Review Article

Effect of calcium ion on the separation of rhodochrosite and calcite

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Abstract

The effect of calcium ion on the separation of rhodochrosite and calcite was systematically investigated based on flotation tests, zeta potential measurements, and scanning electron microscopy analysis. The flotation results showed that the separation of rhodochrosite and calcite was inefficient due to rhodochrosite and calcite being similar in many physical and chemical properties, which could make the separation of rhodochrosite from calcite inefficient. The separation of rhodochrosite and calcite can be significantly improved by adding sodium hexa metaphosphate (SH) because SH could depress calcite flotation while it did not bring an impact on rhodochrosite flotation. However, when calcium ion was added into this flotation system, the separation of rhodochrosite and calcite deteriorated as SH also depressed rhodochrosite flotation under this condition. The solution chemical calculation and scanning electron microscopy analysis illustrated that the formation of calcite precipitation coated on the rhodochrosite surface was the main reason because calcium ion increased the depression effect of SH on rhodochrosite.

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1. Introduction

As the primary source of manganese, pyrolusite is steadily getting depleted and rhodochrosite (MnCO₃) becomes one of the major sources of manganese oxide. Although manganese carbonate resources are very rich in China, there are fewer and fewer high-quality resources due to the over-exploitation of manganese ore. To meet manganese market demand in the future, it is significant to develop low-grade rhodochrosite for a marketable product. Especially, the flotation is one of the most effective methods to increase the recovery of fine grained and low-grade rhodochrosite.

Calcite is one of the most common and important components in sedimentary rocks. And calcite is an extensive carbonate gangue in the flotation of rhodochrosite, smithsonite, celestite and apatite [1–3]. It is easy to enter the rhodochrosite flotation concentrate because of naturally hydrophobic, thus reducing concentrate grade [4]. Being a calcium type gangue mineral, large quantities of calcite in flotation concentrates can cause problems during smelting. Rhodochrosite and calcite are calcite-group minerals that show similar flotation behavior due to the same crystal structure and similar chemical composition. Therefore, it is difficult to achieve effective separation of rhodochrosite from calcite in conventional flotation. Flotation separation of valuable carbonate minerals and calcite is extremely complex because of the interaction between minerals and dissolved metal ions.

The dissolution characteristics of rhodochrosite and calcite play an important role in determining the interactions occurred in the bulk solution or on the mineral surfaces [2,5]. The dissolved species of minerals could participate in some reactions such as hydrolysis, complexation, adsorption, and bulk precipitations, which could affect the selective interaction between reagent and mineral [6–8]. In addition, some agents such as CaO, which used as pH regulator and the water used in actual production also increase the content of the cations, which also effect rhodochrosite flotation in the pulp. Although some reagents such as starch, sodium hexa metaphosphate (SH), and sodium silicate are usually used as calcite depressants in rhodochrosite flotation, the separation process shows relatively low selectivity in practice due to their similar surface properties and dissolved species [9–11]. Moreover, few literatures are focused on the effect of metal ions on flotation separation of rhodochrosite and calcite.

In this study, the effect of calcium ion (Ca²⁺) on the separation of rhodochrosite and calcite was investigated. The flotation tests were used to examine the flotation regularity of rhodochrosite and calcite in the absence and presence of Ca²⁺. To clarify the reasons on the difficulty in flotation separation of rhodochrosite and calcite, the electro-kinetic zeta potential measurements, solution chemistry calculations, scanning electron microscopy, accompanying with the flotation results, were systematically carried out.

2. Experimental

2.1. Samples and reagents

Both calcite and rhodochrosite used in this study were obtained from Changsha, Hunan Province, China. The results of mineralogy and X-ray powder diffraction confirmed that the purity of both samples was higher than 95%. The obtained samples were ground and then sieved to collect the −100 μm fraction for the microflotation and scanning electron microscopy tests. Hydrochloric acid (HCl) and sodium carbonate (Na₂CO₃) were used as pH regulators. Sodium oleate (NaOŁ) and sodium hexametaphosphate (SH) were used as collector and depressant, respectively. Calcium chloride (CaCl₂) was dissolved to prepare a predefined concentration of Ca²⁺ solution. All the reagents used in this study were of analytical grade. The water used in actual production has a certain degree of hardness. A certain amount of calcium and magnesium ions in water, which also affect the flotation separation of rhodochrosite and calcite. In order to eliminate the effect of ions in water on rhodochrosite flotation, for researching convenience, deionized double distilled water was used for all tests.
2.2. Flotation tests

Single mineral flotation tests were carried out in a mechanical agitation flotation machine. The impeller speed was fixed at 1800 r/min. The mineral suspension was prepared by adding 2.0 g of minerals to 40 mL of solutions. The pH of the mineral suspension was adjusted to a desired value using Na₂CO₃ or HCl. The slurry was conditioned for 3 min after adding the depressant of SH. Subsequently, the collector of NaOHL was introduced into the slurry for 3 min and then flotation was carried out for a total of 3 min. The floated and tailing fractions were collected separately and dried and weighed for calculations.

2.3. Zeta potential measurements

The samples used for zeta potential measurements were prepared as follows. The samples of 20 mg in the size –5 μm were added to desired amounts of solution and then magnetically stirred for 10 min, and adjusted pH using HCl or Na₂CO₃. Zeta potential measurements of rhodochrosite were carried out using a zeta plus potential meter. At each condition, the zeta potentials of minerals were measured and an average value of three individually measurements was accredited. Potassium nitrate was used to maintain the ionic strength at 10⁻³ mol/L.

2.4. Scanning electron microscopy

A scanning electron microscope (SEM, CAMSCAN CS44FE) equipped with an energy dispersive X-ray spectrometer (EDS) was used to observe the morphology and characterize the elemental composition of the rhodochrosite samples. The samples used for SEM observation were prepared with the same conditioning regime as the flotation tests, and then filtered and washed thoroughly with deionized double distilled water. The prepared samples were dried in a vacuum oven at 25 °C for 24 h.

3. Results and discussion

3.1. Effect of Ca²⁺ on the separation of rhodochrosite and calcite

The effect of pH on the flotation recovery of rhodochrosite and calcite is shown in Fig. 1. As shown in this figure, the flotation recoveries of rhodochrosite and calcite were very high over the entire pH range tested. Such high recovery could be attributed to the chemisorptions of oleate on rhodochrosite and calcite at alkaline conditions [12,13]. The flotation recoveries of rhodochrosite and calcite increased slightly as the pH increased. According to the results shown in Fig. 1, it can be concluded that it is difficult to separate rhodochrosite and calcite without the addition of depressant.

The effect of pH on the floatability of rhodochrosite and calcite in the presence of SH is shown in Fig. 2. The results illustrated that SH had a significant depression effect on calcite in the pH range of 7–12. The recovery of calcite decreased from 90% to 20% in the absence and presence of SH at pH 11. Different from calcite, the rhodochrosite flotation was not obviously influenced by SH addition at alkaline conditions. The rhodochrosite was depressed by SH addition when pH further decreased. Therefore, it is possible to separate rhodochrosite and calcite at alkaline conditions by using SH as depressant.

In order to investigate whether SH is suitable for separating calcite from rhodochrosite, the samples of rhodochrosite and calcite were mixed by mass ratio of 1:1 and floated at pH 11 using NaOHL and SH as collector and depressant, respectively, and the result is presented in Table 1. In the mixed sample, the theory grades of Mn and Ca are 23.91% and 20.00%, respectively. The results showed that the grades of Mn and Ca in the concentrate were only slightly different from those in raw ore, illustrating that it is unfavorable to separate rhodochrosite and calcite by using SH as depressant. Therefore, it demonstrates that there are some other factors to affect the flotation.
separation of rhodochrosite and calcite in the mixed minerals slurry.

Salt-type minerals are commonly characterized by their higher solubility in water, where the extent of dissolution is remarkably higher than in most oxide/silicate systems. The dissolved species from one mineral frequently undergo hydrolysis or chemical reaction with other mineral surface in pulp, resulting in surface conversion of mineral and subsequently surface properties and flotation performance, making it difficult to separate such minerals without additional treatment [14].

The effect of Ca$^{2+}$ on the depression of rhodochrosite (Fig. 3(a)) and calcite (Fig. 3(b)) using SH as depressant is shown in Fig. 3. As shown in Fig. 3(a), it can be seen that the addition of Ca$^{2+}$ significantly affected rhodochrosite flotation in the pH range of 7–11.5, especially at pH 10, of which the rhodochrosite recovery decreased from 92% to 60%. It should be noted that a strange phenomenon in Fig. 3(a) is that the addition of Ca$^{2+}$ increased the depress effect of SH on rhodochrosite flotation. The higher the pH, the stronger the depression effect. Different from the rhodochrosite, the result in Fig. 3(b) showed that the depression effect of SH on calcite was not influenced by Ca$^{2+}$. These results illustrate that the presence of Ca$^{2+}$ interferes with the separation of rhodochrosite and calcite.

Fig. 4 shows the effect of SH concentration on the flotation performance of rhodochrosite and calcite in the absence and presence of Ca$^{2+}$. It showed that the separation of rhodochrosite and calcite could be realized at a concentration of 120 mg/L in the absence of Ca$^{2+}$. However, both rhodochrosite and calcite are depressed by SH in the presence of Ca$^{2+}$.

### 3.2. The depression mechanism of Ca$^{2+}$ to rhodochrosite flotation

The Ca$^{2+}$ could participate in some reactions such as hydrolysis, complexation, adsorption, and even surface or bulk precipitation [15,16]. The complex equilibria involving all such reactions can be expected to determine the interfacial properties of the particles and their flotation behaviors. The concentrations of each species were calculated based on various solution equilibria of the ions. The corresponding results are plotted as logC–pH diagram as shown in Fig. 5. The reactions for controlling the system of CaCO$_3$ are listed in Table 2.

The species distribution diagrams can be calculated according to the equilibria equation and the results are shown in Fig. 5. The results illustrated that the CaCO$_3$ precipitation began to form when pH was above 9.8, while Ca(OH)$_2$ precipitation was not generate.

In order to further confirm whether Ca$^{2+}$ formed precipitation and adsorbed on the surface of rhodochrosite or not,

### Table 1 – Results of separation of rhodochrosite and calcite.

<table>
<thead>
<tr>
<th>SH concentration (mg/L)</th>
<th>Product</th>
<th>Productivity (%)</th>
<th>Mn grade (%)</th>
<th>Ca grade (%)</th>
<th>Mn recovery (%)</th>
<th>Ca recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Concentrate</td>
<td>98.66</td>
<td>24.03</td>
<td>20.06</td>
<td>98.68</td>
<td>98.71</td>
</tr>
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<td></td>
<td>Tailing</td>
<td>1.34</td>
<td>23.71</td>
<td>19.83</td>
<td>1.32</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>Raw ore</td>
<td>100</td>
<td>24.02</td>
<td>20.05</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>Concentrate</td>
<td>80.33</td>
<td>25.78</td>
<td>19.46</td>
<td>87.53</td>
<td>75.52</td>
</tr>
<tr>
<td></td>
<td>Tailing</td>
<td>19.67</td>
<td>14.98</td>
<td>25.76</td>
<td>12.47</td>
<td>24.48</td>
</tr>
<tr>
<td></td>
<td>Raw ore</td>
<td>100</td>
<td>23.66</td>
<td>20.70</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>Concentrate</td>
<td>75.33</td>
<td>26.17</td>
<td>18.11</td>
<td>80.56</td>
<td>69.85</td>
</tr>
<tr>
<td></td>
<td>Tailing</td>
<td>24.67</td>
<td>19.28</td>
<td>23.88</td>
<td>19.44</td>
<td>30.15</td>
</tr>
<tr>
<td></td>
<td>Raw ore</td>
<td>100</td>
<td>23.90</td>
<td>19.53</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig. 4 – Effect of SH concentration on the depression of rhodochrosite and calcite in the absence and presence of Ca\(^{2+}\) (c(NaOL) = 1 × 10\(^{-4}\) mol/L and c(Ca\(^{2+}\)) = 5 × 10\(^{-4}\) mol/L).

Fig. 5 – Effect of pH on hydrolysis species distribution of Ca\(^{2+}\) in the system of CaCO\(_3\) (C\(_{Ca}\) = 2.0 × 10\(^{-4}\) mol/L).

Table 2 – Reaction of Ca\(^{2+}\) and equilibrium constant in the system of CaCO\(_3\).

<table>
<thead>
<tr>
<th>Equilibrium equation</th>
<th>Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO(_3)(s) = Ca(^{2+}) + CO(_3^{2-})</td>
<td>-8.35</td>
</tr>
<tr>
<td>Ca(^{2+}) + CO(_3^{2-}) = CaCO(<em>3)(</em>{aq})</td>
<td>3.06</td>
</tr>
<tr>
<td>Ca(^{2+}) + OH(^-) = Ca(OH)(^{2+})</td>
<td>1.4</td>
</tr>
<tr>
<td>Ca(^{2+}) + 2OH(^-) = Ca(OH)(<em>2)(</em>{aq})</td>
<td>2.77</td>
</tr>
<tr>
<td>Ca(OH)(<em>3)(</em>{aq}) = Ca(^{2+}) + 2OH(^-)</td>
<td>-5.22</td>
</tr>
<tr>
<td>H(^+) + CO(_3^{2-}) = HCO(_3^{-})</td>
<td>10.33</td>
</tr>
<tr>
<td>H(^+) + HCO(_3^{-}) = H(_2)CO(_3)</td>
<td>6.35</td>
</tr>
</tbody>
</table>

SEM-EDS analysis of rhodochrosite samples treated by Ca\(^{2+}\) and Na\(_2\)CO\(_3\) were measured and the results are shown in Fig. 6. It was found that CaCO\(_3\) precipitations were coated on the surface of rhodochrosite in SEM image. Particularly, the spectrum showed that the peaks Ca and Mn were surely existed, confirming that CaCO\(_3\) precipitations were formed on the surface of rhodochrosite.

As a direct surface chemistry investigation of the mineral, electro-kinetic studies were undertaken to rhodochrosite at different conditions as a function of pH in 10\(^{-3}\) M KNO\(_3\). Fig. 7 shows the effect of NaOL on the zeta potential of rhodochrosite in the absence and presence of Ca\(^{2+}\). The zeta potential of rhodochrosite negatively increased as the pH increased from 7.5 to 11.30 without Ca\(^{2+}\) addition for Line 1, indicating that collector ion of NaOL adsorbed on the surface of rhodochrosite. Such result is consistent with the flotation results shown in Fig. 1. Lines 2 and 3 are the zeta potential curves in the presence of Ca\(^{2+}\) without and with NaOL, respectively. It was found that the addition of NaOL had a negligible effect on zeta potential of rhodochrosite, indicating that the adsorption of collector ion on the surface of rhodochrosite did not occur at this condition.

Based on the results of floatation tests and surface analysis, it can be concluded that Ca\(^{2+}\) is formed to CaCO\(_3\) precipitation and subsequently adsors on the surface of rhodochrosite. Although SH addition has little effect on rhodochrosite, the results indicate that CaCO\(_3\) precipitation coated on the surface of rhodochrosite makes rhodochrosite surface property similar to calcite in response to SH addition. And there is not
only Ca\textsuperscript{2+} dissolved from calcite, some reagents and water used in flotation process may also increase the content of Ca\textsuperscript{2+} in pulp. The influence of these calcium ions on the flotation separation of rhodochrosite and calcite cannot be ignored. Therefore, a novel way is expected to be proposed by preventing Ca\textsuperscript{2+} from forming precipitation and coating on the surface of rhodochrosite in order to achieve effective flotation separation of rhodochrosite and calcite. The flotation methods and corresponding mechanisms are still unknown now, which will be further investigated in the near future.

4. Conclusions

(1) The rhodochrosite and calcite are difficult to be separated without the addition of depressant as they are similar in many physical and chemical properties.

(2) SH is an effective reagent for the separation of rhodochrosite and calcite as SH depressed calcite flotation, while it did not affect the rhodochrosite flotation.

(3) The presence of Ca\textsuperscript{2+} increased the depression effect of SH on rhodochrosite, which was unfavorable for the separation of rhodochrosite and calcite.

(4) The formation of CaCO\textsubscript{3} precipitation coated on the surface of rhodochrosite made the separation performance deteriorated because Ca\textsuperscript{2+} increased the depress effect of SH on rhodochrosite.

Conflicts of interest

The authors declare no conflicts of interest.

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