Effect of dextrin on flotation separation and surface properties of chalcopyrite and arsenopyrite

Jingshen Dong, Quanjun Liu and S. H. Subhonqulov

ABSTRACT

The flotation separation and mechanism of dextrin on chalcopyrite and arsenopyrite surface were investigated using micro-flotation tests, zeta potential measurements, infrared spectroscopy, contact angle measurement and surface adsorption experiments. The micro-flotation test showed that dextrin had obvious inhibitory effect on arsenopyrite flotation, but had no inhibitory effect on chalcopyrite flotation. After treating the surface of arsenopyrite with dextrin, the infrared spectra showed that new characteristic peaks, indicating that chemical adsorption and significant interaction between dextrin and arsenopyrite particles. Zeta potential measurements, contact angle measurement and surface adsorption experiments showed that the selective adsorption of dextrin added a large number of hydrophilic groups to the surface of arsenopyrite, but had little effect on chalcopyrite. In addition, the macromolecular chain structure of dextrin may hinder the attachment of collector molecules to arsenopyrite. The combined effect of these two aspects makes the arsenopyrite treated with dextrin lose its hydrophobicity and enables the separation of chalcopyrite and arsenopyrite.

Key words | arsenopyrite, chalcopyrite, dextrin, flotation, separation

HIGHLIGHTS

- The flotation separation of chalcopyrite and arsenopyrite was enabled by dextrin.
- The effect of dextrin on the surface properties of arsenopyrite is greater than on chalcopyrite.
- Dextrin adsorbed onto the arsenopyrite surface by both physical and chemical adsorption.

INTRODUCTION

Copper is a common metal, and it is indispensable in electronic technology, the construction industry, mechanical processing, light industry and other fields. Chalcopyrite (CuFeS₂) is an important copper-bearing mineral, accounting for 70% of the Earth’s copper resources (Córdoba et al. 2008; Li et al. 2013). However, sulfide ores always contain other sulfide and nonsulfide minerals (Huang et al. 2012). An example is chalcopyrite, which usually coexists with arsenopyrite (Rincon et al. 2019), galena (You et al. 2013), sphalerite (Piao et al. 2014), and pyrite (Chen et al. 2010). Among them, arsenic is an inorganic pollutant that has a series of adverse effects on the water environment and human health (Long et al. 2014). In order to prevent discharge into the water, arsenic pollution must be strictly controlled in the process of mineral processing.

At present, the most commonly used technology to separate copper-bearing ore from other ores is froth flotation (Liu et al. 2017), and separation of different ores is a common problem in flotation process. However, in the flotation separation of chalcopyrite and arsenopyrite, it is difficult to separate chalcopyrite and arsenopyrite because of the similar floatability of chalcopyrite and arsenopyrite and the activation of copper ions on arsenopyrite (Yu...
Thus, the separation of chalcopyrite and arsenopyrite requires the use of selective depressant, collectors and surfactant (Deng et al. 2017a; Huang et al. 2020b), which has gained more and more attention. Inorganic compounds have long been used as the main depressant of sulfide ore separation, but caused many problems, such as poor selectivity, high dosage, and environmental problems (Mu et al. 2016; Deng et al. 2017b; Huang et al. 2020a).

In recent years, some organic depressants, such as tannin, starch, dextrin, locust bean gum, and polyacrylamides, have been widely used in flotation (Wiese et al. 2008). The reasons for their wide use are their many sources, biodegradability and relatively low price (Bicak et al. 2007; Han et al. 2019). Dextrin naturally degrades to carbon dioxide and water. Hence, natural, bio-degradable, non-toxic agents such as dextrin are gaining in importance and hold promise to function as a selective depressant (López Valdivieso et al. 2004). Dextrin is obtained from starch by partial thermal degradation under acidic conditions. The treatment leads to the breakdown of dextrin macromolecules, resulting in smaller molecules that are more branched (Braga et al. 2014; Pereira et al. 2018).

In order to reduce the pollution of arsenic-containing minerals to the water environment, in this study, the effect of dextrin on the flotation behavior and surface properties of chalcopyrite and arsenopyrite was investigated using sodium butyl xanthate (NaBX) as the collector through micro-flotation tests and zeta potential measurements, infrared spectroscopy, contact angle measurement and surface adsorption experiments.

**EXPERIMENTAL**

**Materials and reagents**

The chalcopyrite and arsenopyrite samples used in this study were sourced from Yunnan province, China. The ore samples were crushed and picked over by hand to remove all other gangue minerals. The lumps of chalcopyrite and arsenopyrite were then pulverized into smaller particle sizes and screened to separate the different size fractions. The X-ray diffraction pattern of the mineral samples is shown in Figure 1; the peaks only correspond to the crystal phase of chalcopyrite and arsenopyrite. The chemical analysis (Table 1) also shows that the purity of the two mineral samples was relatively high. A size fraction of smaller than 74 μm and larger than 38 μm was used in the mineral flotation test and surface adsorption experiments. A portion

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**Figure 1 |** X-ray diffraction patterns of chalcopyrite (a) and arsenopyrite (b).

**Table 1 |** Chemical composition of chalcopyrite and arsenopyrite (mass fraction, %)

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>S</th>
<th>Cu</th>
<th>As</th>
<th>SiO₂</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>30.31</td>
<td>35.72</td>
<td>33.18</td>
<td>0.03</td>
<td>0.11</td>
<td>0.09</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>34.20</td>
<td>19.01</td>
<td>0.21</td>
<td>45.24</td>
<td>0.13</td>
<td>0.03</td>
<td>0.12</td>
<td>0.07</td>
</tr>
</tbody>
</table>
with a particle size smaller than 5 \( \mu \text{m} \) was used for the zeta potential, and the infrared spectroscopy analysis.

NaBX (Zhuzhou Flotation Reagents Ltd, China) was used as the collector for chalcopyrite and arsenopyrite. Dextrin (Sinopharm Group Chemical Reagent Co., Ltd) was used as the depressant for arsenopyrite. Terpenic oil (Zhuzhou Flotation Reagents Ltd, China) was used as the frother. The pH value of the pulp was adjusted with hydrochloric acid and sodium hydroxide solutions. Except for commercial NaBX, all other reagents were analytical grade. Pure deionized water was used in all experiments.

**Micro-flotation tests**

A small-scale mechanical agitation flotation machine was used for the micro-flotation experiments at room temperature. 2 g of pure mineral sample was mixed with a small amount of deionized water and treated with an ultrasonic wave for 3 min, the supernatant was removed, and the mineral sample was mixed with 40 mL deionized water and placed in the flotation cell. Then the pH values were adjusted to the specified value by adding dilute HCl or NaOH solutions. Specified concentrations of dextrin solution were added to the ore pulp to condition for 3 min (if necessary). Then, the pulp was conditioned with NaBX for 5 min, and terpenic oil for 1 min; the rate of agitation was 1,500 rpm. The 3 min flotation time was used for all the micro-flotation experiments.

After the flotation experiments, the flotation recovery was calculated from the mass of the dried product after filtration, drying, and weighing. All experiments were repeated three times, and the averages were recorded as flotation recovery. The mixed flotation of chalcopyrite and arsenopyrite was selective separation of chalcopyrite and arsenopyrite with 1:1 artificial ratio of flotation mineral and dextrin as the inhibitor. The experimental process for the mixed mineral flotation was the same as that for the single mineral flotation.

**Zeta potential measurements**

The zeta potential of mineral samples were measured by a zeta potential analyzer (Zetasizer Nano S90) in 1 \( \times \) 10\(^{-3} \) mol/L KNO\(_3\) background electrolyte solution. The KNO\(_3\) solution was used to maintain the ionic strength of the mineral suspension. The mineral suspensions (0.01% mass fraction) of chalcopyrite and arsenopyrite were dispersed in electrolyte solutions. After adding the required flotation reagent, the pH of the resulting suspension was adjusted to specific values using hydrochloric acid or sodium hydroxide, and stirred for a certain time using a magnetic stirring apparatus. After the suspension was left to settle for 5 min, the fine mineral particles were transferred to the measurement vessel and the zeta potential was determined at room temperature. Each sample was measured three times and the average value was recorded.

**Contact angle measurement**

The contact angles were measured with a video contact angle measuring instrument (JY-82B, Chengde, China). Pure mineral block samples were used for testing. Before each test, the samples are manually polished with 100 mesh, 800 mesh, 1,500 mesh and 2,000 mesh silicon carbide sandpaper to expose a fresh surface of the sample. Before each contact angle measurement, the crystal samples were rinsed with deionized water, followed by blow-drying. After the mineral surface interacted with the dextrin, the surface is quickly dried, and then transferred to the contact angle measuring instrument platform. The contact angle of the mineral surface was measured by the droplet method. At least three drops were released and measured for each sample and the average value recorded.

**Adsorption experiments**

2 g pure mineral samples was mixed with 40 mL deionized water and the pH of the solution was controlled at 8. Dextrin solution was then added as necessary and the mixture was stirred for 3 min. Then the pulp was mixed with 10 mg/L NaBX solution and conditioned for a specific time. After the specific time, about 10 mL of the supernatant was taken by dropper and centrifuged for 3 min in a centrifuge at 2,000 rpm. After centrifugation, the clear solution of the upper layer was poured out, and the absorbance test was carried out using the spectrophotometer (UV-765, Shanghai, China). The adsorbed amounts of NaBX were expressed using the following equation:

\[
\Gamma = \frac{(C_0 - C)V}{sm}
\]

where \( \Gamma \) is the amount of NaBX adsorbed onto the chalcopyrite or arsenopyrite surface, \( C_0 \) is the initial NaBX concentration, \( C \) is the final NaBX concentration, \( V \) is the total volume of the flotation solution, \( m \) is the weight of the chalcopyrite or arsenopyrite sample, \( s \) is the specific surface area of the chalcopyrite or arsenopyrite sample.
**Infrared spectroscopic analysis**

The arsenopyrite samples were treated by the following method. Firstly, the arsenopyrite samples (smaller than 5 μm) were treated with ultrasonic wave for 3 min to remove the oxide film on the mineral surface, and then a specific weight of the mineral was placed into the beaker. After adjusting the pH value, an appropriate amount of dextrin solution was added and stirred at room temperature for 3 hours. After several washes and filtration, the samples were dried in a vacuum drying chamber and prepared for infrared spectroscopy measurements. Infrared spectroscopy spectra measurement used a Fourier-transform infrared spectrometer (Nicolet iS10, Thermo Fisher Scientific, USA), using scanning wave number ranges from 400 to 4,000 cm⁻¹.

**RESULTS AND DISCUSSION**

**Micro-flotation tests study**

**Single mineral flotation study**

At pH = 8, the relationship between the recovery of flotation and the concentration of NaBX was determined (Figure 2). When the NaBX concentration was 10 mg/L, the flotation recovery of arsenopyrite was 72.33%. With the increase of NaBX concentration, the flotation recovery of arsenopyrite increased slightly and stabilized at about 87% when the NaBX concentration exceeded 30 mg/L. NaBX concentration changes had no significant effect on the floatability of chalcopyrite. Regardless of NaBX concentration, the flotation recovery of chalcopyrite always exceeded 96% at this pH value. Even in the absence of NaBX, chalcopyrite still had a higher flotation recovery. This result indicates that chalcopyrite exhibits good floatability, which is consistent with the results of previous studies (Fuerstenau & Sabacky 1984). At the concentration of NaBX of 10 mg/L, both chalcopyrite and arsenopyrite showed high flotation recovery. With the increase of the collector concentration, the flotation separation of chalcopyrite and arsenopyrite became more difficult. Therefore, it is necessary to add a selective depressant to separate chalcopyrite and arsenopyrite. In the subsequent flotation test, the concentration of NaBX was maintained at 10 mg/L.

*Figure 3* shows the effect of dextrin concentration on the flotation performance of chalcopyrite and arsenopyrite. The recovery of chalcopyrite did not change significantly with the increase in dextrin concentration. However, the presence of dextrin had a significant effect on arsenopyrite. When the dextrin concentration was 30 mg/L, the flotation recovery of arsenopyrite decreased to 68.10%; when the dextrin concentration increased to 200 mg/L, the flotation recovery of arsenopyrite was only 29.86%, and the flotation recovery of chalcopyrite was still 92.11%. This shows that dextrin has an obvious depressive effect on arsenopyrite, but has no depressive effect on chalcopyrite. Therefore, dextrin is an effective
depressant for the flotation separation of chalcopyrite and arsenopyrite.

**Mixed mineral flotation study**

Further, a mixed flotation experiment of chalcopyrite-arsenopyrite (1:1 mass ratio of chalcopyrite and arsenopyrite) was carried out to demonstrate the selective separation of chalcopyrite and arsenopyrite using dextrin as the depressant. According to the single mineral flotation, the suitable flotation conditions were: dextrin 100 mg/L, NaBX 10 mg/L, and pH = 8. The flotation recovery of chalcopyrite and arsenopyrite in concentrate and tailings after flotation of mixed minerals are shown in Table 2. It can be seen from Table 2 that the flotation recovery of chalcopyrite in concentrate products is about 71%, while the flotation recovery of arsenopyrite is less than 29%. Compared with the results of single mineral flotation, the flotation recovery of chalcopyrite with mixed minerals decreased slightly.

**Zeta potential measurement results**

The main function of the flotation agent is to adsorb onto the mineral/solution interface, thereby affecting the surface electrical properties of the mineral (Feng et al. 2019). The zeta potential of chalcopyrite and arsenopyrite under different dextrin concentrations was determined using NaBX as a collector in a wide pH range (Figure 4). As in previous studies, the isoelectric point of the chalcopyrite was obtained at pH = 6. As shown in Figure 4(a), the presence or absence of dextrin has no significant effect on the zeta potential of chalcopyrite, indicating that the interaction is weak. Regardless of the presence or absence of dextrin, the tendency of NaBX to reduce the zeta potential of chalcopyrite is similar, indicating that dextrin has no obvious effect on the adsorption of chalcopyrite to xanthate and has no obvious effect on its hydrophobicity. Figure 4(b) shows that the zeta potential increases, after the interaction of arsenopyrite with dextrin, indicating that dextrin can adsorb onto its surface. In the absence of dextrin, NaBX can be adsorbed onto the mineral surface, thereby reducing the zeta potential, and in the presence of dextrin, the zeta potential hardly decreased, indicating that the presence of dextrin reduces the adsorption of xanthate onto the mineral surface. Zeta potential measurement results show that dextrin and arsenopyrite can strongly interact, hindering the adsorption of xanthate, thereby reducing the floatability of arsenopyrite minerals.

In the mixed arsenopyrite-chalcopyrite system, dextrin was selectively adsorbed on the surface of arsenopyrite to achieve flotation separation of chalcopyrite and

<table>
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<th>Products</th>
<th>Ratio (wt%)</th>
<th>Recovery (%) CuFeS₂</th>
<th>FeAsS</th>
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</thead>
<tbody>
<tr>
<td>Concentrate</td>
<td>51.6</td>
<td>71.12</td>
<td>28.88</td>
</tr>
<tr>
<td>Tailing</td>
<td>48.4</td>
<td>28.88</td>
<td>71.12</td>
</tr>
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</table>

*Table 2* | Flotation results for mixed minerals (1:1 mass ratio of chalcopyrite and arsenopyrite) (100 mg/L dextrin, 10 mg/L NaBX, pH = 8)
arsenopyrite. This is consistent with the results of the micro-flotation test research.

Contact angle experiment results

The contact angle is the most intuitive characterization to judge the hydrophilicity/hydrophobicity of minerals. The larger the contact angle is, the stronger the hydrophobicity of minerals is. Figure 5 shows that both chalcopyrite and arsenopyrite treated with deionized water have high hydrophobicity, which is consistent with the results of the micro-flotation test. After dextrin (20 mg/L) treatment, the contact angle of chalcopyrite did not significantly change, while the contact angle of arsenopyrite decreased from 69.3° to 28.9°, and the surface of arsenopyrite changed from being hydrophobic to being hydrophilic. The results of the contact angle experiment show that the selective adsorption of dextrin to arsenopyrite is stronger than that of chalcopyrite, which reduces the hydrophobicity of arsenopyrite.

Adsorption experiment results

Because the addition of dextrin greatly reduced the floatability of arsenopyrite, the floatability of mineral particles was mainly affected by the amount of NaBX adsorbed onto the mineral surface. The amounts of NaBX adsorbed onto mineral surfaces in the presence and absence of dextrin were investigated through adsorption experiments on the surfaces of chalcopyrite and arsenopyrite. As shown in Table 3, in the absence of dextrin, the adsorption capacity of arsenopyrite to NaBX was similar to that of chalcopyrite. However, in the presence of dextrin, the adsorption capacity of arsenopyrite to NaBX decreased significantly. When the dextrin treatment time was 4 min, the adsorption amount of NaBX on the arsenopyrite surface was only 0.135 mg/m², whereas that of chalcopyrite was 0.216 mg/m². With the increase of time, the amount of NaBX adsorbed on the surface of chalcopyrite was not affected significantly. These results show that dextrin clearly depressed the adsorption of NaBX onto the arsenopyrite surface, but not onto the chalcopyrite surface. Dextrin is selectively adsorbed onto the surface of arsenopyrite, which greatly hinders the adhesion of the collector to the surface of minerals, thus reduces the hydrophobicity and floatability of arsenopyrite surface. The results of the adsorption experiments show that dextrin is an effective depressant for the flotation separation of arsenopyrite from chalcopyrite, which is consistent with the results of the flotation tests.

Infrared spectroscopy analysis

The surface properties of arsenopyrite treated with dextrin were analyzed by infrared spectroscopy (Figure 6). The spectrum of dextrin showed a strong wide absorption peak around 3,450 cm⁻¹, which was attributed to the stretching vibration of the -OH groups (Hasan et al. 2019; Pan et al. 2019). The absorption peak at 2,928 cm⁻¹ was attributed to the antisymmetric stretching of -CH₂ groups (Pan et al. 2019). The absorption peak of the C-O antisymmetric deformation vibration occurred at 1,654 cm⁻¹ and that of the C-O-C stretching vibration at 985–1,162 cm⁻¹ (Wang & Chen 2009). The infrared spectrum of dextrin shows that the dextrin molecules contained a large number of -OH groups,

<table>
<thead>
<tr>
<th>Time/min</th>
<th>Chalcopyrite (mg/m²)</th>
<th>Arsenopyrite (mg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.201</td>
<td>0.081</td>
</tr>
<tr>
<td>2</td>
<td>0.213</td>
<td>0.112</td>
</tr>
<tr>
<td>3</td>
<td>0.215</td>
<td>0.123</td>
</tr>
<tr>
<td>4</td>
<td>0.216</td>
<td>0.135</td>
</tr>
<tr>
<td>3 (untreated dextrin)</td>
<td>0.211</td>
<td>0.220</td>
</tr>
</tbody>
</table>

Table 3 | Amounts of NaBX adsorbed on arsenopyrite and chalcopyrite surfaces (pH = 8, 10 mg/L NaBX, 50 mg/L dextrin)

Figure 5 | Contact angle of chalcopyrite and arsenopyrite surface in the absence and presence of 20 mg/L dextrin.
which could improve the hydrophilicity of minerals after being adsorbed onto the surface of mineral.

In the infrared spectrum of arsenopyrite treated with dextrin, the stretching vibration of -OH adsorbed in arsenopyrite was transferred from 3,425.96 cm\(^{-1}\) to 3,427.91 cm\(^{-1}\), and the characteristic peaks intensity increased, indicating that -OH in dextrin adsorbed onto the arsenopyrite surface. A new absorption peak at 2,924.53 cm\(^{-1}\) was attributed to the antisymmetric deformation of -CH\(_2\). In fact, the infrared spectrum of the surface of the interaction between dextrin and arsenopyrite was almost completely replaced by the peak of dextrin, which indicates that dextrin adsorbs strongly onto the surface of arsenopyrite. It is also possible that the hydrophilic molecules of dextrin cover the hydrophobic molecules and reduce the floatability of the mineral. In addition, these results not only indicated that dextrin exhibited chemical adsorption onto the surface of arsenopyrite, but also the adsorption of dextrin involved hydrogen bonding in addition to the intermolecular effect; in other words, dextrin was adsorbed onto the arsenopyrite surface by both physical and chemical adsorption.

In the infrared spectrum measured after the interaction of chalcopyrite and dextrin (Figure 7), the newly generated -OH stretching vibration absorption peak was located at 3,455.38 cm\(^{-1}\). Other absorption peaks did not change significantly. The results of infrared spectroscopy, flotation tests and zeta potential measurements show that dextrin interacted weakly with chalcopyrite, which had no effect on the floatability of chalcopyrite.

On the basis of the aforementioned results, a schematic diagram of the selective adsorption of dextrin onto chalcopyrite and arsenopyrite surfaces is presented in Figure 8. As shown in Figure 8, in the mixed arsenopyrite-chalcopyrite system, dextrin macromolecules are selectively adsorbed onto the surface of arsenopyrite. On the one hand, the adsorption of dextrin added a large number of hydrophilic groups on the surface of arsenopyrite; on the other hand, the macromolecular chain structure of dextrin may hinder the attachment of collector molecules. The combined action of the two aspects makes arsenopyrite lose its hydrophobicity, but has no effect on chalcopyrite.
CONCLUSION

This study revealed the effect of dextrin on flotation separation and the surface properties of chalcopyrite and arsenopyrite at pH = 8. The results of micro-flotation showed that dextrin had an obvious inhibitory effect on arsenopyrite at this pH and the depression behavior was enhanced with an increase of dextrin concentration.
However, regardless of the presence or absence of dextrin, chalcopyrite always showed good floatability in flotation. The zeta potential and infrared measurements analysis showed that dextrin adsorbs onto the surface of arsenopyrite by physical adsorption and chemisorption, and only a small amount of dextrin interacts with the surface of chalcopyrite. Contact angle experiment results showed that dextrin can selectively adsorb onto the surface of arsenopyrite and make it hydrophilic. The results of adsorption experiments showed that dextrin was selectively adsorbed onto the surface of arsenopyrite, which greatly hindered the adhesion of the collector to the surface of minerals. The adsorption of dextrin added a large number of hydrophilic groups on the surface of arsenopyrite. In addition, the macromolecular chain structure of dextrin may hinder the attachment of collector molecules.

This study will provide a reference for the effect of organic inhibitors on the flotation separation of chalcopyrite and arsenopyrite, thus reducing the environmental pollution by arsenopyrite.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


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