Flotation of Copper Ores with High Cu/Zn Ratio: Effects of Pyrite on Cu/Zn Separation and an Efficient Method to Enhance Sphalerite Depression

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Abstract: Porphyry copper deposits are important sources of copper and typically processed by flotation to produce copper concentrates. As mining areas become deeper, the amounts of impurities, such as sphalerite, can be increased in copper ores, so the appropriate depression of sphalerite floatability should be achieved to obtain saleable copper concentrates. In this study, the flotation behaviors of chalcopyrite and sphalerite in model samples mimicking copper ores with high Cu/Zn ratios (i.e., the ratio of chalcopyrite/sphalerite = 13:1) were investigated with zinc sulfate as a depressant for sphalerite. In addition, the effect of pyrite—a major gangue mineral in copper ores—on the depression of sphalerite floatability with zinc sulfate was examined. When sphalerite and chalcopyrite coexisted, the floatability of the former was effectively depressed by zinc sulfate (Zn recovery: <12%), whereas the presence of pyrite promoted the release of Cu due to the galvanic interaction between pyrite and chalcopyrite, which resulted in the elimination of the effectiveness of zinc sulfate for depressing sphalerite floatability (Zn recovery: >90%). Despite the presence of much higher amounts of chalcopyrite and pyrite than sphalerite, the application of nitrogen (N2) gas limiting the galvanic interaction between pyrite and chalcopyrite by reducing the dissolved oxygen (DO) concentration in the system effectively depressed the floatability of sphalerite (Zn recovery: <30%).

Keywords: flotation; porphyry copper deposits; chalcopyrite; sphalerite; pyrite; galvanic interaction

1. Introduction

Copper (Cu) has excellent electrical and thermal conductivities, high corrosion resistance, and outstanding malleability and ductility, which make it an essential component in various applications (e.g., building and construction, electrical and electronic products, industrial machinery and equipment, transportation, etc.) [1,2]. Moreover, copper is one of 17 critical metals used across a variety of clean energy generation and storage technologies, so its demand is projected to increase continuously to achieve a low-carbon future [3,4].
Porphyry copper deposits (PCDs) are the most important sources of copper worldwide, accounting for more than 60% of the annual production of copper and they constitute about 65% of known copper ore resources [5]. Ores excavated from these deposits are typically processed by flotation—a separation technique based on the difference in surface wettabilities of minerals—to recover copper sulfides (mostly chalcopyrite (CuFeS$_2$)) while removing associated gangue minerals such as pyrite (FeS$_2$) and quartz (SiO$_2$) [6,7]. After a multi-stage flotation of copper ores, the produced copper concentrates are processed via pyrometallurgical routes to produce copper metal [8].

To meet the high forecasted demand for copper, mining industries are finding it necessary to mine ores at increasingly deeper positions since copper reserves are finite and easy-to-mine ore deposits are dwindling [9–11]. In the case of PCDs, as mining areas become deeper laterally, it could be extended to the peripheral zone, where the amount of sphalerite (ZnS) increases compared to the ore zone [12]. When processing copper ores containing sphalerite via flotation, the depression of sphalerite floatability is an important issue for producing saleable copper concentrates because the impurities in copper concentrates have a negative impact on copper smelting and penalties are imposed for their treatment in the smelting process [13–15]. In general, Cu-Zn sulfide ores consisting of a Cu/Zn ratio of 0.4–1.1 (w/w) [16–20] are processed by a two-step flotation: (i) the selective flotation of Cu minerals while depressing sphalerite using zinc sulfate (ZnSO$_4$)—a sphalerite depressant—and other gangue minerals such as pyrite (FeS$_2$) and silicate minerals under alkaline conditions, and (ii) the recovery of sphalerite after its activation using copper sulfate (CuSO$_4$) [21,22]. However, it is unclear whether the conventional approach for Cu-Zn and Cu-Zn-Pb ores (i.e., depression of sphalerite using zinc sulfate) is effective in Cu/Zn separation in the processing of the copper ores excavated from PCDs with a much lower level of Zn (e.g., a Cu/Zn ratio of 7:1 (w/w)) compared to Cu-Zn or Cu-Zn-Pb sulfide ores [23]. Thus, this study investigated the flotation behaviors of chalcopyrite and sphalerite in ores with high Cu/Zn ratios such as PCDs. Specifically, flotation tests of a single mineral (chalcopyrite or sphalerite) and mixed minerals (chalcopyrite and sphalerite with and without pyrite—a major impurity of PCDs) were conducted. Finally, a method to enhance sphalerite depression in the flotation of the chalcopyrite–sphalerite–pyrite mixture was proposed.

2. Materials and Methods
2.1. Minerals and Reagents

Four types of minerals were used in this study: chalcopyrite (CuFeS$_2$, Copper Queen Mine, Cochise County, AZ, USA), sphalerite (ZnS, Kamioka Mine, Hida, Japan), pyrite (FeS$_2$, Huanzala Mine, Huanuco, Peru), and quartz (SiO$_2$, 99% purity, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan). They were characterized by X-ray fluorescence spectroscopy (XRF, EDXL300, Rigaku Corporation, Tokyo, Japan) and X-ray powder diffraction (XRD, MultiFlex, Rigaku Corporation, Tokyo, Japan). The chemical and mineralogical compositions of these samples are summarized in Table 1 and shown in Figure 1, respectively. The XRD pattern of chalcopyrite (Figure 1a) showed that it contains impurities such as ferro-actinolite (Ca$_2$(Fe$^{2+}$, Mg)$_5$Si$_8$O$_{22}$(OH)$_2$), sphalerite, and quartz, whereas those of sphalerite and pyrite (Figure 1b,c) showed that these samples are highly pure as indicated by the absence of peaks from common minerals such as quartz. The samples were ground using a vibratory disc mill (RS 200, Retsch Inc., Haan, Germany) and screened to obtain a size fraction of $\sim 75 + 38 \, \mu m$. For the flotation experiments, potassium isopropyl xanthate (PIPX, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) as a collector, methyl isobutyl carbinol (MIBC, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) as a frother, and zinc sulfate (ZnSO$_4$, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) as a depressant for sphalerite were used. Sodium hydroxide (NaOH, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) and sulfuric acid (H$_2$SO$_4$, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) were used as pH adjusters.
Table 1. The chemical composition of mineral samples based on XRF.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>28.3</td>
<td>0.5</td>
<td>32.8</td>
<td>17.7</td>
<td>11.0</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>–</td>
<td>54.0</td>
<td>6.4</td>
<td>32.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Pyrite</td>
<td>–</td>
<td>–</td>
<td>42.3</td>
<td>52.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Note: “–” denotes below detection limit.

Figure 1. XRD patterns of mineral samples: (a) chalcopyrite (CuFeS\textsubscript{2}), (b) sphalerite (ZnS), and (c) pyrite (FeS\textsubscript{2}). Note differences in the scales of the y-axes.

2.2. Experimental Methods

2.2.1. Flotation

Flotation experiments were carried out using an agitator-type flotation machine (ASH-F30H, Kankyo-kanri Engineering, Akita, Japan) equipped with a 400 mL flotation cell under the following conditions: pH, 9; temperature, 25 °C; impeller speed, 1000 rpm; air flow rate, 1 L/min. The mixtures of ground sphalerite, chalcopyrite, pyrite, and quartz (−75 + 38 µm) were used as model samples. Three types of model samples were prepared: (i) 18 g of chalcopyrite or sphalerite and 2 g of quartz, (ii) 13 g of chalcopyrite, 1 g of sphalerite, and 6 g of quartz, (iii) 13 g of chalcopyrite, 1 g of sphalerite, 4 g of pyrite, and 2 g of quartz. The ratios of Cu and Zn in model samples (ii) and (iii) were based on the Cu ore sample obtained from South America. Meanwhile, quartz was added to not only adjust the amount of the model samples to 20 g but also to check the entrainment of minerals into the froth products.

Prior to the flotation experiments, each mineral sample was deslimed with 300 mL of distilled water, respectively [24]. After desliming, each mineral sample was mixed and repulped to 400 mL with distilled water containing various concentrations of zinc sulfate (0, 1, or 10 kg/t) in the flotation cell and conditioned with MIBC for 3 min, and then the
flotation experiments were carried out based on the flowchart consisting of conditioning with PIPX for 3 min, followed by froth recovery for 3 min, which was repeated until the cumulative PIPX dosage reached 500 g/t (Figure 2). After flotation, froth and tailings were dried at 105 °C for 24 h and analyzed by XRF to determine the recovery of Cu, Zn, Fe, and Si. Some experiments were carried out in duplicate to ascertain that the differences observed were statistically significant.

Figure 2. Flotation procedure with sequential addition of the collector (PIPX).

2.2.2. Contact Angle Measurements

Contact angle measurements were carried out in a solution containing 50 ppm zinc sulfate, 5 ppm PIPX, and 20 µL/L MIBC at pH 9 and 25 °C. A small cuboid crystal of sphalerite and pyrite (~10 mm (w) × 10 mm (d) × 10 mm (h)) was obtained by cutting the sphalerite and pyrite mineral specimens using a diamond cutter and fixed inside a plastic holder using Technovit® non-conductive resin (Kulzer GmbH, Wehrheim, Germany). The mineral surface was polished with a polishing machine (SAPHIR 250 M1, ATM GmbH, Mammelzen, Germany) against silicon carbide papers of increasing grit numbers (P180 → P320 → P600 → P1200), followed by polishing with diamond suspensions (3 and 1 µm). After this, the polished mineral sample was cleaned using an ultrasonicator (W-113 MK-II, Honda Electronics Co., Ltd., Toyohashi, Japan) for 5 min to remove any residually attached diamond particles, washed thoroughly with distilled water, and then immediately used for the experiments. The sphalerite and pyrite surfaces were reacted with a solution containing 50 ppm zinc sulfate in the flotation cell and conditioned for 3 min after adding
the following reagents in sequence: 5 ppm PIPX and 20 µL/L MIBC. The concentrations of zinc sulfate, PIPX, and MIBC were the same as that used in the flotation experiments: 1 kg/t zinc sulfate, 100 g/t PIPX, and 20 µL/L MIBC, respectively. Bubble contact angles on the surfaces of sphalerite and pyrite were measured using the captive bubble method. A high-magnification digital microscope (VHX-1000, Keyence Corporation, Japan) and AutoCAD 2023 (Autodesk, Inc., San Rafael, CA, USA) were used to measure the bubble contact angles. The experiments were conducted in triplicates at various spots on the mineral surface to ascertain that the differences observed were statistically significant.

3. Results and Discussion
3.1. Single Mineral Flotation of Chalcopyrite or Sphalerite

To investigate the floatabilities of chalcopyrite and sphalerite, single mineral flotation experiments of chalcopyrite or sphalerite were carried out without Zn depressants. The Cu recovery in the absence of PIPX was 58% but significantly increased to 86% by adding 20 g/t PIPX because chalcopyrite has a high affinity with xanthate [25–28]. As the PIPX dosage increased from 20 to 200 g/t, the Cu recovery was mildly increased to 95% and remained constant after 200 g/t PIPX (Figure 3a). On the other hand, the Zn recovery was lower than 30% even at 500 g/t PIPX (Figure 3b) because sphalerite has a low affinity with xanthate, thus adding PIPX cannot improve the floatability of sphalerite [29].

![Figure 3. Results of single mineral flotation of (a) chalcopyrite or (b) sphalerite.](image)

3.2. Effects of Chalcopyrite on the Floatability of Sphalerite

To investigate how the flotation behaviors of chalcopyrite and sphalerite are affected when they coexist in the absence of Zn depressants, flotation tests of mixed minerals (chalcopyrite and sphalerite) were conducted with various PIPX dosages. Compared to the results of the single mineral flotation of sphalerite (Figure 4a), the mixed mineral flotation results show that sphalerite floated together with chalcopyrite, indicating that the coexistence of chalcopyrite improved the floatability of sphalerite (Figure 4b). To elucidate why the floatability of sphalerite increased in the presence of chalcopyrite, the mixture of sphalerite and chalcopyrite was conditioned in the flotation cell following the flotation procedure, and the surface of sphalerite was analyzed by a scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS, JSM-IT200TM, JEOL Co., Ltd., Tokyo, Japan). Figure 5 shows the SEM photomicrograph of sphalerite after conditioning with chalcopyrite and the corresponding elemental maps of Zn, S, Cu, Fe, and O. The map of Cu was detected on the surface of sphalerite after conditioning with chalcopyrite and associated with the maps of S and O, whereas that of Cu did not correspond to that of Fe. These indicate that sphalerite was activated by Cu$^{2+}$ dissolved from chalcopyrite, that is, a
CuS-like and/or Cu(OH)$_2$-like layer was formed on the surface of sphalerite as described in Equation (1) [30].

\[ \text{ZnS} + \text{Cu}^{2+} = \text{CuS} + \text{Zn}^{2+} \]  

(1)

Cu$^{2+}$ was dissolved from copper oxides formed on the surface of chalcopyrite and caused unwanted activation of sphalerite [31,32]. The copper activation of sphalerite caused an increase in the floatability of sphalerite because xanthate was readily adsorbed on the Cu-compounds present on the sphalerite surface as illustrated in Figure 6. Thus, the

![Figure 4](image-url)  

**Figure 4.** Flotation results of sphalerite in the absence of Zn depressants (a) without chalcopyrite and (b) with chalcopyrite. Note that the data at 100 g/t of collector in Figure 4b were absent due to the lack of froth amounts for the XRF.

![Figure 5](image-url)  

**Figure 5.** SEM photomicrograph of sphalerite after conditioning with chalcopyrite in the flotation cell with the corresponding elemental maps of Zn, S, Cu, Fe, and O.
increase in the floatability of sphalerite in the presence of chalcopyrite made the separation of sphalerite from chalcopyrite difficult without the aid of Zn depressants.

![Diagram of copper activation of sphalerite](image)

**Figure 6.** A schematic diagram of copper activation of sphalerite in the presence of chalcopyrite.

To depress the floatability of sphalerite in the presence of chalcopyrite, the effect of zinc sulfate, a conventional depressant, on sphalerite floatability was investigated. Figure 7 shows the flotation results of chalcopyrite and sphalerite with and without 1 kg/t zinc sulfate. As illustrated in Figure 7a, sphalerite was recovered as froth together with chalcopyrite in the absence of zinc sulfate; however, when zinc sulfate was added as a depressant for sphalerite, the Zn recovery was dramatically decreased to ~12% even at 500 g/t PIPX (Figure 7b). Meanwhile, the floatability of chalcopyrite was not affected by zinc sulfate; >90% of Cu recovery was achieved irrespective of the presence of zinc sulfate at >50 g/t PIPX (Figure 7). These results indicate that zinc sulfate is effective in depressing the floatability of sphalerite even in the presence of chalcopyrite. The possible mechanisms of how zinc sulfate could depress the floatability of sphalerite in the presence of chalcopyrite are as follows: (i) adsorption of zinc precipitates such as Zn(OH)$_2$ on the surface of sphalerite, rendering the surface of sphalerite hydrophilic where the adsorption of the collector is limited, (ii) inhibition of Cu activation by zinc precipitates, and/or (iii) deactivation of Cu-activated sphalerite via reverse reaction of Equation (1) [29,33].

![Flotation results](image)

**Figure 7.** Flotation results of sphalerite and chalcopyrite with zinc sulfate (a) 0 kg/t and (b) 1 kg/t. Note that the data at 100 g/t of collector in Figure 7a and those at 100 and 200 g/t of collector in Figure 7b were absent due to the lack of froth amounts for the XRF.
3.3. Effects of Pyrite on Sphalerite Floatability in the Presence of Chalcopyrite

Copper ores contain not only valuable minerals such as chalcopyrite and sphalerite but also gangue minerals such as pyrite—a major gangue mineral of sulfide ores. The presence of pyrite has been reported to have a significant impact on the flotation behavior of minerals [34–39]. Although the addition of zinc sulfate improved the flotation separation of chalcopyrite from the chalcopyrite–sphalerite binary mixed minerals system, it is necessary to further investigate whether zinc sulfate would also be effective in the presence of pyrite. To clarify this, flotation tests of mixed minerals consisting of chalcopyrite, sphalerite, and pyrite were conducted with zinc sulfate (Figure 8). When pyrite coexisted with sphalerite and chalcopyrite, the recovery of Zn was dramatically increased (Figure 8b) compared to that in the absence of pyrite (Figure 8a). Though the amount of zinc sulfate increased from 1 to 10 kg/t, the floatability of sphalerite was high (>80%) (Figure 8c). These results indicate that pyrite inhibits the depressive effect of zinc sulfate toward sphalerite in the presence of chalcopyrite, which could be attributed to two possible mechanisms: (i) the reduced amount of zinc precipitates adsorbed onto the sphalerite surface by pyrite is not the reason for losing the depressive effect of zinc sulfate toward sphalerite.

3.4. Mechanisms of Losing the Depressive Effect of Zinc Sulfate toward Sphalerite in the Presence of Both Pyrite and Chalcopyrite

3.4.1. Effects of Pyrite on the Hydrophilicity of Sphalerite

One of the considerable mechanisms of depressing sphalerite floatability with zinc sulfate may be due to the adsorption of zinc precipitates such as Zn(OH)₂ on the surface sphalerite, rendering its surface hydrophilic, thus limiting the adsorption of a collector [29,33]. If Zn precipitates are adsorbed onto the surface of not only sphalerite but also pyrite, it would result in reducing the amount of Zn precipitates adsorbed onto the surface of sphalerite, and thus the depression of sphalerite floatability by zinc sulfate may not be achieved. To investigate whether pyrite affects the adsorption of Zn precipitates on sphalerite, the contact angles of sphalerite in the absence and presence of pyrite were measured using a small cuboid crystal of sphalerite and pyrite under the same conditions as the flotation experiments; 50 ppm zinc sulfate, 5 ppm PIPX, and 20 μL/L MIBC at pH 9 and 25 °C. As shown in Figure 10, the difference in the contact angles between the sphalerite and air bubble in the absence and presence of pyrite was almost negligible, indicating that the reduced amount of Zn precipitates adsorbed onto the sphalerite surface by pyrite is not the reason for losing the depressive effect of zinc sulfate toward sphalerite.
Figure 9. A schematic diagram of two possible mechanisms for why pyrite inhibits the depression of sphalerite with zinc sulfate in the presence of chalcopyrite: (i) the reduced amount of zinc precipitates adsorbed onto the surface of sphalerite due to the presence of pyrite whose surface also attracts zinc precipitates, (ii) galvanic interaction between chalcopyrite and pyrite that promotes the anodic half-cell reaction of chalcopyrite, releasing more Cu$^{2+}$ into the aqueous solution.

Figure 10. The contact angle of sphalerite in the absence and presence of pyrite.

3.4.2. Effects of the Galvanic Interaction between Chalcopyrite and Pyrite on the Floatability of Sphalerite

Pyrite is known to strongly affect the floatability of target minerals due to their electrochemical interactions with each other [40,41]. When pyrite and chalcopyrite are in contact, they form a galvanic cell where the former (i.e., pyrite) acts as a cathode due to a higher rest potential, whereas the latter (i.e., chalcopyrite) having a lower rest potential
behaves as an anode [42]. The formation of a galvanic cell is well-known to enhance the dissolution of minerals or metals that act as anodes while it protects the cathode from corrosion [43–48]. That is, the dissolution of chalcopyrite as an anodic reaction (Equation (2)) is accelerated via the galvanic interaction, whereas on the surface of pyrite, the reduction reaction of dissolved oxygen (DO) as a cathodic reaction (Equation (3)) occurs [49].

\[
\text{CuFeS}_2 = \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}^0 + 4e^- \quad (2)
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \quad (3)
\]

This indicates that the amount of dissolved Cu\(^{2+}\) in the flotation pulp would increase due to the galvanic interaction between chalcopyrite and pyrite, and the degree of sphalerite activation by Cu\(^{2+}\) would also be enhanced, resulting in the difficulty in depressing sphalerite floatability by zinc sulfate. Therefore, the enhanced dissolution of chalcopyrite due to the galvanic interaction with pyrite is one of the possible mechanisms that inhibits the ability of zinc sulfate to depress sphalerite floatability in the presence of both pyrite and chalcopyrite.

To investigate the effect of the galvanic interaction between chalcopyrite and pyrite on the floatability of sphalerite, mixed minerals flotation experiments of chalcopyrite, sphalerite, and pyrite with 1 kg/t zinc sulfate were carried out, where the amount of DO in the flotation pulp was limited. DO is an essential reactant for the galvanic interaction to take place, and thus the effect of the galvanic interaction between chalcopyrite and pyrite on the floatability of sphalerite can be clarified by conducting flotation experiments in the absence and presence of oxygen in the system. For the flotation under anaerobic conditions, ultrapure nitrogen (N\(_2\)) gas (99.99%) was introduced to distilled water for 15 min before conditioning to remove DO from the flotation pulp, and froth recovery was also conducted by injecting N\(_2\) gas instead of air to limit the appearance of oxygen in the system. As shown in Figure 11, the recovery of Zn was dramatically decreased under anaerobic conditions; at 100 g/t PIPX, Zn recoveries under aerobic and anaerobic conditions were ~90% and ~20%, respectively. As confirmed in Figure 8c, when the galvanic interaction between pyrite and chalcopyrite occurred, it was impossible to depress the floatability of sphalerite even with the addition of 10 kg/t zinc sulfate. These results indicate that the effects of the galvanic interaction between pyrite and chalcopyrite on sphalerite floatability were minimized when the amount of DO in the flotation pulp was limited by employing N\(_2\) gas, resulting in effective depression of sphalerite floatability in the presence of both chalcopyrite and pyrite. Therefore, the galvanic interaction between pyrite and chalcopyrite would be the most likely mechanism for pyrite inhibiting the depression of sphalerite floatability with zinc sulfate in the presence of chalcopyrite.

![Figure 11](image-url)  
**Figure 11.** Flotation results of chalcopyrite, sphalerite, and pyrite in the presence of 1 kg/t zinc sulfate (a) with air and (b) with N\(_2\) gas.
3.5. A Proposed Method to Efficiently Depress Sphalerite in Flotation of Cu Ores with a High Cu/Zn Ratio

Figure 12 shows the proposed method to efficiently depress sphalerite in the flotation of Cu ores with a high Cu/Zn ratio. When chalcopyrite and pyrite coexisted with sphalerite, zinc sulfate lost its ability to depress sphalerite floatability (Figure 8). This is most likely due to the galvanic interaction between chalcopyrite and pyrite that enhances the dissolution of chalcopyrite, and thus the amount of dissolved Cu$^{2+}$ in the flotation pulp would be increased. As a result, Cu activation of sphalerite could be enhanced, so zinc sulfate becomes inefficient in depressing sphalerite (Figure 9ii). The cathodic reaction, i.e., the reduction of DO occurring on the pyrite surface (Equation (3)), is the first step of the galvanic interaction, and as a result, zinc sulfate becomes effective in depressing sphalerite floatability. As the ratio of pyrite to chalcopyrite in copper ores increased, the galvanic interaction between them would become more intensive, which negatively would affect the floatability of chalcopyrite [50]. Copper ores contain not only chalcopyrite but also other copper sulfide minerals (e.g., chalcocite and bornite), which could also form a galvanic cell with pyrite due to their lower rest potential than pyrite [51]. Therefore, the application of N$_2$ gas to limit the galvanic interaction of copper sulfide minerals with pyrite could be a promising method to achieve Cu/Zn separation by effectively depressing sphalerite floatability in the actual processing of copper ores containing many mineralogical species such as several copper sulfide minerals and pyrite.

![Figure 12](image_url)

**Figure 12.** A schematic diagram of the proposed efficient method to depress sphalerite in flotation of Cu ores containing sphalerite and pyrite with zinc sulfate.

4. Conclusions

In this paper, the flotation behaviors of chalcopyrite and sphalerite in model samples mimicking Cu ores with high Cu/Zn ratios were investigated. The recovery of Zn was low in the single mineral flotation of sphalerite, but it dramatically increased when chalcopyrite coexisted due to the activation of sphalerite by Cu$^{2+}$ dissolved from chalcopyrite. The addition of zinc sulfate successfully depressed the sphalerite floatability; however, the presence of pyrite inhibited its ability to depress sphalerite floatability most likely due to the galvanic interaction between pyrite and chalcopyrite. The application of N$_2$ gas that limits the galvanic interaction between pyrite and chalcopyrite by reducing the DO concentration in the system is an effective option to depress sphalerite with zinc sulfate, although the amounts of chalcopyrite and pyrite are much higher than sphalerite. Typically, copper ores contain not only chalcopyrite but also other copper sulfide minerals (e.g., chalcocite and bornite), which could form a galvanic cell with pyrite. Therefore, the application of N$_2$ gas to limit the galvanic interaction of copper sulfide minerals with pyrite could be a promising method to achieve Cu/Zn separation by effectively depressing sphalerite floatability in...
the actual processing of copper ores containing many mineralogical species such as several copper sulfide minerals and pyrite.

**Author Contributions:** Conceptualization, K.A., M.I. and K.H.; methodology, K.A., M.I. and I.P.; investigation, K.A. and N.O.; data curation, S.J., T.S., T.O. and R.S.M.; writing—original draft preparation, K.A.; writing—review and editing, M.I., N.O., S.J., I.P., K.H., T.K., T.T., T.S., T.O., R.S.M. and N.H.; visualization, K.A.; supervision, T.K. and N.H.; project administration, T.T. and K.S.; funding acquisition, M.I. All authors have read and agreed to the published version of the manuscript.

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