The Improvement Effect of Dispersant in Fluorite Flotation: Determination by the Analysis of XRD and FESEM-EDX

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Different dispersants were added in the dispersion process to improve the efficiency of fluorite flotation. The types and dosage of dispersant on the improvement of fluorite flotation were investigated; when the sodium polyacrylate (SPA) was used as the dispersant and its addition is 0.5%, the concentrate grade of CaF$_2$ increased from 90% to 98% and the fluorite recovery increased from 81% to 85%. Methods of X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), and Energy dispersive X-ray spectrometer (EDX) were used to characterize the sample. According to the analysis of results, the optimal sample consisted of CaF$_2$ and very little CaCO$_3$ in the size range of 0–5 µm. It could be concluded that the mechanism of improvement for the concentrate grade and recovery of CaF$_2$ was attributed to the change of potential energy barrier which caused the separation of particles with different charge. All results indicate that SPA has a great potential to be an efficient and cost-effective dispersant for the improvement of fluorite flotation.

1. Introduction

Fluorite, which is a kind of mineral with the highest level of fluoride content, derives its name from the Latin word “flurum.” The main chemical component of fluorite is CaF$_2$, and fluorite also contains traces of impurity elements such as silicon, aluminum, magnesium, strontium, yttrium, cerium, and uranium and other foreign matters like asphalt, ferric oxide, and so forth [1]. Fluorite is a kind of equiaxial crystal, often featuring in a cube and octahedron, and it also shapes into a monocristalline of rhombic dodecahedron or irregular granular aggregate. Fluorite is characterized by the vitreous luster, crispness, shell-shaped fractures, and complete cleavages along the octahedron. With its relative density of 3.18 and melting point of 1360 °C, it is insoluble in water or acid [2]. It has been a long time since humans began to make use of fluorite. Early in the 15th century, Agricola found the features of “Flares” in fluorites and employed them as a metallurgical flux [3]. Fluorite is the most important industrial mineral containing fluorine. It not only is widely used in the industrial sectors such as metallurgy, chemicals, ceramics, building materials, machinery, electrical machinery, aviation, agriculture, medicine, and precise instruments, but also serves as the important energetic materials in the cutting-edge science and emerging industries such as atomic energy, the rockets, and aerospace. Fluorite ore can produce products of different specifications through mineral processing [4]. With the development of industrial technology, there is a growing demand for high-quality fluorite ore (with the contents of CaF$_2$ more than 93%) [5]. However, there is less rich ore and poorer ore in terms of the fluorite ore resources in China, with the contents of CaF$_2$ in fluorite ore about 35 to 40% on average [6]. Therefore, we must adopt efficient mineral processing ways so as to improve the contents of CaF$_2$.

At present, we commonly adopt the flotation method to remove the mineral impurities except fluorite in the fluorite ore to improve the content of CaF$_2$, among which the dispersion process is a very important technique and the selection of dispersants will have a direct impact on the contents of CaF$_2$ of the final products [7]. In this work, we chose four types of dispersants, studying the dispersion effect of them on the fluorite purification to produce a high-grade
Table 1: The effect of dispersants on the concentrate grade and recovery of CaF₂.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Dispersant</th>
<th>Grade (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR</td>
<td>—</td>
<td>90</td>
<td>81</td>
</tr>
<tr>
<td>FSS</td>
<td>SS</td>
<td>92</td>
<td>82</td>
</tr>
<tr>
<td>FPAM</td>
<td>PAM</td>
<td>95</td>
<td>82</td>
</tr>
<tr>
<td>FHPMC</td>
<td>HPMC</td>
<td>92</td>
<td>83</td>
</tr>
<tr>
<td>FSPA</td>
<td>SPA</td>
<td>98</td>
<td>85</td>
</tr>
</tbody>
</table>

The objectives of this study is to explore the best dispersant in increasing the concentrate grade and recovery of CaF₂.

2. Experimental

2.1. Materials. The fluorite ore used in this work was mined from Inner Mongolia, which mainly consists of 77.12% CaF₂, 11.35% CaCO₃, 9.71% SiO₂, and a little clay. The sample was dried at 95°C to constant mass and then milled to less than 45μm. The dispersants supplied from Aladdin Co. Ltd. are all analytical reagents, including silica sol (SS), polyacrylamide (PAM), hydroxypropyl methyl cellulose (HPMC), and sodium polyacrylate (SPA), and the corresponding samples with different dispersants are FSS, FPAM, FHPMC, and FSPA, respectively.

2.2. Experimental Methods. For the preparation of high-grade fluorite concentrate, the slurry with 200 g fluorite ore and 700 mL water was ground in a ball mill for 20 min while the dispersant was added in this dispersion process, and then, by the process of rougher flotation and cleaner flotation, the final fluorite concentrate was obtained. The fluorite concentrate was dried at 95°C to constant mass and weighed, of which the composition was analyzed. From the procedure, the concentrate grade and recovery of fluorite were calculated to choose the best dispersant in increasing the concentrate grade and recovery. The sample prepared with the best dispersant was characterized by different methods, including X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy dispersive X-ray spectrometer (EDX). XRD was performed on a Rigaku D/max-3Bx diffractometer with Cu Kα radiation, in the range of 30°–65° 2θ and at a step size of 0.02°. FESEM micrographs were performed by the Hitachi SU8010 operating at the accelerating voltage of 15 kV and FESEM images were taken at different magnifications. The instrument was equipped with the energy dispersion X-ray spectroscopy.

3. Results and Discussion

3.1. Effects of Dispersants. Table 1 shows the effect of dispersants (0.5% addition) on the concentrate grade and recovery of CaF₂. As can be seen from Table 1, without the addition of dispersant, the concentrate grade and recovery of CaF₂ were 90% and 81%, and, with the addition of dispersant, it could increase the concentrate grade and recovery of CaF₂ but with a different effect. The concentrate grade of CaF₂ was in the range of 92–98% and the recovery was in the range of 82–85% with the addition of dispersant. In particular, with the addition of SPA, the concentrate grade and recovery of FSPA were 98% and 85%, which increased about 8% and 4% compared with FR. It can be attributed to the dispersion effect which dispersed the mineral particles equably in the solution and thus prevented other minerals such as calcite and quartz from being entered into the concentrate [8]. Hence, the addition of dispersant has great influences on the concentrate grade and recovery of CaF₂.

3.2. The Effect of Dispersant Amount. The amount of dispersant is an important parameter determining the concentrate grade and recovery of CaF₂. The effect of SPA amount on the concentrate grade and recovery is shown in Figure 1, which indicates that the dispersant amount has great influence on both of concentrate grade and recovery. It is observed that the concentrate grade of CaF₂ increases obviously with the increase of SPA addition all the while, and the increases are much stronger in the low SPA addition than in the high
addition, which can be attributed to the dispersion effect [9]. As the dispersibility of raw ore is poor, the impurity is hard to separate. With the addition of SPA, the dispersibility is improved and causes the increase of concentrate grade. However, the recovery of CaF$_2$ increases with the increase of dispersant at first but reaches the maximum value when the dispersant addition is 0.5% and then declines. It shows that too much dispersant addition makes a bad effect on the recovery of CaF$_2$ and the best amount of SPA addition is about 0.5%.

3.3. XRD Characterization. XRD pattern reveals the microstructure and composition of sample. The XRD pattern of FSPA is presented in Figure 2. As can be seen, the FSPA consists of fluorite (CaF$_2$) with peaks at 1.931, 1.926, 1.647, and 1.643 Å (corresponding to 46.1, 47.2, 55.7, and 56.3$^\circ$, resp.). The peaks are strong and sharp, reflecting an ordered and high-crystallinity structure, which show that the disposal of floatation does not change the crystallinity structure of fluorite [10, 11]. Meanwhile, the peaks of calcite, quartz, and other minerals are almost not observed, which indicate the high concentrate grade of CaF$_2$. As already introduced, fluorite, calcite, and quartz are the main minerals in the fluorite ore; the result suggests that, with the SPA addition, the other minerals such as calcite and quartz can be removed drastically from the concentrate and a high concentrate grade of CaF$_2$ can be obtained.
3.4. FESEM-EDX Characterization. The FESEM micrographs of FSPA are presented in Figure 3. As it can be seen in Figure 3, the microappearance of FSPA is irregular platelet and pile on each other, and its size is in the range of 0–5 µm, and its appearance is consistent with the typical characteristics of fluorite [12]. The particle size of FSPA is very fine due to the addition of dispersant, which is beneficial for the flotation. As the main minerals in the fluorite ore are fluorspar, calcite, and quartz which have their isoelectric point (IEP) at different pH, the addition of dispersant changes the pH of slurry and endows the minerals with different charges, which are beneficial for the separation of the minerals and getting the high concentrate grade of CaF$_2$ [13, 14]. It can be explained that the existence of potential energy barrier between particles keeps from the approach of particles, which causes the aggregative stability of colloidal suspensions, but the interaction energies of electrical double layer and van der Waals cause the potential energy barrier to arise and the particles with different charge to separate [15–17]. Meanwhile, the sample was characterized by the method of EDX in order to analyze the composition of the sample. Figure 4 shows the results of FESEM-EDX analysis of FSPA. As it can be seen in Figure 4, the EDX spectra reveal the presence of calcium, fluorine, and carbon (Ca = 52.12 wt%, F = 43.80 wt%, and C = 4.08 wt%), which indicate that the sample consists of CaF$_2$, and little of CaCO$_3$ may be residual [18]. In addition, Si is not detected in the sample which suggests the quartz had been removed completely. The result shows the high concentrate grade of CaF$_2$, and in this system the quartz, compared with calcite, is easier to be removed with the addition of dispersant.

4. Conclusion

The final results presented in this paper demonstrated the influence of dispersants in the floatation of fluorite. It was shown that all the dispersants exhibited certain effects in increasing the concentrate grade and recovery of CaF$_2$, and SPA presented high improvement in the purification of fluorite ores by floatation. With the addition of SPA in the slurry, the sample with high concentrate grade and recovery of CaF$_2$ was prepared, and when the addition of SPA is 0.5%, FSPA obtained the highest concentrate grade (98%) and recovery (85%). FSPA were characterized by several methods, including XRD, FESEM, and EDX. According to the analysis of results, the optimal sample consisted of CaF$_2$ and very little CaCO$_3$ in the size range of 0–5 µm. It can be concluded that the mechanism of improvement for the concentrate grade and recovery of CaF$_2$ could be attributed to the change of potential energy barrier which caused the separation of particles with different charges.

Generally speaking, in the practical application, the addition of dispersant is technically and economically reliable for the floatation of fluorite, including (a) the high concentrate grade of CaF$_2$, (b) the increasing recovery of ore fluorite, and (c) the finer particles. Meanwhile, the addition of dispersant is cost-effective and has a high recovery for CaF$_2$ from the slurry. Furthermore, the dispersion disposal with SPA as the dispersant in the fluorite flotation could increase the concentrate grade from 90% to 98% while the fluorite recovery was increased from 81% to 85%. Hence, in order to increase the concentrate grade and recovery of CaF$_2$, the SPA can be used as the potential dispersant in the fluorite floatation.

Conflict of Interests

The authors declare no conflict of interests regarding the publication of this paper.

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References


