Agglomeration-flotation of finely ground chalcopyrite using surfactant-stabilized oil emulsions: Effects of co-existing minerals and ions

Vothy Hornn [1], Ilhwan Park [2, *], Mayumi Ito [2], Hiromasa Shimada [1], Tomoki Suto [1], Carlito Baltazar Tabelin [3], Sanghee Jeon [2], Naoki Hiroyoshi [2]

[1] Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

[2] Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan

[3] School of Minerals and Energy Resources Engineering, The University of New South Wales, Sydney, NSW, Australia

* Corresponding author – e-mail: i-park@eng.hokudai.ac.jp; address: Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Hokkaido, Japan.

Abstract: Flotation rate of finely ground chalcopyrite (< 5 μm) is low due to the low collision probability between air bubbles and the mineral particles. In this study, effects of emulsifiers in the presence of co-existing minerals and ions on agglomeration-flotation of finely ground chalcopyrite were investigated. Anionic emulsifiers (SDS, KAX) can be used to improve Cu recovery in the agglomeration-flotation of chalcopyrite and quartz because addition of emulsifiers could stabilize the oil-water emulsion and produce smaller oil droplets. When Ca^{2+} and quartz co-existed, SDS used as emulsifier was consumed by Ca^{2+} adsorbed on quartz surface, resulting in low Cu recovery due to the coalescence of oil droplets. On the other hand, emulsified oil stabilized by KAX was not affected by the presence of Ca^{2+} and quartz, so high Cu recovery could be obtained.

Keywords: agglomeration; emulsified oil; emulsifiers; flotation; fine chalcopyrite.

1. Introduction

Flotation is the most commonly used technique to recover valuable minerals not only from sulfide ores like complex Cu-Pb-Zn sulfides (Aikawa et al., 2020; Bulatovic, 2007), Cu-Ni-Co sulfides (Liu et al., 2021; Zhao et al., 2015), porphyries (Hornn et al., 2020a; Park et al., 2020a, 2020b, 2021), seafloor massive sulfides (Aikawa et al., 2021; Nakajima et al., 2011), Li-silicates (Tabelin et al., 2021a) but also from electronic wastes (Jeon et al., 2018). Despite its widespread adoption, flotation efficiency dramatically drops when particle sizes become too

small (Jiangang et al., 2012). A comprehensive review by Trahar (1981) noted that chalcopyrite recovery by flotation decreased from ~95% to 50% when the median particle size decreased from 20 to 3 μm. This low recovery of fine mineral particles in flotation has been attributed to the low collision probability between fine particles and air bubbles (Dai et al., 2000; Miettinen et al., 2010; Trahar and Warren, 1976). As high-grade ores become depleted, low-grade deposits will increasingly become important resources for critical metals like copper. Unfortunately, target minerals in low-grade ores typically have finer grain size than those in high-grade ores, so fine grinding is required for liberation. This means that fine particle generation will become a challenging problem in the mining industry especially in conventional mechanical flotation circuits that do not operate efficiently with fine particles, resulting in the loss of valuable minerals to tailings.

One promising approach to improve the flotation recovery of fine particles is to increase their apparent size by agglomeration. Oil agglomeration—a technique to agglomerate fine particles under intense mixing conditions using oil as a bridging liquid—is economically promising because oil is relatively inexpensive. This method has been extensively studied for coal cleaning (Alonso et al., 1999; Slaghuis and Ferreira, 1987) and was recently applied to flotation of finely-ground sulfide minerals like molybdenite (Jiangang et al., 2012), sphalerite/galena (Song et al., 2001), and chalcopyrite (Hornn et al., 2020b). Although effective, the main drawback of oil agglomeration is its huge oil volume requirement of up to 0.1–1.0% and 5–10% for agglomeration-screening and agglomeration-flotation techniques, respectively (Laskowski and Ralston, 1992). To address this issue, several authors proposed using emulsified oil in the agglomeration step because emulsification reduced oil droplet size and oil dosage (Bensley et al., 1977; Hornn et al., 2020a; Sahinoglu and Uslu, 2013; van Netten et al., 2016). One previous work of the authors, for example, studied agglomeration-flotation of finely-ground chalcopyrite (D_{50} = 3.5 μm) using emulsified oil prepared by an ultrasonic homogenizer and confirmed that Cu recovery increased from ~50 to ~80% when agglomeration was operated at a high agitation speed (15,000 rpm) (Hornn et al., 2020b). At a low agitation speed (1000 rpm) during agglomeration, however, the agglomeration efficiency decreased due to instability of emulsified oil, so Cu recovery only slightly improved to ~60%. These previous results suggest that intense agitation is required to disperse oil droplets into water and maintain their small size, a high energy input prerequisite that makes the process costly and difficult to integrate into existing flotation circuits.

In a follow-up study of the authors, it was reported that stabilizing emulsified oil with surfactants eliminated the need for intense agitation during the agglomeration step, and thus, the process could be easily integrated into existing flotation circuits (Hornn et al., 2020c). Sodium dodecyl sulfate (SDS), for example, not only stabilized

oil droplets but also reduced the oil droplet size from ~3.9 to ~1.2 μm, limited the coagulation of emulsified oil in suspension, and improved Cu recovery from ~60% to ~98% even at low agitation strength.

Although promising, the applicability of surfactant-stabilized emulsified oil agglomeration-flotation to real sulfide ores remains unclear because the experiments were done using chalcopyrite and deionized (DI) water only. In other words, the effects of co-existing minerals and ions found in real flotation circuits on the efficiency of this technique remain unclear. Because Cu-sulfide ores contain not only chalcopyrite but also gangue minerals like quartz, it is important to understand how gangue minerals affect agglomeration-flotation using surfactant-stabilized oil emulsion. Moreover, significant amounts of Ca^{2+} are typically present during flotation because of (i) the use of pH modifiers (e.g., CaO and/or $Ca(OH)_2$) to depress pyrite floatability (Mu and Lauten, 2016), and (ii) the recirculation of process water containing Ca^{2+} (Dzingai et al., 2020; Ikumapayi et al., 2012). In addition, seawater, which contain about 400 ppm Ca^{2+}, is often used for the beneficiation of porphyry copper deposits located in semi-arid areas (e.g., Chile) due to the shortage of fresh water (Cisternas and Galvez, 2018; Tabelin et al., 2021b). This means that significant amounts of Ca^{2+} are found in flotation circuits, so its effect on the recovery of chalcopyrite via agglomeration-flotation using surfactant-stabilized emulsified oil should be investigated. In this paper, the effects of coexisting mineral (i.e., quartz) and ions (e.g., Ca^{2+} and other elements present in seawater) on agglomeration-flotation of finely-ground chalcopyrite using emulsified oil stabilized by anionic surfactant (SDS or potassium amyl xanthate (KAX)) were investigated.

2. Materials and Methods

2.1 Mineral samples

The chalcopyrite and quartz (99% of purity) used in this study were obtained from Copper Queen Mine, Arizona, USA and Wako Pure Chemical Industries Co., Ltd., Japan, respectively. The chalcopyrite sample was characterized by X-ray fluorescence (XRF) (EDXL300, Rigaku Corporation, Japan) and X-ray powder diffraction (XRD, Multiplex, Rigaku Corporation, Japan), and its chemical composition is summarized in Table. 1. XRD analysis indicated that chalcopyrite is the major mineral in the sample while actinolite ($Ca_2Mg_3Fe_2Si_8O_{22}(OH)_2$), quartz and sphalerite are found in minor amounts.

Table 1. Elemental compositions of chalcopyrite sample.

Elements	Cu	Fe	S	Zn	Si	Ca	Others
wt.%	26	27	26	0.8	6	2	12.2

The finely-ground chalcopyrite sample having median particle diameter (D_{50}) of 3.5 µm was prepared as follows: (i) crushing and grinding using a jaw crusher (1023-A, Yoshida Manufacturing co., Ltd, Japan) and a vibratory disc mill (RS100, Retsch Inc., Germany), (ii) screening of ground products to obtain a size fraction less than 75 µm, and (iii) additional grinding of–75 µm fraction in the vibratory disc mill. The quartz sample (particle dimeter of less than 500 µm) was ground separately in the same manner as the chalcopyrite sample. The median particle diameter (D_{50}) of the quartz sample was 6 µm. The particle size distribution of chalcopyrite and quartz samples used in this study were measured using a laser diffraction (Microtrac® MT3300SX, Nikkiso Co., Ltd., Japan) in water after sonication (Fig. 1).

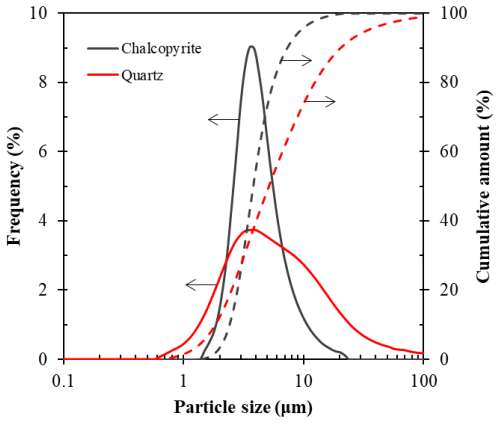

Figure 1. Particle size distributions of finely-ground chalcopyrite and quartz samples.

2.2 Methods

2.2.1 Preparation of emulsified oil with emulsifiers

Two types of emulsifiers—SDS and KAX (Tokyo Chemical Industry Co., Ltd., Japan)—were used in the experiments. These two emulsifiers were chosen because the former is the most commonly used emulsifier while the latter is a typical collector in flotation. First, 10 mL of kerosene (Wako Pure Chemical Industries, Ltd., Japan) and 40 mL of DI water were mixed with and without 0.1 g of emulsifier (SDS or KAX), the concentration of which is 2000 ppm. Afterwards, emulsification of the mixture was carried out using an ultrasonic homogenizer (ULTRA-TURRAX, IKA, Germany) for 60 s. After emulsification, oil droplet size was immediately analyzed by laser diffraction.

2.2.2 KAX conditioning and agglomeration

KAX conditioning and agglomeration were conducted on finely-ground chalcopyrite sample or chalcopyrite/quartz mixture (1:1, w/w). Before agglomeration, 20 g of sample (chalcopyrite or mixture) was

suspended in 400 mL of distilled water (with and without 400 ppm Ca^{2+} prepared using calcium chloride ($CaCl_2$, Wako Pure Chemical Industries, Ltd., Japan)), then the suspension was conditioned with the surface modifier, KAX (200 g $_{KAX}$/t $_{sample}$), for 5 min at 1000 rpm in the flotation cell (FT-1000, Heiko, Japan). Calcium concentration was decided based on the concentration of Ca^{2+} in process water (100–500 ppm) and seawater (~400 ppm) (Ikumapayi et al., 2012). After KAX conditioning, 15 L $_{kerosene}$/t $_{sample}$ of emulsified oil (with and without emulsifier) was added to the suspension, and agglomeration was carried out at 1000 rpm for 30 min in the flotation cell. The particle size of agglomerates was determined by a laser diffraction analyzer.

2.2.3 Flotation tests

Flotation was carried out immediately after agglomeration process. After 30 min agglomeration, 25 μL/L of frother (Methyl isobutyl carbinol, MIBC, Tokyo Chemical Industry Co., Ltd., Japan) was added, and the suspension was stirred for 3 min at 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 by XRF.

The classical first-order flotation kinetic model was applied to assess the influence of variables on the flotation kinetics:

$$R_t = R_\infty[1 - \exp(-kt)] \quad (1)$$

where R(t) and R_∞ are the recovery of chalcopyrite and/or quartz at time t and an infinite time, and k is the first-order rate constant. A nonlinear least square regression was used to calculate R_∞ and k from the best fit with experimental data. The obtained R_∞ and k were used for calculating the modified rate constant (Equation (2)) and the selectivity index of mineral I over mineral II (Equation (3)) (Xu, 1998):

$$K_M = R_\infty \cdot k \quad (2)$$

$$S.I.(I/II) = (K_M\ of\ mineral\ I)/(K_M\ of\ mineral\ II) \quad (3)$$

2.2.4 FT-IR measurements

The untreated and treated quartz samples with SDS and/or Ca^{2+} were analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, FT/IR-6200 HFV and ATR Pro One attachment equipped with a diamond prism, Jasco Analytical Instruments, Japan) to check whether SDS is adsorbed on its surface or not. Suspension containing quartz with and without 400 ppm Ca^{2+} were prepared. The suspensions were then conditioned with 2000 ppm SDS for 15 min in a beaker with magnetic stirrer at 300 rpm. Afterwards, the residue

was recovered from the suspension by filtration, dried in the vacuum oven at 40 °C for 24 h, and analyzed by ATR-FTIR.

3. Results and discussion

3.1 Agglomeration-flotation of finely-ground chalcopyrite using emulsified oil stabilized by SDS or KAX

3.1.1. Single-mineral system (chalcopyrite only)

The effects of anionic emulsifier (SDS or KAX) on agglomeration and flotation of finely-ground chalcopyrite were investigated. Agglomeration in this study consisted of two stages: (1) conditioning in the flotation cell with 200 g/t of KAX as a surface modifier rendering the chalcopyrite surface more hydrophobic; (2) agglomeration using 15 L/t of emulsified oil containing 0 or 2000 ppm of emulsifier (SDS or KAX). Figures 2 and 3 show the apparent particle size distribution after agglomeration and the size distribution of oil droplets with and without SDS or KAX. The results showed that when SDS or KAX were used, the size of agglomerate was larger (D_{50} = 9.2 μm (SDS) and 10.1 μm (KAX)) than that without any emulsifier (D_{50} = 4.6 μm). The droplets size of emulsified oil modified by emulsifiers was relatively smaller (D_{50} = 1.5 μm (SDS) and 1.1 μm (KAX)) than that without emulsifiers (D_{50} = 2.8 μm). When the size of oil droplets become smaller, the number of oil droplets in the cell increases. Because frequency of collision between the oil droplets and particles in agglomeration system is proportional to the number of oil droplets, it is reasonable to assume that the number of oil droplets attached on particle surface, induced by the collision of oil droplet and particle, become larger resulting in bigger agglomerate size when emulsified oil stabilized by emulsifier was used.

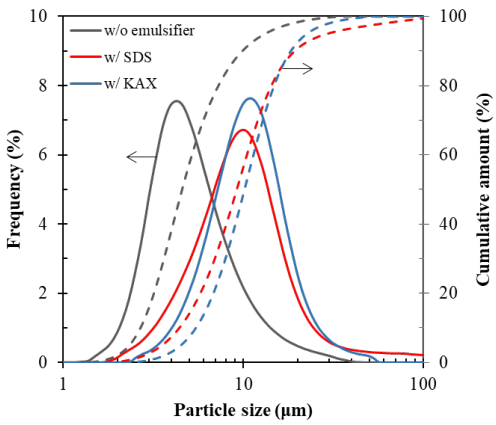

Figure 2. Particle size distribution of chalcopyrite after agglomeration using emulsified oil with and without emulsifier.

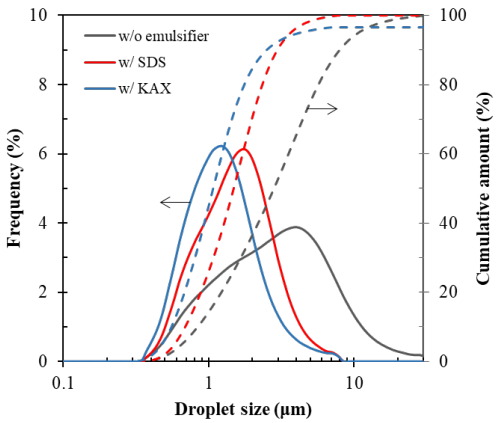

Figure 3. Oil droplet size distribution of emulsified oil after emulsification with and without emulsifiers.

Figure 4 shows the results of flotation of agglomerates generated using emulsified oil with and without emulsifier. As illustrated in Figure 4, Cu recovery after agglomeration with SDS or KAX was >97%, which was higher than that without emulsifier (~68%). This improved Cu recovery could be explained by the larger apparent size of agglomerates that improved collision probability between air bubbles and agglomerates (Fig. 2). The collision probability (P_c) between air bubbles and agglomerates is mathematically expressed as follows:

$$P_c = A\left(\frac{D_p}{D_b}\right)^n \tag{4}$$

where, D_p and D_b are the particle and bubble diameters, respectively, and A and n are empirical constants dependent on the flow regime (Yoon, 2000).

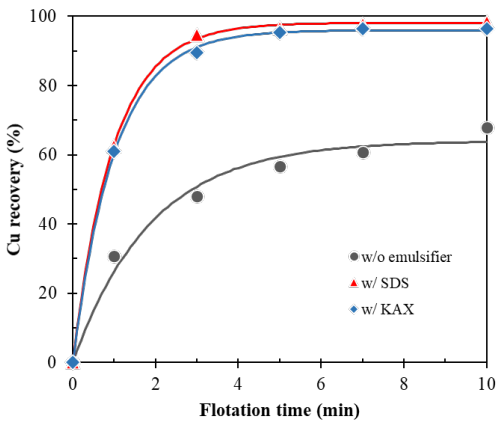

Figure 4. Effects of emulsifiers on the agglomeration-flotation of finely-ground chalcopyrite.

3.1.2. Mixed minerals system (chalcopyrite and quartz)

Agglomeration-flotation experiments of a chalcopyrite/quartz mixture using emulsified oil stabilized by SDS or KAX were conducted to check whether this technique can selectively recover finely-ground chalcopyrite or not. As shown in Fig. 5(a), Cu recovery improved when surfactant-stabilized emulsified oil was used during

agglomeration. After flotation for 10 min, Cu recovery increased from ~57% (without emulsifier) to ~81% (with SDS) and ~85% (with KAX). In contrast, both emulsifiers had minimal effects on Si recovery, indicating that they had little interactions with quartz (Fig. 5(b)). The calculated selectivity indices of Cu/Si obtained with no emulsifier, with SDS, and with KAX were also close to each other at around 11, 16, and 14, respectively. Based on these results, Cu recovery and separation efficiency were unaffected by the presence of quartz during agglomeration-flotation of finely-ground chalcopyrite using surfactant-stabilized emulsified oil.

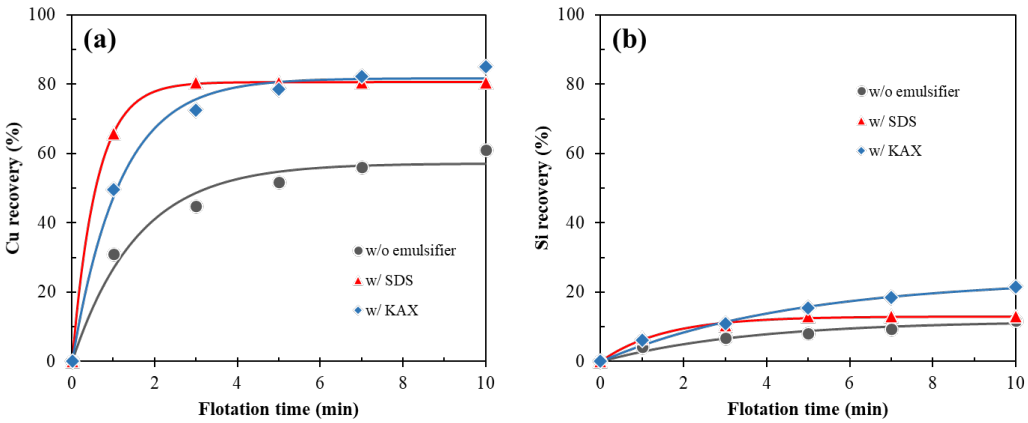

Figure 5. Effects of emulsifiers on the agglomeration-flotation of a chalcopyrite/quartz mixture: (a) Cu recovery and (b) Si recovery.

3.2. Effects of calcium ions on the agglomeration-flotation

3.2.1. Single-mineral system (chalcopyrite only)

The effects of Ca^{2+} on agglomeration-flotation using SDS or KAX as emulsifier were carried out in the absence and presence of 400 ppm of Ca^{2+}. As shown in Fig. 6(a), the presence of Ca^{2+} had insignificant effect on Cu recovery using SDS as an emulsifier. This result is further supported by the first-order kinetic model showing that ultimate recovery (R_∞) and rate constant (k) were almost the same with Ca^{2+} (R_∞ = ~100%; k = 1.1 min^{-1}) and without Ca^{2+} (R_∞ = 98%; k = 0.9 min^{-1}). Similarly, the flotation results obtained using KAX as an emulsifier were not affected by Ca^{2+} (Fig. 6(b)). Based on these results, Ca^{2+} had negligible effects on the recovery of chalcopyrite via agglomeration-flotation using emulsified oil stabilized by SDS or KAX.

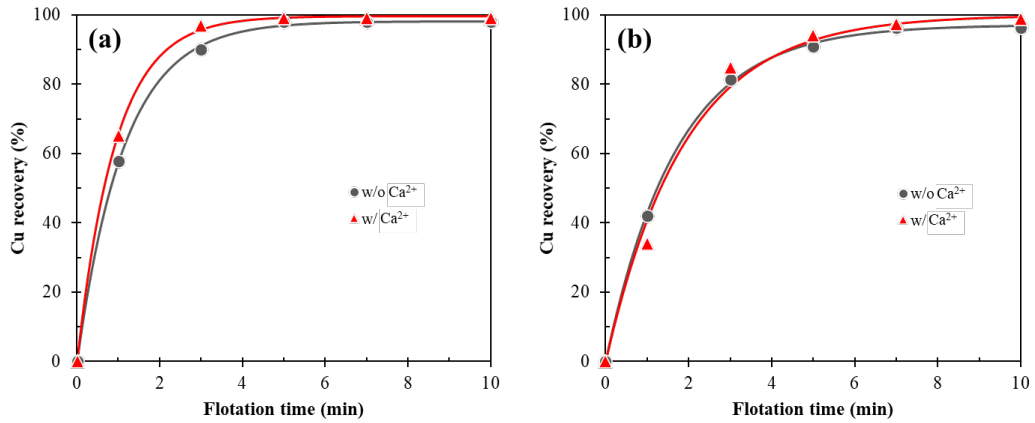

Figure 6. Copper recovery as a function of flotation time with and without 400 ppm Ca^{2+} during agglomeration-flotation of finely-ground chalcopyrite using (a) SDS or (b) KAX as emulsifier.

3.2.2. Mixed minerals system (chalcopyrite and quartz)

Agglomeration-flotation of the mixture of chalcopyrite and quartz was carried out using emulsified oil with SDS or KAX in the absence and presence of 400 ppm of Ca^{2+}. As shown in Fig. 7(a), the presence of Ca^{2+} lowered the ultimate Cu recovery from 81% to 44% when SDS was used as an emulsifier. In comparison, Ca^{2+} had negligible effect on Cu recovery when KAX was used (Fig. 6(b)). For Si recovery, the effects of Ca^{2+} were insignificant in both types of surfactants.

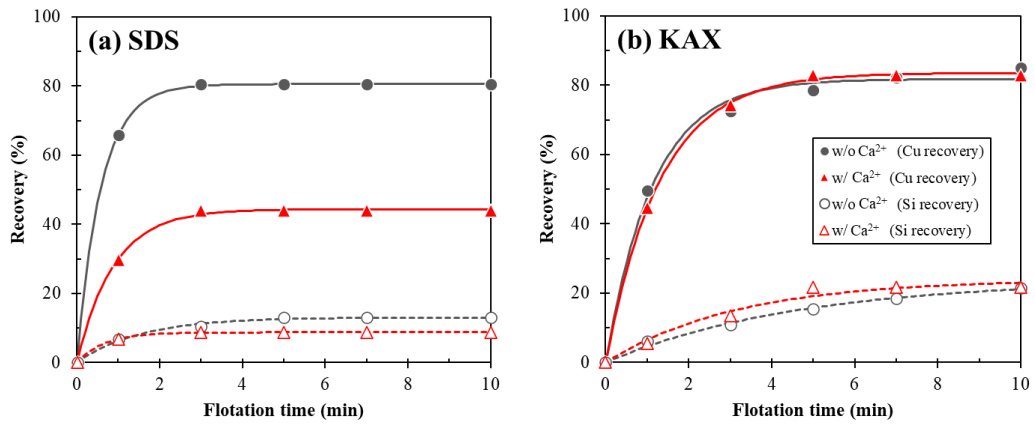

Figure 7. Copper and silicon recovery as a function of flotation time with and without 400 ppm Ca^{2+} during agglomeration-flotation of chalcopyrite and quartz mixture using (a) SDS or (b) KAX as emulsifier (Collector: KAX).

To elucidate the mechanisms suppressing the recovery of finely-ground chalcopyrite in the presence of quartz and Ca^{2+} when SDS is used, the size distribution of oil droplets in emulsion prepared with SDS was measured with and without quartz and Ca^{2+} (Fig. 8). As described in the previous section, oil droplet size of emulsified oil modified with SDS was smaller than those without SDS, resulting in high Cu recovery rate due to

higher collision probability. The median size of oil droplets with SDS slightly increased from 1.2 μm without Ca^{2+} to 1.5 μm with Ca^{2+} and were still smaller than that without emulsifier (~2.8 μm). This explains why Cu recovery rate in a single mineral system was high and unaffected by Ca^{2+} (Fig. 6(a)). When quartz was added together with Ca^{2+}, the median size of oil droplets increased to ~4.5 μm. In addition, a clear oil layer on top of kerosene/water emulsion was also observed when both quartz and Ca^{2+} are present with SDS (see photos in Fig. 8), suggesting that quartz and Ca^{2+} promoted kerosene droplets to coalesce into larger oil droplets. At concentrations above 50 ppm, Ca^{2+} has been reported to adsorb on minerals like quartz, silicates and iron-oxyhydroxides when their surface charge potentials are negative (Kou et al., 2016; Tabelin et al., 2012, 2017b, 2020; Wang et al., 2019). Meanwhile, SDS has a strong chemical affinity for Ca^{2+} (Subrahmanyam and Forssberg, 1990), so in the presence of quartz and Ca^{2+}, it is possible for SDS to be removed from solution, lower its concentration available to stabilize small oil droplets in solution, increase the size of oil droplets, and decrease the Cu recovery rate.

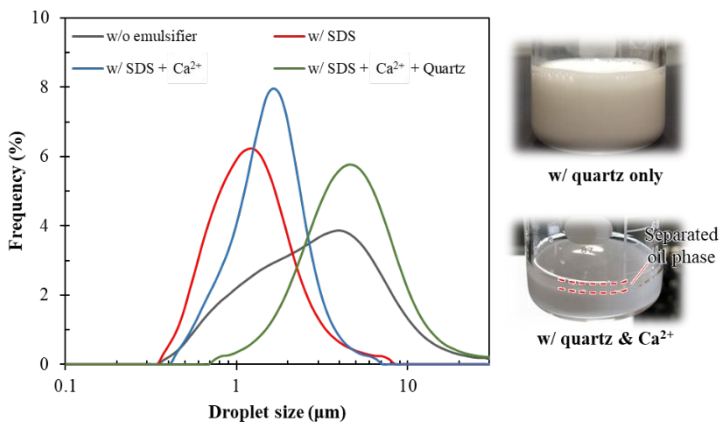

Figure 8. The size distribution of oil droplets with and without SDS, quartz and/or Ca^{2+}.

To verify this deduction, SDS adsorption on quartz with Ca^{2+} was further characterized by ATR-FTIR (Fig. 9). IR spectra of quartz treated with and without SDS showed only IR-signatures of quartz (i.e., Si—O symmetric bending and Si—O symmetric stretching) observed at 1165, 1089, 1059, 795, 778, 692, 520, and 451 cm^{-1} (Kumar and Rajkumar, 2014; Shahack-Gross, 1997; Tabelin et al., 2017b). In comparison, IR spectrum of quartz treated with SDS and Ca^{2+} showed additional peaks at 2957, 2917, 2872, 2849, 1245, 1211, 965, and 855 cm^{-1}. In the 3000–2800 cm^{-1} region, the absorption bands of hydrophobic tail of SDS (e.g., asymmetric and symmetric stretching bands of —CH_3 at 2957 and 2872 cm^{-1} and —CH_2— at 2917 and 2849 cm^{-1}) were observed. In addition, the absorption bands of hydrophilic sulfonate head (e.g., asymmetric and symmetric stretching bands of OSO_3^- at 1245, 1211, and 965 cm^{-1} and C—O—S stretching at 855 cm^{-1}) were detected in the 1300–800 cm^{-1} region (Gao and Chorover, 2010; Viana et al., 2012; Zeng et al., 2017). These results support our earlier deduction that SDS

adsorption onto quartz was promoted by Ca^{2+} and is a key process in the observed increase in oil droplet size when both quartz and Ca^{2+} are present.

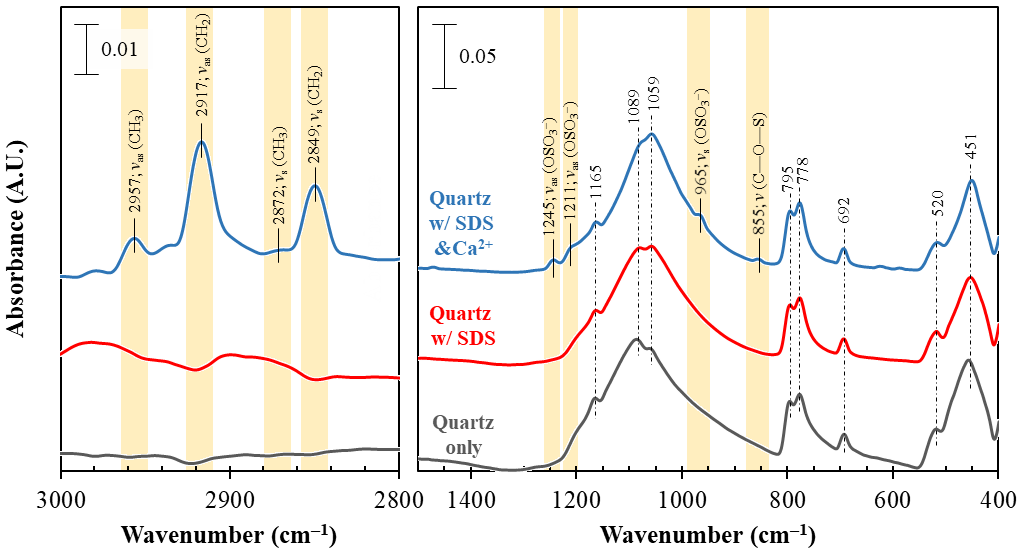

Figure 9. FT-IR spectra of quartz only, quartz treated with SDS with and without Ca^{2+}.

Based on these results, SDS cannot be used as an emulsifier when Ca^{2+} and quartz are present because fine oil droplets are destabilized and become larger, which decreased the efficiency of agglomeration-flotation to recover finely-ground chalcopyrite. Between the two surfactants, KAX is better when processing Cu-sulfide ores containing impurities like quartz via agglomeration-flotation in a high Ca^{2+} solution.

4. Conclusions

In this study, the effects of co-existing quartz and ions on agglomeration-flotation of finely-ground chalcopyrite using surfactant-stabilized emulsified oil were investigated. The findings of this study are summarized as follows:

1. Addition of emulsifiers (e.g., SDS or KAX) reduced the size of oil droplets, so it was effective in increasing the size of finely-ground chalcopyrite, resulting in improving Cu recovery.
2. The presence of either quartz or Ca^{2+} in the agglomeration-flotation process using emulsified oil stabilized by SDS or KAX had almost no effect on the recovery of chalcopyrite.
3. However, when both quartz and Ca^{2+} co-existed, Cu recovery obtained with SDS significantly decreased because of the adsorption of SDS on Ca^{2+}-activated quartz, causing the reduction of SDS amount available for emulsifying oil droplets.

4. On the other hand, KAX could improve the agglomeration-flotation of finely-ground chalcopyrite even in the presence of both quartz and Ca^{2+}, so KAX is a better emulsifier than SDS when processing Cu ores in a high Ca^{2+} solution.

Acknowledgments

This study was supported by a collaborative research program between Hokkaido University and Sumitomo Metal Mining Co., LTD.

CRediT authorship contribution statement

Vothy Hornn: Investigation, Writing – original draft.

Ilhwan Park: Conceptualization, Writing – original draft, Writing – review & editing, Visualization.

Mayumi Ito: Conceptualization, Writing – review & editing.

Hiromasa Shimada: Investigation.

Tomoki Suto: Investigation.

Carlito Baltazar Tabelin: Conceptualization, Writing – review & editing.

Sanghee Jeon: Conceptualization, Writing – review & editing.

Naoki Hiroyoshi: Conceptualization, Writing – review & editing, Supervision.

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