Original Article

Flotation studies of fluorite and barite with sodium petroleum sulfonate and sodium hexametaphosphate

Zhijie Chen\textsuperscript{a}, Zijie Ren\textsuperscript{a,b,}\textsuperscript{*}, Huimin Gao\textsuperscript{a,b}, Renji Zheng\textsuperscript{a}, Yulin Jin\textsuperscript{c}, Chunge Niu\textsuperscript{c}

\textsuperscript{a} School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China
\textsuperscript{b} Hubei Key Laboratory of Mineral Resources Processing and Environment, Wuhan University of Technology, Wuhan 430070, China
\textsuperscript{c} Refining & Petrochemical Research Institute, PetroChina Karamay Petrochemical Co., Ltd., Karamay 834000, China

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\textbf{A B S T R A C T}

The development of new collectors to separate fluorite from barite is urgently needed in mineral processing. In this study, the flotation behavior of fluorite and barite was studied using sodium petroleum sulfonate (SPS) as a collector with sodium hexametaphosphate (SHMP) as a depressant. The performance of reagents on minerals was interpreted by infrared spectroscopic analysis and zeta potential measurement. The flotation results showed that SPS performed well in a wide pH region (7–11) even at a low temperature (5°C), while the flotability of fluorite and barite were almost the same. At pH 11, the presence of SHMP obviously depressed fluorite rather than barite and SHMP exhibited good selective inhibition to fluorite. Fourier-transform infrared spectra and zeta potential results showed that: (1) SPS can adsorb on fluorite and barite surfaces and (2) SHMP had little effect on the adsorption of SPS on a barite surface, although it interfered with the adsorption of SPS on a fluorite surface through strong adsorption.

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1. Introduction

Fluorite (CaF\textsubscript{2}), an important non-metallic mineral, is widely employed in chemical manufacturing, metallurgy, and the glass and ceramic industries [1,2]. Consequently, high-grade fluorite is in great demand to meet the rapid development of related industries. However, in most cases, fluorite is tightly associated with gangue, such as barite (BaSO\textsubscript{4}), calcite (CaCO\textsubscript{3}), and quartz (SiO\textsubscript{2}) [1,3]. Thus, these less appealing fluorite resources require advanced beneficiation methods.

The abundant barite–fluorite type ores around the world are hard to treat, and the most efficient way is by froth flotation [3]. Until now, (sodium) oleate has been the most often used collector, and almost all the flotation theories and applications have been developed within an oleate system. Several studies show that oleate has strong collecting ability at relatively high temperatures but is quite sensitive to slimes, low
temperature (lower than 15 °C) [4,5], and hard-water ions [6]. To solve this problem, many meaningful attempts have improved the performance of these collectors in the flotation of scheelite and apatite [4–7]. Nevertheless, little attention has been given to design innovative flotation collectors for the separation of fluorspar from barite.

In this study, the anionic collector sodium petroleum sulfonate (SPS) was used as a collector to float fluorite and barite at a relatively low temperature. SPS normally contains molecules with different weights and polarities [8]. The main functional component of SPS is sulfonate, which has a highly hydrophilic sulfonic group connected with alkyl (RSO3Na) [9]. As reported, SPS has been extensively applied in the flotation of silicate and iron ores [9–11], but seldom have researchers examined the performance of SPS in the flotation of fluorite or barite.

Apart from collectors, depressants are vital to achieve desirable separation results in fluorite ore beneficiation. Depressants can be divided into three categories, namely, metal ions (Al3+, Fe3+, Mg2+, Cu2+, Fe2+), inorganic inhibitors (sodium silicate, sodium sulfide, and sodium hexametaphosphate (SHMP)), and macromolecular inhibitors (starch, tannin extract, and polyacrylamide). Among these commonly used inhibitors, SHMP is often used as a depressant, dispersant, stabilizer of mineral suspensions, precipitating agent of some metal ions, and softening agent of hard water. Consequently, SHMP has been used extensively in mineral processing [12] and was therefore selected as an inhibitor in our study to achieve selective recovery of one mineral over another.

In this study, the flotation behavior of both fluorite and barite and their separation were, for the first time, studied in the presence of SPS. SHMP was used as a depressant to achieve the separation of fluorite and barite. The interaction of SPS and SHMP with both minerals was studied by Fourier-transform infrared (FTIR) analysis, zeta potential measurement, and contact angle measurement. The purpose of this work was to uncover the underpinning mechanisms responsible for the flotability of fluorite and barite using SPS and SHMP.

2. Experimental

2.1. Materials

High-grade fluorite and barite samples were collected from the Wuling mountain area, China. The purities of fluorite and barite were over 97% based on X-ray diffraction (XRD, Fig. 1) and X-ray fluorescence (XRF) spectrometer analysis (Table 1). It can be seen that the characteristic peaks of fluorite and barite samples corresponded quite well to the standard patterns of fluorite (JCPDS card No. 35-0816) and barite (JCPDS card No. 24-1035). The samples were ground in a porcelain ball mill and then dry-screened to obtain particles with sizes ranging from −74 to +45 μm and used for micro-flotation tests. Samples used for infrared spectrum and zeta potential measurements were achieved by further grinding of the course particles, while samples with −45 μm were used for XRD and XRF measurements.

Analytical grade sodium hydroxide and hydrochloric acid were prepared as 1% solutions for pH adjustment. The SPS employed in this work was supplied by PetroChina Karakym Petrochemical Co., Ltd. and had a molecular weight of ~300 g/mol, an aromatic compound content of ~20%, a saturated hydrocarbon content of ~80%, and a small number of polar compounds. Analytical-grade SHMP was used as a depressant. Deionized water with a resistivity value of 18.25 MΩ cm was used throughout the experiments and
Table 1 – Main chemical composition of fluorite and barite samples (%).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>S</th>
<th>Ca</th>
<th>Ba</th>
<th>Mg</th>
<th>Si</th>
<th>F</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorite</td>
<td>0.19</td>
<td>50.78</td>
<td>0.24</td>
<td>0.04</td>
<td>0.22</td>
<td>47.59</td>
<td>0.79</td>
</tr>
<tr>
<td>Barite</td>
<td>33.63</td>
<td>1.34</td>
<td>64.18</td>
<td>0.13</td>
<td>0.19</td>
<td>0.02</td>
<td>0.30</td>
</tr>
</tbody>
</table>

LOI, loss-on-ignition.

spectroscopic-grade KBr was applied in FTIR spectra measurement.

2.2. Micro-flotation test

The micro-flotation tests were conducted with an RK/FGC flotation machine. Two grams of particles was placed in a 40-mL Flexiglas cell, which was then filled with a certain amount of deionized water. The pulp was continuously stirred at 1800 rpm for 2 min using a pH regulator and 2 min with or without the depressant before the collector was introduced and the pulp was then conditioned for 2 min. The pH of the slurry was monitored before flotation, followed by flotation for 5 min. For single mineral flotation tests, the floated and tailing fractions were collected separately and dried afterwards before being weighed. For artificially mixed minerals flotation, the concentrates and tailings were assayed (Chinese standards GB/T 5195.1-2006) to acquire the grades of fluorite and barite, before calculating the recovery amounts.

All flotation tests, except the temperature-based experiments, were carried out at 15 °C. In addition, the temperature of each test refers to the initial water temperature of each conditioning process.

2.3. FT-IR spectra

The infrared spectra were recorded by a Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, U.S.) in the 4000–500 cm⁻¹ region through KBr disks. Two-gram mineral samples (∼2 µm) were mixed with a certain amount of deionized water and reagents corresponding to the flotation test. The suspension was then stirred for 10 min, settled for 10 min, and then the solution was filtered. The treated sample was first dried in a vacuum desiccator at room temperature before a tiny amount of the dried powder was used for FTIR measurement. The IR spectra were obtained at a spectral resolution of 4 cm⁻¹.

2.4. Zeta potential measurement

The zeta potential was measured by a 90Plus Zeta Particle Size Analyzer (Brookhaven Instruments Corporation, U.S.). The particle size of the ground powder was finer than 2 µm for zeta potential measurement tests. The suspensions (0.1% mass fraction) with 1.00 × 10⁻³ M KCl solution were dispersed in a beaker and magnetically stirred for 10 min with and without flotation reagents at various pH values. After 5 min, the supernatant was obtained for zeta potential measurements.

Fig. 2 – Effect of pH value on recovery of fluorite and barite using SPS (c_{SPS} = 0.28 g/L).

3. Results and discussion

3.1. Flotation of fluorite and barite with SPS

The effect of pH value on the flotability of fluorite and barite is illustrated in Fig. 2. The results stated that the recoveries of both fluorite and barite increased drastically when pH was increased from 2 to 7, while there still being relatively high levels in recoveries (over 80%) of two minerals in the pH range 7–11. As indicated, recoveries of both minerals slightly increased when the pH value was beyond 7; therefore, the pH value of 7 was chosen to perform the conditional experiments. Obviously, barite showed higher recovery than fluorite in a strong acidic environment (pH 2). The maximum recoveries of fluorite and barite were 81.89% and 83.24% reached at pH 11, respectively. As observed, fluorite showed a quite similar flotation response to barite in the pH range 3–11.

The flotation response of fluorite and barite as a function of SPS dosage is shown in Fig. 3. An increase in the SPS concentration had a positive influence on the recoveries of both fluorite and barite when the pH was fixed at 7. The recoveries of both fluorite and barite increased rapidly when the SPS concentration was increased from 0.1 to 0.3 g/L. With a further increase in the SPS dosage, the recoveries of both fluorite and barite almost remained stable. As a result, a SPS dosage of 0.3 g/L–0.5 g/L was preferred in the flotation tests.

To investigate the effect of water temperature on the performance of SPS, a series of flotation tests were conducted
from 5 to 25°C with the pH value and SPS concentration fixed at 7 and 0.3 g/L, respectively (Fig. 4). Both fluorite and barite showed an incremental recovery when the water temperature rose from 5 to 25°C. The recovery of fluorite climbed slowly from 75.40% (5°C) to 81.36% (25°C); for barite, the recovery grew slightly from 72.69% to 78.64%. Therefore, it can be concluded that SPS functions well at low temperatures and its performance is not sensitive to temperature.

3.2. Effect of SHMP on flotability of fluorite and barite

The above flotation results indicate that the flotability of fluorite and barite in different cases seems to be similar. Thus, it is problematic to separate fluorite from barite using SPS as a collector without depressants. To handle this problem, SHMP was applied as an inhibitor to separate fluorite from barite. The impact of pH value and SHMP concentration was investigated, and the results are shown in Figs. 5 and 6.

Fig. 5 illustrates that SHMP has a strong inhibition on both fluorite and barite in the pH range 3–11, and fluorite has a lower recovery than barite. The recovery of fluorite decreased as the pH value increased from 3 to 11, and the final value was 6.60%. However, barite showed a different pattern as its recovery increased when the pH value was above 7 after a decrease in the acidic condition, and the final value was 38.04%. Furthermore, the maximum difference in recovery between fluorite and barite was achieved with the pH fixed at 11.

The flotability of fluorite and barite as a function of SHMP concentration is shown in Fig. 6. An increase in the SHMP dosage had a negative influence on the recoveries of both fluorite and barite when the pH was fixed at 11. The recovery of fluorite decreased more rapidly than barite when the SHMP concentration was increased to $2.29 \times 10^{-6}$ M and the difference in recovery was about 60%. With a further increase in the SHMP dosage, the difference in recovery between fluorite and barite reduced.

Fig. 6 – Effect of SHMP dosage on recovery of fluorite and barite (pH 11, $C_{\text{SPS}} = 0.3$ g/L).

Fig. 5 – Effect of pH value on recovery of fluorite and barite with SHMP ($C_{\text{SPS}} = 0.3$ g/L, $C_{\text{SHMP}} = 2.78 \times 10^{-6}$ M).

Fig. 3 – Effect of SPS dosage on recovery of fluorite and barite (pH 7).

Fig. 4 – Effect of water temperature on recovery of fluorite and barite using SPS (pH 7, $C_{\text{SPS}} = 0.3$ g/L).
Table 2 – Flotation results of artificial mixed minerals with the reagent scheme of “SPS (0.3 g L⁻¹) + SHMP (1.28 × 10⁻⁴ mol L⁻¹)” at pH 11.

<table>
<thead>
<tr>
<th></th>
<th>Yield/%</th>
<th>Grade/%</th>
<th>Recovery/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fluorite</td>
<td>Barite</td>
<td>Fluorite</td>
</tr>
<tr>
<td>Concentrate</td>
<td>70.98</td>
<td>6.26</td>
<td>93.74</td>
</tr>
<tr>
<td>Tailing</td>
<td>29.02</td>
<td>70.84</td>
<td>29.16</td>
</tr>
<tr>
<td>Raw material</td>
<td>100.00</td>
<td>25.00</td>
<td>75.00</td>
</tr>
</tbody>
</table>

Fig. 7 – Infrared spectra of minerals treated by SPS.

3.3. Flotation of artificial mixed minerals

Flotation tests on artificially mixed minerals of fluorite (0.5 g) and barite (1.5 g) were conducted three times to measure the separation efficiency of SHMP, and the average results are summarized in Table 2. The concentrate contained 93.74% barite with a low fluorite contamination, with the recovery of barite being 88.71%, while that of fluorite was 17.77%. Therefore, fluorite can be significantly removed with the selected reagent scheme. Obviously, the effective separation of barite from fluorite was possible using SHMP as a depressant.

3.4. FTIR spectrum analyses

FTIR spectroscopic analyses were conducted to uncover the interaction mechanism of SPS with the fluorite and barite surfaces, and the results are shown in Fig. 7.

The infrared spectrum of SPS shows that the broad band around 3442 cm⁻¹ was attributed to the –OH bond stretching vibration, while the frequencies at 2932 cm⁻¹ and 2853 cm⁻¹ were attributed to the stretching vibration of the alkyl groups [1,13]. The frequencies at 1630 cm⁻¹, 1575 cm⁻¹, and 1452 cm⁻¹ were the result of the vibration of the C=O bond of the benzene ring, and the frequency at 826 cm⁻¹ arose from the out-of-plane C–H bond deformation vibration [14]. Typically, frequencies at 1184 cm⁻¹ and 1051 cm⁻¹ are assigned to the stretching vibration of S=O bonds [14,15], which verifies the existence of sulfonic groups.

After treatment with SPS, several new peaks occurred compared with the pure fluorite spectrum. The frequencies at 2953 cm⁻¹, 2925 cm⁻¹, 2868 cm⁻¹, and 1383 cm⁻¹ were attributed to the alkyl groups in SPS, demonstrating that SPS has strong adsorption on a fluorite surface. The frequencies located at 1131 cm⁻¹, 590 cm⁻¹, and 748 cm⁻¹ in SPS shifted to 1123 cm⁻¹, 983 cm⁻¹, and 719 cm⁻¹, respectively. These obvious shifts reveal that the SPS-fluorite interaction may occur through chemical bonding [16,17].

The spectra of SPS, barite, and barite treated with SPS show some differences. The characteristic bands of barite occurred at 1181 cm⁻¹, 1084 cm⁻¹, 982 cm⁻¹, 630 cm⁻¹, and 610 cm⁻¹. Frequencies at 1181 cm⁻¹ and 1084 cm⁻¹ were attributed to the asymmetric stretch vibration of SO₄²⁻. The frequency at 982 cm⁻¹ was the result of the symmetric stretch vibration of SO₄²⁻. In addition, frequencies at 632 cm⁻¹ and 610 cm⁻¹ were the result of the bending vibrations of SO₄²⁻ [18]. With the adsorption of SPS, new bands were observed at 2924 cm⁻¹ and 2854 cm⁻¹, which were attributed to the alkyl groups in SPS, illustrating that SPS adsorbed on the barite surface. In the range 1200–500 cm⁻¹, several characteristic bands of barite and SPS were almost the same, so it is difficult to examine the interaction form at these frequencies.

The flotation results with SHMP show that SHMP has a strong interaction with minerals, and the hidden mechanism was investigated through FTIR (Fig. 8). The infrared spectrum of SHMP shows that frequencies at 1280 cm⁻¹ and 1161 cm⁻¹ were attributed to the P=O bond, the frequencies at 1110 cm⁻¹ and 1007 cm⁻¹ to the P–O bond, and the frequency at 893 cm⁻¹ to the P–O–P bond [19,20].

With the adsorption of SHMP, several characteristic bands of fluorite shifted. The frequencies located at 1635 cm⁻¹ (–OH stretching vibration), 1414 cm⁻¹, and 1171 cm⁻¹ in fluorite shifted to 1631 cm⁻¹, 1455 cm⁻¹, and 1177 cm⁻¹, respectively. These obvious shifts reveal that SHMP-fluorite interaction may occur through chemical bonding. Compared with Fig. 7, Fig. 8
shows several features: (1) both of the two curves contain the characteristic bands of SPS, indicating that SPS can still adsorb on the fluorite surface in the presence of SHMP and (2) frequencies at 1575 cm⁻¹, 1108 cm⁻¹, 1045 cm⁻¹, and 876 cm⁻¹ disappeared with the addition of SHMP; in addition, substantial shifts cannot be seen.

For barite, the addition of SHMP had little effect on its spectrum, and there was almost no shift when compared with that of fluorite. Furthermore, there was no new band or apparent shift. Therefore, it can be concluded that SHMP has a weak adsorption on a barite surface.

3.5. Zeta potential measurement results

To better understand the adsorption of SPS and SHMP on fluorite and barite, the electrokinetic potential of fluorite and barite in the absence and presence of SPS and SHMP were measured, and the results are plotted in Figs. 9 and 10.

As shown in Fig. 9, fluorite and barite exhibited an isoelectric point at pH 9.2 and pH 4.7, respectively. These results are in the range of previous reports [1,2,21]. It can be seen that SPS has an obvious impact on fluorite and barite surfaces. Zeta potentials for both fluorite and barite showed a substantial decrease in the presence of SPS. Fig. 9 indicates that SPS can adsorb on both fluorite and barite surfaces in a wide pH range (3–11), even if the mineral surface is negatively charged.

The addition of SHMP had a negative impact on the zeta potentials of fluorite and barite, demonstrating that SHMP can adsorb on fluorite and barite surfaces easily; however, the extent is different. SHMP drastically reduced the zeta potential for fluorite with an average decline of 20.14 mV in the 3–11 pH range. For barite, the average decrease was about 3.37 mV. These results indicate that the interaction between SHMP and fluorite is stronger than that of barite. The “SHMP + SPS” addition resulted in different zeta potential variations in the fluorite and barite flotation systems. The addition of SPS caused a slight reduction in the zeta potential of the “fluorite + SHMP” surface, indicating that SPS cannot favorably adsorb on a fluorite surface treated with SHMP. In the case of barite, the decrease of the zeta potential of the “barite + SHMP” surface was noticeable with the addition of SPS, showing that SPS can further adsorb on a “barite + SHMP” surface easily.
average reduction of the “barite + SHMP” surface was 24.91 mV, which was higher than that of the “fluorite + SHMP” surface (3.95 mV). This distinction can explain the selective inhibition for fluorite with the addition of “SHMP + SPS.”

To research the selective depression performance of SHMP, the species distribution diagram of SHMP shows that HPO$_4^{2-}$ and H$_2$PO$_4^-$ are the main components in the pH range 3–11 [20]. As reported, these anionic species have strong complexation ability with metal ions, especially Ca$^{2+}$ ions, and the complexes are soluble [12,19,22]. Since Ca$^{2+}$ ions were on the surface of fluorite, SHMP could absorb on the surface of fluorite more easily than that of barite. Hence, the zeta potentials on the surface of fluorite decreased more dramatically, and SHMP occupied the Ca sites which were active sites for the adsorption of anionic collector SPS. As a result, less SPS adsorbed on the surface of fluorite with the presence of SHMP, and the recovery of fluorite showed a considerable reduction.

4. Conclusions

SPS was used as a collector to study the flotation behavior of fluorite and barite with SHMP as a depressant. The flotation results showed that SPS performed well in an alkaline pulp even at a low temperature (5 °C), while the floatability of fluorite and barite were almost the same. At pH 11, the presence of SHMP obviously depressed fluorite rather than barite and SHMP exhibited good selective inhibition to fluorite. Flotation results of artificially mixed minerals indicated that the reagent scheme of 1.28 × 10$^{-4}$ mol L$^{-1}$ of SHMP and 0.3 g L$^{-1}$ of SPS at pH 11 obtained selective separation of barite from fluorite. FTIR spectra and zeta potential results showed that SPS adsorbs on fluorite and barite surfaces; however, SHMP had little effect on the adsorption of SPS on a barite surface, although it interfered with the adsorption of SPS on a fluorite surface through strong adsorption.

Conflict of interest

The authors report no conflicts of interest.

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