The Effect of New Modified Fatty Acid (CY-23) Collector on Chlorite/Hematite Separation

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1. Introduction

Chlorite distributes in nature widely and is one of the most common minerals in sedimentary, low-grade metamorphic, and hydrothermal metamorphic rocks [1–3]. Reports of the separation of chlorite and other minerals are often seen [4–7]. Being an iron-bearing silicate mineral type gangue mineral, it is difficult to be separated from weak magnetic iron ore. Chlorite is enriched in iron concentrate during strong magnetic separation, which reduces the grade of iron concentrate. Despite these facts, the reports of separation of chlorite and weak magnetic iron ore minerals have seldom been reported, especially in the aspects of mechanism of the interaction between the reagents and minerals.

Flotation separation of chlorite and hematite is a complex process. The collector can be adsorbed on the surface of the chlorite instead of adsorption on the surface of hematite. Therefore, it is very important to develop highly selective collector. It was reported that the selective flotation and collection of hematite can be achieved by using the fatty acids collector to some extent [8, 9].

In the present work, the new collector CY-23 is a modified fatty acid collector with ether-based oxygen atom containing lone pair electrons, which can be composed of chelate with metal ion along with carboxyl oxygen, and the ether acid group may also be arranged in a similar crown ether structure to be adsorbed on the mineral surface [10].

2. Materials and Methods

2.1. Samples. The chlorite and hematite used for all experiments were obtained from Yuanjiajun Iron Mine, Shanxi Province, China. Coarse, well-crystallized hematite mineral was ground and screened through 75 μm and 19 μm series sieves. The -75 μm particle samples were used for flotation experiments and -19 μm particle samples were used for adsorption tests, respectively. Mineralogical and X-ray
powder diffraction data confirmed that the hematite sample was of high purity with trace amounts of ilmenite.

The preparation method of chlorite monomer is as follows: First, the artificial selected ore block rich in chlorite was crushed and screened. Then, the minerals with 90.1 mm were conducted with magnetic separation under 2000 Gs intensity to remove the ferromagnetism and iron pollution impurities. Later, the nonmagnetic minerals were removed under 8000 Gs intensity and the purified chlorite was enriched in the high-intensity magnetic concentrate. The chlorite was finally obtained after repeated high-intensity magnetic separation (HIMS). The mineral surface was washed using distilled water and dried in vacuum dryer at low temperature (60°C). Based on a quantitative X-ray diffraction (XRD) analysis [11], the chlorite was of 96% purity with traces of quartz. The sample was screened through 75 μm and 19 μm sieve series. The -75 μm particle samples were used for flotation experiments, and -19 μm particle samples were used for adsorption tests and X-ray photoelectron spectroscopy (XPS) tests, respectively. The chlorite monomer chemical composition was shown in Table 1.

2.2. Test Facilities and Reagents. Equipment included XFG flotation machine, XPS, pH meter, ultraviolet-visible spectrophotometer, rotary vane vacuum filter, and electric thermostat blast oven.

The caustic starch (CS) solution was prepared by using industrial pure corn starch and sodium hydroxide at the weight ratio of 5:1 in cold distilled water, which was then stirred in boiling distilled water. The solutions were freshly prepared each day. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used as pH regulators. All the reagents used in the test including sodium oleate (NaOL) collector and calcium chloride (CaCl₂) were of analytical grade. The structural formula of collector CY-23 was listed in Figure 1. Distilled water was used for all tests.

2.3. Experiments

2.3.1. Flotation Tests. Single mineral flotation tests were carried out by using XFG type laboratory flotation machine with a 40 ml flotation cell, and the impeller speed was fixed at 1900 rpm. The mineral suspension (either chlorite or hematite) was prepared by adding 3.0 g of minerals to 40 ml of distilled water. The sequence of reagent additions was as follows: pH regulators, depressor, activator, and collector. All tests were carried out under room temperature of approximately 25°C. The floated and unflotted products were collected, filtered, dried, and weighed, respectively. The flotation recovery was calculated based on solid weight distributions between the two products.

The chlorite and hematite are mixed in a 1:1 mass ratio, as the mixed mineral; 3.0 g of mixed mineral was used for mixed mineral flotation at every experiment; the flotation procedure was the same as the single mineral flotation tests.

2.3.2. Adsorption Tests. For the adsorption tests, 0.5 g of mineral powder was dispersed into a 100 ml pulp solution after adding distilled water and required reagents in order (the mixing time of each agent is 3 min) in 250 ml erlenmeyer flasks. The suspensions were mixed and placed on a rotator for 1 h until the adsorption process had reached equilibrium. Each sample was then centrifuged, and the residual concentration of collector in solution was analyzed using the ultraviolet-visible spectrophotometer. It was assumed that the amount of collector depleted from solution had adsorbed on the mineral surface, and the absorbance and concentration were in a good linear relationship in respect of concentration range of collector.

2.3.3. XPS Measurements. The measurement was carried out with the aid of ESVALAB 2500 electron spectrometer made by Thermo-VG Scientific Company, USA. The preparation method of XPS test samples was listed as follows: the chlorite was ground to ~2 μm in agate mortar for several hours; then, the samples were put into the distilled water at 25°C, and the pH value was adjusted to 10 with the addition of chlorite and reagents; the solution was stirred in flotation cell for 10 min; afterwards, when solution was stirring for 3 min and the mineral adsorption became equilibrium, the pulp was filtrated and the pulp cake was washed with distilled water at pH 10 for three times; the test samples were obtained after the filtrated cake was dried at a low temperature (60°C).

The XPS element electron binding energy analysis on test samples was conducted with MultiLab 2000 multifunctional surface analysis equipment. The pollutionCls was adopted as the charged calibration standard.

3. Results and Discussion

3.1. Flotation Tests. The effect of pulp pH on the flotation recovery of chlorite and hematite was shown in Figure 2. It was evident from Figure 2 that the flotation recovery of hematite was very high under the pH = 4–10 range, and in the strong acid and strong alkaline condition, the flotation recovery of hematite was very low. Different from hematite, the flotation recovery of chlorite gradually increased with the increase of pH value using NaOL or CY-23 as collector [12, 13].

Table 1: Chemical component analysis results of chlorite/\%.

<table>
<thead>
<tr>
<th>Component</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>MnO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>H₂O⁺</th>
<th>In total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>25.59</td>
<td>1.72</td>
<td>27.49</td>
<td>0.37</td>
<td>18.53</td>
<td>0.63</td>
<td>13.70</td>
<td>0.12</td>
<td>0.02</td>
<td>0.08</td>
<td>11.53</td>
<td>99.78</td>
</tr>
</tbody>
</table>

![Figure 1: Structural formula of collector CY-23.](image)
The flotation collecting ability of collector CY-23 to chlorite is stronger than that of NaOL within the range of pH = 8–11. As it could be observed from Figure 2, the flotation recovery of chlorite was higher than that of hematite within the range of pH = 8–11, with either NaOL or CY-23 as collector. In the actual industrial process, chlorite was often chosen for flotation and hematite was suppressed. The truth is that the content of chlorite is often less than that of hematite in the flotation process of iron ore. Chlorite flotation and hematite inhibition are more in line with the fundamental principles, that is, few flotation and high inhibition during beneficiation process. In the present work, the effect of CY-23 collector on chlorite flotation separation from hematite has been studied.

Macromolecular polysaccharides have been used in the inhibition of chlorite and hematite flotation [14, 15]. Figure 3 showed the effect of CS concentration at pH 10 on flotation recovery of chlorite and hematite. The results in Figure 3 illustrated that CS had a significant depression effect on hematite. When the concentration of CS was 20 mg/L, the flotation recovery of hematite was less than 10%, even when adding NaOL or CY-23 as collector. CS not only influenced the recovery of hematite, but also caused a decrease on the recovery of chlorite in the same conditions.

Figure 4 showed that when hematite was inhibited by CS of 20 mg/L, the flotation recovery of hematite was still less than 15%, even when adding 100 mg/L CaCl₂. It was reported that metal ions are able to impact chlorite flotation [16, 17]. As seen in Figure 4, at the depressant CS dosage of 20 mg/L and the activator CaCl₂ dosage of 100 mg/L, the flotation recovery of chlorite gradually increased to different extent with increasing collector dosage. When the CY-23 dosage is 100 mg/L, the flotation recovery of chlorite was 85%, but the flotation recovery of chlorite was only 53% with the same NaOL dosage. It indicated that the flotation property of collector CY-23 on chlorite is superior to that of NaOL. The reason for that is because there was strong chemical reaction between unsaturated double key and ether-base structure in CY-23 molecule (Figure 1) with metal ions on chlorite surface, which increases the effective reaction density between CY-23 and chlorite surface.

The results of the mixed mineral flotation study were shown in Table 2. Because SiO₂ only exists in chlorite and there is no SiO₂ in hematite, SiO₂ recovery stands for chlorite recovery in this study. From Table 2, it could be seen that, at the collector CY-23 dosage of 100 mg/L, the recovery of SiO₂ was 25.45% in un floated product, which was lower than...
that in the case if using NaOL as collector. It indicated that when the collector CY-23 was used the chlorite content in the unfloated product was less, which inferred that the selective capture ability of the collector CY-23 to chlorite is higher than that of NaOL.

3.2. Adsorption Tests. As shown in Figures 5 and 6, the UV spectra maximum absorption peaks of CY-23 and NaOL were at 233 nm and 238 nm, respectively.

Table 3 exhibited the results of collector adsorption onto chlorite. The results in Table 3 showed that NaOL has not been adsorbed onto chlorite without CS and CaCl₂, and after both CS and CaCl₂ additions, NaOL adsorption rate was only 18.0%. The same cannot be said for the CY-23. As it could be seen, the collector CY-23 adsorption rate was 23.0% in the absence of CS and CaCl₂, and the chlorite flotation recovery was 47% (Figure 2). In the presence of CS and CaCl₂, the adsorption rate of CY-23 on the chlorite surface was 42.2%, and the flotation recovery rate of chlorite was 85% (Figure 4).

3.2.1. XPS Measurements. As shown in Figure 7, the C1s peak on chlorite surface was narrow and symmetric, with single chemical morphology caused by carbon pollution peak. After the reaction with CY-23 and NaOL, the chlorite was in the form of complex C structure. After the reaction between

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Abs</th>
<th>Adsorption rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-23</td>
<td>0.213</td>
<td>23.0</td>
</tr>
<tr>
<td>CS + CaCl₂ + CY-23</td>
<td>0.161</td>
<td>42.2</td>
</tr>
<tr>
<td>NaOL</td>
<td>0.120</td>
<td>6.2</td>
</tr>
<tr>
<td>CS + CaCl₂ + NaOL</td>
<td>0.105</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Table 3: Adsorption rate of collectors on chlorite surface at pH 10.
chlorite and NaOL, the C-H bond peak (number (2) location) appeared on the mineral surface. After the reaction between chlorite and CY-23, there did not exist C-H bond peak with strong C-O bond peak (or C=O) (number (1) location) appearing, and the C-C bond peak position was moved from the number (3) location to number (4) location. This was the same as the solid XPS analysis results of collector CY-23, which indicated that addition of ring structure ether acid group and other functional groups in CY-23 molecule generated C=C and C-O structure and improved the effects of collector CY-23 on chlorite, which made it easy for CY-23 molecule to react with mineral surface.

Figure 8 shows the XPS atlas of surface Mg element before and after the reaction between chlorite and new collector CY-23 and NaOL. Figure 8 shows that the 2p XPS peak of chlorite surface Mg element slightly moved to lower energy after the reaction between NaOL and chlorite; meanwhile, the reduction degree of chlorite after reaction was not enough, and some Mg peaks still stayed in situ after reaction. However, the Mg 2p XPS peak of chlorite surface moved obviously to lower energy by 0.43 eV after reaction with CY-23. It indicated that there occurred chemical bonding reaction on chlorite surface, in which the CY-23 moved into Mg electron cloud and the density of Mg ions electron cloud increases. This result was closely related to the reaction between the unsaturated double keys and ether-based ring structure of new correlation CY-23 molecule.

Figure 9 shows the XPS atlas of surface aluminum element before and after the reaction between chlorite and new collector CY-23 and NaOL. As it could be seen from Figure 9, in the Al 2p photoelectron spectroscopy of chlorite surface after the reaction between NaOL and chlorite, a little structure appeared at 73 eV location, and part of Al elements was reduced. The Al 2p photoelectron spectroscopy of chlorite surface moved obviously to lower energy after reaction with CY-23. It indicated that there occurred strong chemical bonding reaction on chlorite surface in which the CY-23 moves into Al electron cloud.

4. Conclusions

Based on the results of this investigation, the following conclusions can be drawn:

(1) After the chlorite was inhibited by CS, the flotation recovery of chlorite reached 85% by using CaCl\textsubscript{2} as the activator and CY-23 as the collector. Under the same conditions, the recovery of hematite was less than 15%. The results of the mixed mineral flotation experiments showed that the selective capture ability of the collector CY-23 to chlorite was higher than that of NaOL at the same mass concentration.

(2) Adsorption rate of NaOL on the surface of chlorite was only 18%. In the absence of starch and CaCl\textsubscript{2}, the adsorption rate of CY-23 on the surface of chlorite was 23%. In the presence of starch and CaCl\textsubscript{2}, the adsorption rate of CY-23 on the surface of chlorite was 42.2%, and then the flotation recovery of chlorite was 85%.

(3) The results of XPS analysis showed that the photoelectron spectroscopy peaks of Mg2p and Al2p moved towards low energy after collector CY-23 was absorbed on chlorite surface, which indicated that chemical bonding through electron cloud transfer occurred between collector CY-23 and Mg/Al ions of chlorite surface. The chemical reaction promoted the adsorption of CY-23 on chlorite surface and eventually improved the ability of CY-23 to float and collect chlorite. That is to say, there exists stronger reaction between new collector CY-23 and Mg/Al ions on chlorite surface.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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