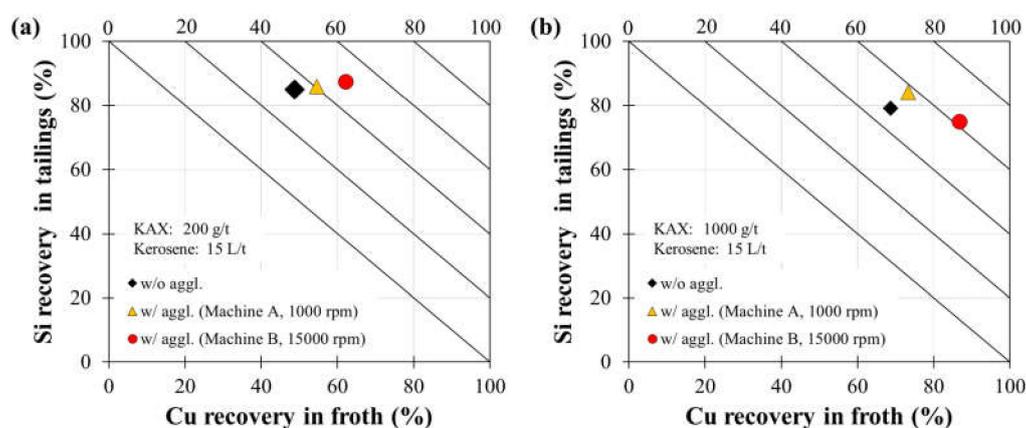
### 3.4. Separation of Finely Ground Chalcopyrite and Quartz by Agglomeration-Flotation

In actual flotation of copper sulfide ores, the ore contains copper (chalcopyrite) and gangue minerals like quartz. To investigate the effects of agitation strength, KAX dosage and kerosene dosage on separation efficiency, agglomeration-flotation experiments were conducted using a mixture of 10 g of chalcopyrite and 10 g of quartz. One of the effects of the coexistence of quartz during flotation is the entrapment of quartz in agglomerate, resulting in a high recovery of quartz in froth. This may cause the decrease in separation efficiency. Flotation kinetics is mainly determined by (1) particle–bubble collision, (2) particle–bubble attachment, and (3) the detachment of a particle from a bubble [33]. The coexistence of quartz may affect flotation kinetics, which can be explained by the following possibilities. The size distribution of finely ground chalcopyrite after agglomeration in the absence and presence of quartz would be different, which means that (1) the collision probability of particle–bubble may also be changed. When quartz is entrapped in agglomerate, the contact angle of agglomerate may decrease, so the (2) attachment and (3) detachment probabilities of particle–bubble will change. According to the flotation results comparing with and without quartz, however, flotation kinetic as well as Cu recovery showed similar values (about 80% Cu recovery) under the condition of 200 g/t KAX, 25 L kerosene/t sample kerosene and 15,000 rpm, indicating that the presence of quartz does not affect Cu recovery.

#### 3.4.1. Effects of KAX Dosage and Agitation Strength on Separation Efficiency

Figure 9 shows the relationship between Cu recovery in froth,  $R_{Cu}$  (%), and Si recovery in tailings,  $R_{Si}$  (%), after agglomeration-flotation under the following conditions: kerosene dosage,

15 L kerosene/t sample; agglomeration time, 30 min; agitation strength, 1000 rpm and 15,000 rpm; KAX dosage, 200g/t and 1000 g/t. In the case of flotation without agglomeration (i.e., control), flotation was conducted after conditioning with KAX and 25  $\mu$ L/L of frother.



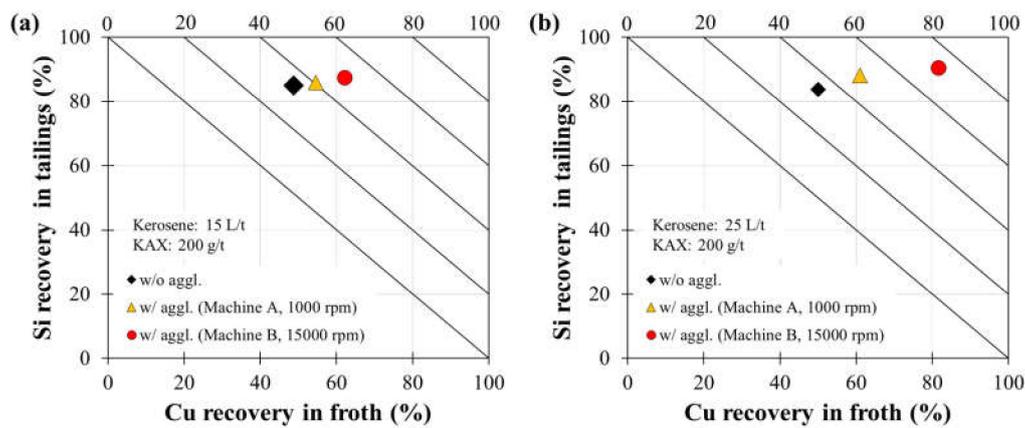
**Figure 9.** Relationship between Cu recovery in froth,  $R_{Cu}$  (%), and Si recovery in tailing,  $R_{Si}$  (%), of chalcopyrite and quartz mixture with different KAX dosage: (a) 200 g/t and (b) 1000 g/t.

With increasing agitation strength and KAX dosage, Cu recovery increased significantly, while Si recovery in tailings was almost constant (around 20%). The separation efficiency,  $\eta$  (%), which can be defined by Equation (1), increased with increasing agitation strength and KAX dosage. These results indicate that quartz may not affect Cu recovery. Even with the presence of quartz, Cu recovery increases with increasing agitation strength and KAX dosage, resulting in the improvement of separation efficiency.

$$\eta (\%) = R_{Cu} (\%) + R_{Si} (\%) - 100 \quad (1)$$

#### 3.4.2. Effects of Kerosene Dosage and Agitation Strength on Separation Efficiency

Figure 10 shows the relationship between Cu recovery in froth,  $R_{Cu}$  (%), and Si recovery in tailing,  $R_{Si}$  (%) after agglomeration-flotation (KAX, 200 g/t; agglomeration, 30 min; agitation strength, 1000 rpm and 15,000 rpm, kerosene dosage, 15 L kerosene/t sample and 25 L kerosene/t sample). The results showed that with increasing agitation strength and kerosene dosage, Cu recovery increased significantly, while Si recovery slightly increased. These results indicate that the separation efficiency,  $\eta$  (%), increased with increasing agitation strength and kerosene dosage. The highest separation efficiency was obtained under the conditions of 200 g/t KAX, 25L kerosene/t sample and 15,000 rpm agitation strength.



**Figure 10.** Relationship between Cu recovery in froth,  $R_{Cu}$  (%), and Si recovery in tailing,  $R_{Si}$  (%), of chalcopyrite and quartz mixture with different kerosene dosage: (a) 15 L kerosene/t sample and (b) 25 L kerosene/t sample.

#### 4. Summary

Agglomeration using emulsified oil is an effective method to improve the floatability of finely ground chalcopyrite ( $D_{50} = 3.5 \mu\text{m}$ ). Agitation strength, kerosene and KAX dosages are important parameters for overall Cu recovery and flotation separation efficiency. The main findings of this study are summarized as follows:

- Strong agitation is important to produce small oil droplets, which increases the number of oil droplets available for a higher frequency of collision with fine particles.
- Increasing kerosene dosage is not effective to improve Cu recovery when low agitation strength is applied, while at high agitation strength, Cu recovery is improved. High agitation strength and high dosage of kerosene provide high Cu recovery.
- Increasing the KAX amount is also effective to improve Cu recovery, probably by assisting the attachment of small oil droplets to mineral particles, of which the hydrophobicity increased by the addition of KAX.
- In the agglomeration-flotation of a mixed sample containing chalcopyrite and quartz with a 1:1 ratio (w/w), Si recovery in froth is low and is not affected by agitation strength, KAX and kerosene dosages, while Cu recovery increases with increasing agitation strength, KAX and kerosene dosages, making separation efficiency higher.

**Author Contributions:** V.H., M.I., S.J., I.P. and N.H. conceived and designed the experiments; V.H. and H.S. performed the experiments and analyzed the data; V.H. wrote the paper. M.I., C.B.T., S.J., and I.P. reviewed and edited the paper. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The authors declare no conflict of interest.

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