Original Article

The depression behavior and mechanism of carboxymethyl chitosan on calcite flotation

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\section*{A B S T R A C T}

The separation of scheelite and calcite by froth flotation is difficulty as these two minerals have similar physicochemical characteristics. To solve this problem, the role of carboxymethyl chitosan in the flotation separation of scheelite from calcite has been studied and the depression mechanism has been discussed. Micro-flotation tests show that carboxymethyl chitosan has strong depression effect on calcite and the depression effect decreased with the increase of pH. However, its depression effect on scheelite is weak. A concentrate with WO\textsubscript{3} grade of 65.21\% and WO\textsubscript{3} recovery of 77.48\% can be achieved in the mixed minerals flotation when carboxymethyl chitosan was used. The adsorption tests show that carboxymethyl chitosan has adsorbed on the calcite surface and the adsorption amount increased with the increase of added amount. The adsorption mechanism of carboxymethyl chitosan on calcite surface was analyzed through the X-ray photoelectron spectroscopy (XPS) tests and the results revealed that carboxymethyl chitosan adsorbed on calcite surface mainly through chemical interaction.

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\section*{1. Introduction}

China is the main producers of tungsten in the world. With the development of economy, the wolframite resources which can be utilized easily by gravity method almost depleted, the utilization of refractory scheelite resources becomes very important. The Shizhuyuan mine is located in Hunan province. The main valuable mineral in the Shizhuyuan ore is scheelite and the gangue minerals are mainly calcite and fluorite. Scheelite is hard to be separated from other calcium minerals by flotation techniques.

The commonly used collectors in the flotation separation of scheelite from calcic gangue minerals are generally fatty acids or fatty acid derivatives [1–3], due to the same Ca\textsuperscript{2+} species on the cleavage, the scheelite and other calcic gangue minerals such as calcite exhibit similar surface reactivity to above collectors [4]. Therefore, it is almost impossible to separate scheelite from calcite without the addition of depressant [5]. Sodium silicate and its solution with metal ions or acids are widely used in the flotation of scheelite as depressants...
[6,7], but the sodium silicate-based depressants have also been proved to be able to adsorb on the scheelite surface and impair flotation performance [8–11]. Furthermore they also have dispersion effect on the mineral particles and make the particles settling slowly in the tailings treatment process. Therefore, the development of a new selective depressant for scheelite flotation is needed. In recent years, polymer depressants, such as sodium algin ate, sodium polycarboxylate and calcium lignosulphonate, have been widely applied in flotation separation of scheelite and calcite [12–14].

Chitosan is a natural cationic polysaccharide that shows many advantages over artificial materials and carboxymethyl ation is one of the most widely-studied modifications for chitosan. In addition to these advantages that are inherited from the parent chitosan, carboxymethyl chitosan also possesses good solubility and amph oteric properties. Both chitosan and carboxymethyl chitosan have been used in mineral flotation [15,16]. The aim of this study is to show the selective flotation of scheelite from calcite using carboxymethyl chitosan as depressant. Adsorption measurements and XPS analysis were conducted to define the depression mechanism of carboxymethyl chitosan to calcite.

2. Materials and methods

2.1. Pure minerals and reagents

The scheelite and calcite samples were purchased from Geological Specimen Factory of Zhejiang University. The minerals were separately crushed and hand-picked to obtain high purity samples. The scheelite sample was then further purified by shaking table. X-ray diffraction measurements showed that there were no other tungsten minerals in scheelite and trace silicate in calcite (Fig. 1).

According to Table 1, the scheelite sample contained 80.50% WO3, representing a high purity of 99.87% scheelite, and that calcite contained 55.47% CaO, indicating a purity of 99.0% calcite. Then samples were further dry-ground using a porcelain ball mill and sieved. The –75 + 38 μm size fractions were used in the flotation test. The calcite particles of –38 μm were used in adsorption tests (with a D90 value of 33.3 μm).

The sample of sodium olate (NaOl) and carboxymethyl chitosan (MW 150,000–200,000, degree of decetylation >75%, degree of carboxylation >60%). The structure of carboxymethyl chitosan is shown in Fig. 2) used in this study was obtained from Aladdin Chemical Technology Co., Ltd. HCl and NaOH were used to regulate the pulp pH. Distilled water was used for all tests.

2.2. Flotation tests

Micro-flotation tests of single minerals and artificially mixed minerals were both conducted to evaluate the ability of carboxymethyl chitosan as a selective depressant in the flotation separation of scheelite and calcite. All the micro-flotation tests were conducted in a XFGG flotation machine with a 50 mL cell.

In single mineral flotation test, 2 g mineral sample was mixed with 40 mL distilled water. The desired pH value (as shown in Fig. 3, 4 and 5) was then adjusted and maintained by adding HCl or NaOH during the conditioning process. The depressant carboxymethyl chitosan and collector NaOl were added respectively and conditioned for 5 min after each reagent addition. The flotation test was carried out for a total of 4 min. The recovery was calculated from the dry weights of the flotation concentrates and tailings.

In mixed minerals flotation, the flotation feed sample was a mixture of scheelite and calcite, and the flotation procedure

| Table 1 – The chemical composition of scheelite and calcite (%) |
|-------------------|--------|--------|--------|--------|--------|
| Sample            | WO3   | Fe     | SiO2   | Al2O3  | CaO   |
| Scheelite          | 80.50 | /      | /      | /      | 19.72 |
| Calcite            | /     | 0.21   | 0.52   | 0.22   | 55.47 |

Fig. 1 – XRD diagrams of scheelite and calcite.

Fig. 2 – structure of monomer carboxymethyl chitosan.
was the same as the single mineral flotation test. After flotation, the concentrate and tailings were collected, dried, weighed, and assayed for WO₃ contents by chemical titration method.

2.3. Adsorption tests

The total organic carbon method (TOC) was used to measure the adsorption amount of carboxymethyl chitosan on calcite. 1 g of mineral was added to 100 mL distilled water and the pH of the pulp was adjusted to a desired value. The depressant was then added and the suspension was stirred for 30 min. The pulps were then centrifuged and the concentration of carboxymethyl chitosan remaining in the supernatant is measured by determining the total organic carbon amount in the supernatant using a TOC analyzer (vario TOC made by ELEMENTAR, Germany) and comparing the value to a known calibration standard curve.

2.4. X-ray photoelectron spectroscopy (XPS) tests

For the XPS tests, 1 g calcite was added into 100 mL distilled water and then the carboxymethyl chitosan solution was added to make the concentration of 100 mg/L. After pH adjustment, the suspension was conditioned for 10 min. The slurries were filtered, and dried in a vacuum desiccator. XPS measurements were conducted on an K-Alpha 1063 X-ray spectrometer (Thermo Fisher, UK). The vacuum in the analyzer chamber was maintained at \( \sim 10^{-10} \) Torr. The binding energy scale of the instrument was calibrated using the Au(4f)/2 (BE = 84.0 eV) lines of metallic gold. Samples were in the form of dry powder mounted on conductive carbon tape. No negative effects resulting from charging or X-ray damage were observed.

3. Results and discussion

3.1. Micro-flotation test results

The flotation recovery of scheelite and calcite at different pH using NaOl as collector were studied and the result is shown in Fig. 3. It is evident from the figure that NaOl has good collecting ability to both scheelite and calcite over the pH range tested and it is difficult to separate scheelite from calcite without the addition of depressant.

When the pulp pH was kept at 7 and the collector concentration was fixed at \( 1.2 \times 10^{-4} \) mol/L, different concentrations of carboxymethyl chitosan were added to investigate its depressing effect on scheelite and calcite flotation. As shown in Fig. 4, by increasing the concentration of carboxymethyl chitosan, calcite tended to have lower recoveries and it was completely depressed with only 20 mg/L carboxymethyl chitosan. Different from calcite, the recovery of scheelite changed little with the increase of carboxymethyl chitosan concentration.

The effect of pH on the flotation behavior of scheelite and calcite was shown in Fig. 5. The results show that carboxymethyl chitosan has strong depression effect on calcite and the depression effect decreased with the increase of pH. For scheelite, the depression effect of carboxymethyl chitosan is weak. The results illustrate that the flotation separation of scheelite and calcite can be achieved in the pH range of 6–11 when carboxymethyl chitosan was used as depressant.

3.2. Scheelite and calcite mixture flotation

According to the single mineral micro-flotation tests of scheelite and calcite, the recovery difference of scheelite and calcite
is the largest at pH 7 when carboxymethyl chitosan is used as depressant. So the separation of the two minerals was studied at pH 7 using different dosages of carboxymethyl chitosan and the best results achieved are shown in Table 2. When carboxymethyl chitosan was not added, the recovery of scheelite is 83.91% but the grade is low. With the addition of 30 mg/L carboxymethyl chitosan, the concentrate recovery was 77.48% and the grade is 65.21%, representing a scheelite content of 80.91%. This result illustrates that a certain degree of selectivity can be achieved.

3.3. The adsorption behavior and mechanism of carboxymethyl chitosan on calcite surface

Fig. 6 shows the adsorption behavior of carboxymethyl chitosan on calcite surface. The results illustrate that the adsorption amount of carboxymethyl chitosan on calcite surface increased with the increase of added amount and no adsorption saturation was achieved in the tested concentration range.

X-ray photoelectron spectroscopy tests were performed to study the adsorption mechanism of carboxymethyl chitosan on calcite. The XPS spectrum of N 1s, Ca 2p were collected on calcite before and after interacted with carboxymethyl chitosan.

The narrow scans of N 1s were shown in Fig. 7a and b. It can be seen from Fig. 7a that the intensity of nitrogen on calcite surface is extremely weak and can be considered as coming from background noise, indicating that there was no nitrogen on the calcite sample [17]. After treated with carboxymethyl chitosan, the nitrogen element appeared on calcite surface and the spectrum was fitted by three peaks, which assigned to the $\text{−C−N}$ (398.9 eV), $\text{−NH}_2$ (399.7 eV) and $\text{−NH}−\text{C}−\text{═O}$ (400.6 eV) [18], respectively.

Table 2 – The flotation separation results of mixed minerals (pH = 7; c(NaOCl) = $1.2 \times 10^{-4}$ mol/L).

<table>
<thead>
<tr>
<th>Carboxymethyl chitosan (mg/L)</th>
<th>Feed grade (%)</th>
<th>Yield/%</th>
<th>WO$_3$ grade/%</th>
<th>WO$_3$ recovery/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 mg/L</td>
<td>26.56</td>
<td>31.55</td>
<td>65.21</td>
<td>77.48</td>
</tr>
<tr>
<td>0 mg/L</td>
<td>26.54</td>
<td>86.26</td>
<td>25.82</td>
<td>83.91</td>
</tr>
</tbody>
</table>

Fig. 6 – The adsorption behavior of carboxymethyl chitosan on calcite surface at pH 7.

Fig. 7 – The resolved narrow scan N$_{1s}$ spectrum for (a) calcite; (b) calcite treated with carboxymethyl chitosan.

Fig. 8 presents the resolved narrow scan Ca 2p spectrum for calcite treated with or without carboxymethyl chitosan. The scan spectrum of Ca 2p for calcite are shown in Fig. 8a, it can be seen that there are two peaks appear at the 348.0 eV and 351.9 eV which are assigned to Ca 2P3/2 and 2P1/2, respectively [19]. After treated with carboxymethyl chitosan, the peak of Ca 2P3/2 and 2P1/2 shift downwardly to 346.9 eV and 351.1 eV respectively. The shifts of peaks indicating that the interaction mechanism of carboxymethyl chitosan with calcite is a chemical interaction between the Ca on calcite surface and the $\text{−COOH}$ of carboxymethyl chitosan.

4. Conclusions

Carboxymethyl chitosan was used in the flotation separation of scheelite from calcite with NaOCl as collector. In single mineral flotation with NaOCl as a collector, carboxymethyl chitosan (30 mg/L) can depress calcite, but not scheelite in the pH range from 6 to 11. The recovery difference between scheelite and calcite is up to 70 percentage points. The mixture mineral flotation test shows that the flotation separation of scheelite and calcite can be achieved by using carboxymethyl chitosan as depressant at pH 7. A concentrate with WO$_3$ grade of 65.21% and WO$_3$ recovery of 77.48% was achieved when the mixture feed grade is 26.65%. In XPS measurements, the nitrogen element can be detected on the surface of calcite after
carboxymethyl chitosan adsorption and the shifts of peaks of Ca 2p spectrum can be attributed to the bonds formed between Ca and –COOH.

Conflicts of interest

The authors declare no conflicts of interest.

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References


Fig. 8 – The resolved narrow scan Ca 2p spectrum for (a) calcite; (b) calcite treated with carboxymethyl chitosan.