

# The Effect of Oleic Acid Emulsification using SPE on Fluorite and Dolomite Flotation\*\*

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Collector OA, oleic acid, is widely used industrially for fluorite flotation. Low selectivity, dispersibility and collecting capability of the OA collector are always observed. In this study, compared with flotation of dolomite, a collector mixture of OA and SPE (styrylphenol polyoxyethylene ether) demonstrated significantly better performances for the fluorite. An optimal mass ratio 4:1 OA:SPE was found, and the recovery of fluorite was increased from over 85% to more than 94% compared with pure OA. Furthermore, the dosage of the collector agent was reduced from 50 mg mL<sup>-1</sup> to 20 mg mL<sup>-1</sup>, which did not negatively

impact the recovery of dolomite. The results from the contact angle tests indicated that SPE selectively increased the surface hydrophobicity of fluorite but had little effect on dolomite. Besides, zeta potential measurements and IR analyses revealed that the addition of SPE led to strong chemical adsorption on the surface of fluorite, resulting in a significant difference in the flotation performances of the two minerals. Therefore, SPE-emulsified OA is corroborated to prompt more selectivity and collecting capability on flotation of fluorite over dolomite.

## Introduction

Fluorite (CaF<sub>2</sub>) is one of the most important fluorine-bearing minerals and widely used in, chemistry, metallurgy, cements, ceramics and various other industries.<sup>[1,2]</sup> Furthermore, fluorite resources also occupy an extremely crucial position in the development of a powerful nation.<sup>[3,4]</sup> With the fantastic spur both in industry and economy, fluorite resources are consumed in large quantities, making the use of complex and refractory ores an inexorable trend.

However, the exploitation of this ore means a more complex process, which causes serious environmental and economic problems. Therefore, research on the utilization of complex fluorite resources must be strengthened. Carbonate-fluorite ore is one of the main types of fluorite ores, usually in coexistence with other gangue minerals like dolomite, calcite, and others.<sup>[5,6]</sup> It is difficult to separate fluorite and dolomite efficiently due to their extremely similar floatability. An effective way to improve the flotation separation of fluorite and dolomite lies in the

development of a collector system with strong collection capacity and high selectivity. The most commonly used collectors for the separation of fluorite and dolomite are fatty acids and their soaps. Among such collectors, oleic acid is currently the most widely used in the field of oxide ore. However, the dosage of oleic acid is high due to its poor selectivity, dissolution and dispersibility.

In recent years, emulsifiers have been widely used in ore flotation because they can enhance the selectivity, solubility and collection capacity of collectors.<sup>[7,8]</sup> Using RP emulsifier emulsified kerosene as collector, the flotation of coal has been studied and the recovery rate increased by 8%.<sup>[9]</sup> Billi et al. reported that using kerosene-emulsified dodecylamine as collector could significantly improve the recovery of zinc oxide.<sup>[10]</sup> In the flotation of other minerals, Rubio,<sup>[11]</sup> Guo,<sup>[12]</sup> and other researchers<sup>[13,14]</sup> have carried out similar collector emulsification studies and have achieved acceptable flotation effects. Nevertheless, only few studies about using SPE as emulsifier in the flotation separation of fluorite and dolomite have been reported. Thus, the purpose of this study is to identify whether SPE could be used as an emulsifier to improve the collection performance and selectivity of oleic acid in fluorite and dolomite flotation systems.

## Materials and Methods

### Materials and Reagents

The fluorite and dolomite samples were obtained from Baotou, Inner Mongolia Province, China. After the samples were ground with a ceramic ball mill, the products were then dry sieved and the products in the 37–74 μm size range were collected for micro-flotation experiments. The fraction with size (<37 μm) were ground to less than 5 μm with a mortar for zeta potential

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[\*\*] SPE = Styrylphenol polyoxyethylene ether.

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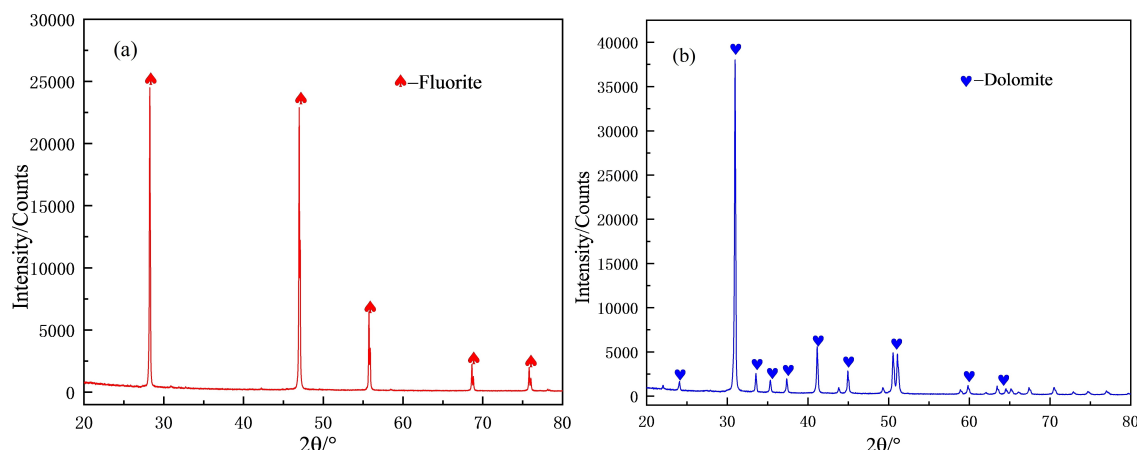


Figure 1. PXRD plots of fluorite (a) and dolomite (b).

and IR measurements. The results from powder X-ray diffraction (PXRD) are shown in Figure 1. The purities of fluorite and dolomite samples were 98.78% and 98.93%, respectively, which met the desired requirement for this research.

Analytically pure oleic acid (OA,  $C_{18}H_{34}O_2$ ), obtained from Sinopharm Chemical Reagent Co. Ltd, was used as the collector. Analytically pure styrylphenol polyoxyethylene ether (SPE, Figure 2) was provided by Jiangsu Haia Reagents, China. Solution pH values during the experiments were regulated using  $0.05 \text{ mol L}^{-1}$  hydrochloric acid (HCl) and  $0.1 \text{ mol L}^{-1}$  sodium hydroxide (NaOH) stock solutions. All reagents used in this

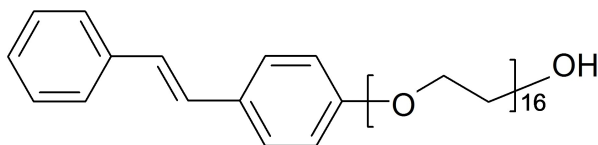


Figure 2. Chemical structure of styrylphenol polyoxyethylene ether (SPE).



Figure 3. Flotation machine used in this study.

experiments were analytically pure and supplied by Sinopharm Chemical Reagent Shanghai Co., Ltd, China. Distilled (DI) water with a minimum resistivity of  $18.2 \text{ M}\Omega \times \text{cm}$  was used throughout the tests.

### Micro-Flotation Experiments

Micro-flotation experiments were performed in an RK/FGC flotation machine (Figure 3) from Rock Grinding Equipment Manufacturing Co. Ltd., Wuhan, China with a 40 mL plexiglass cell at an impeller speed of 1800 rpm. In single mineral flotation experiments, 2 g single mineral samples were added into the flotation cell containing 35 mL of DI water and the pulp was conditioned for 1 min. A desired pH value of mineral suspensions was adjusted by adding NaOH or HCl.

After conditioning, the collector was added and agitated for 3 min. The flotation lasted for 5 min before the products (concentrate and tailing) were collected, dried, and weighed. The dry weights of the two products were measured and used to calculate the recovery, and the reported results were averaged over at least three repeated tests. The flowsheet for the micro-flotation experiments is presented in Figure 4.

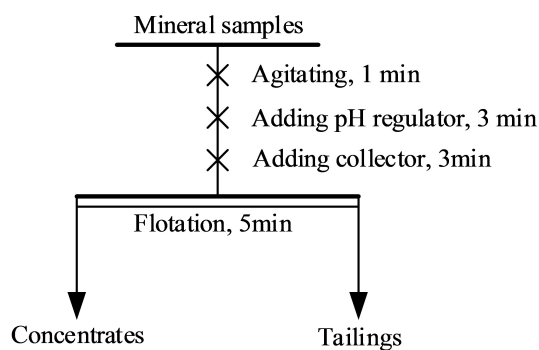


Figure 4. Flowsheet of micro-flotation experiments.

## Contact Angle Measurements

A JY-82C contact angle apparatus (Dingsheng Testing Equipment Co. Ltd., Chengde, China) was employed to measure the contact angle of exposed mineral surfaces with and without the reagent treatment using the sessile drop technique.<sup>[15]</sup> The prepared samples with smooth flat surfaces were conditioned with reagents in a beaker containing a certain amount of DI water, similar to the reagent flowsheet of the flotation process, and then washed and dried before contact angle measurements through the sessile drop technique. Each measurement was conducted three times and the average value was considered as the reported result.

## Zeta Potential Measurements

Zeta potentials for fluorite and dolomite were determined using an automatic potential analyzer (Zetasizer Nano ZS90, Malvern Co., Ltd., Britain) with a sample cell. In each measurement, 20 mg of the purified mineral sample were added to 50 mL of  $1 \times 10^{-3} \text{ mol L}^{-1}$  KCl as a background electrolyte. After the pH regulation, the pre-determined amount of collector was added for 5 min of conditioning. Subsequently, the suspension was left to settle for more than 30 min, and the supernatant liquor was taken and added to a sample cell for the Zeta potential measurements under the same conditions at 25 °C. The averages of at least three independent zeta potential measurements were adopted as the final results reported in this study.<sup>[16]</sup>

## FTIR Measurements

The FTIR spectra were recorded using a Spectrum One FTIR spectrometer (Version BM, Perkin Elmer Instrument Co., USA) at 25 °C in the spectral range of 500–4000  $\text{cm}^{-1}$ . After being subjected to the same treatment as in the micro-flotation tests, the solid mineral samples were washed at least three times with DI water, adjusted to the desired pH, and vacuum dried at 40 °C for 24 h. FTIR spectra were collected using KBr pellets.<sup>[17]</sup>

# Results and Discussion

## Micro-Flotation Results

In the collector OA system, the flotation results of fluorite and dolomite in the absence and presence of SPE as the emulsifier as a function of pH are showed in Figure 5.

In the absence of SPE, Figure 5 shows that the fluorite recovery increases with the increase of pH. A maximum of approximately 85% recovery at  $\text{pH } 9 \pm 0.2$  is found, followed by a remarkable decrease at  $\text{pH} > 9 \pm 0.2$ . In contrast, the dolomite recovery remains constant at approximately 83% in the pH range of 6.02–12.16. After adding the SPE-emulsified OA in advance, the recovery of fluorite was increased from over 85%

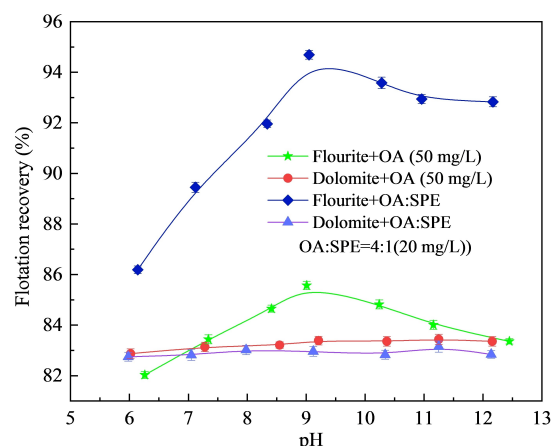


Figure 5. Effect of pH on the flotation behavior of fluorite and dolomite.

to more than 94% at  $\text{pH } 9 \pm 0.2$ , but the addition of SPE-emulsified OA did not strongly affect the recovery of dolomite in the whole pH range of 5.98–12.14. These results suggest that SPE-emulsified OA had a stronger floatability impact on fluorite than on dolomite. The optimum pH of  $9 \pm 0.2$  was chosen for further experiments concerning the mass ratio of OA and SPE.

Figure 6 details the influence of the mass ratio of OA and SPE on the flotation recovery of fluorite and dolomite at  $\text{pH } 9 \pm 0.2$ . As can be seen, the collecting capability of OA is greatly affected by the mass ratio of OA and SPE. When  $\text{OA:SPE} < 4:1$ , that is with an increase of the concentration of SPE, the amount of micelles of SPE in the pulp decreases, which weaken the competitive adsorption of SPE and OA with fluorite and dolomite. The highest recovery of fluorite at  $\text{pH} = 9 \pm 0.2$  of approximately 95% as well as for dolomite was found for  $\text{OA:SPE} = 4:1$  and afterwards slowly decreased. When the concentration of SPE continues to decrease, the dispersibility of OA decreased, which was not conducive to the adsorption of OA and led to a decrease in recovery of fluorite and dolomite. When SPE-emulsified OA was used as collector, the flotation recovery of dolomite was decreased slightly compared with

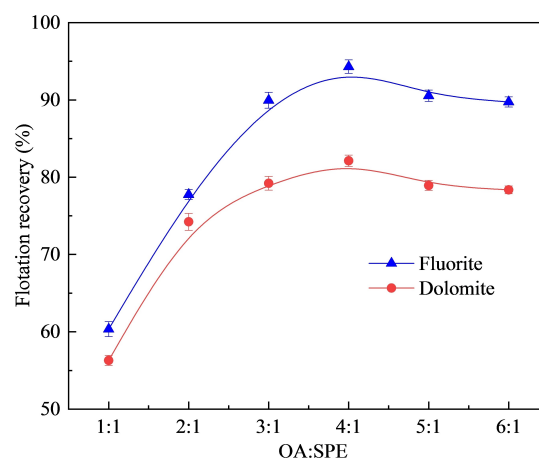


Figure 6. Effect of the mass ratio of OA and SPE on the flotation behavior of fluorite and dolomite at  $\text{pH } 9 \pm 0.2$ .

using only OA. These findings indicated that SPE-emulsified OA as a collector apparently is selective for fluorite and not for dolomite. Thus, a fixed mass ratio of OA:SPE=4:1 was chosen for further tests of collector concentration.

Figure 7 shows the influence of collector concentration on the flotation of fluorite and dolomite at pH  $9 \pm 0.2$  when using OA and SPE-emulsified OA, respectively. As shown in Figures 7(a) and 7(b), the flotation recovery of fluorite was considerably higher in the presence of SPE, and SPE slightly influenced the recovery of dolomite. When only OA was used as a collector, the fluorite and dolomite recovery were, at maximum, 85.66% and 83.15%, respectively, at an OA concentration of  $50 \text{ mg L}^{-1}$ . When OA was emulsified by SPE, the fluorite and dolomite recovery were, at maximum, 94.69% and 82.04%, respectively, at a collector concentration of  $20 \text{ mg L}^{-1}$ . Thus, the flotation of fluorite can be enhanced by using SPE-emulsified OA while simultaneously greatly reducing the dosage of collector, indicating that the collection capacity of SPE-emulsified OA is stronger than that of pure OA.

### Contact Angle Analysis

The hydrophilicity or hydrophobicity of the mineral surface is usually represented by the wettability. Wettability is closely related to the floatability of mineral, which is generally measured by the contact angle. In general, the larger the

contact angle, the weaker the hydrophilicity of the mineral surface will be.<sup>[18–19]</sup> Thus, the contact angles for fluorite and dolomite surface with and without OA and SPE have been measured and results are shown in Figures 8 and 9. Without flotation chemicals (Figures 8a and 9a), the contact angle of fluorite and dolomite were  $81.13^\circ$  and  $74.35^\circ$ , respectively. Similar findings had also been reported in the previous literature.<sup>[15–17]</sup> The contact angle of fluorite and dolomite after treatment with OA (Figures 8b and 9b) dramatically increased to  $90.87^\circ$  and  $88.06^\circ$ , respectively, illustrating that OA could significantly enhance their hydrophobicity, which matched well with their good floatability using OA alone. When used SPE-emulsified OA as collector, the contact angle of fluorite sharply increased to  $115.32^\circ$  (Figure 8c). In contrast, only a slightly increased contact angle of dolomite was observed (Figure 9c), suggesting that SPE-emulsified OA further increased the hydrophobicity of the fluorite surface but had little effect on dolomite. The results were consistent with the micro-flotation test.

### Zeta Potential Measurements

The zeta potential is the electrical potential for the interfacial double layer at the location of the slipping plane relative to a point in the bulk solution away from the interface.<sup>[20–21]</sup> In order to understand the adsorption mechanisms between the miner-

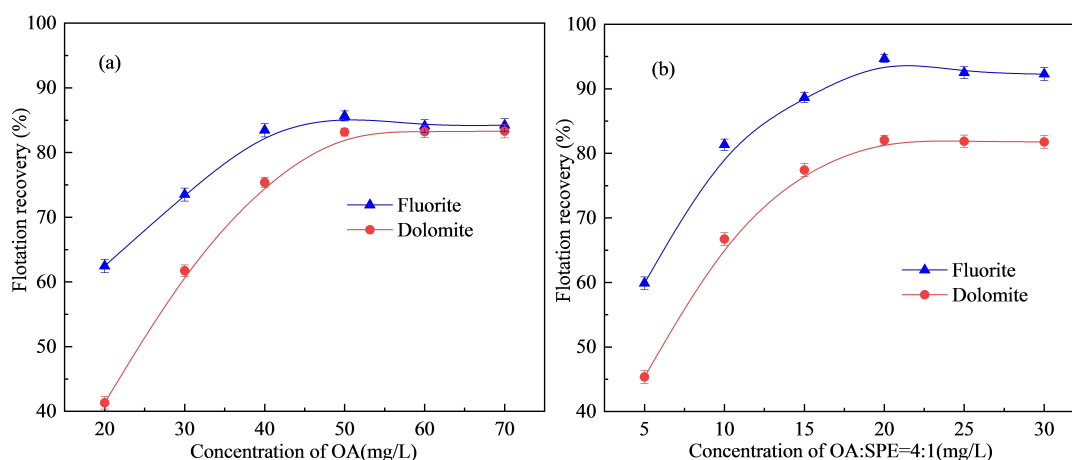


Figure 7. Effect of collector concentration on the flotation behavior of fluorite and dolomite.

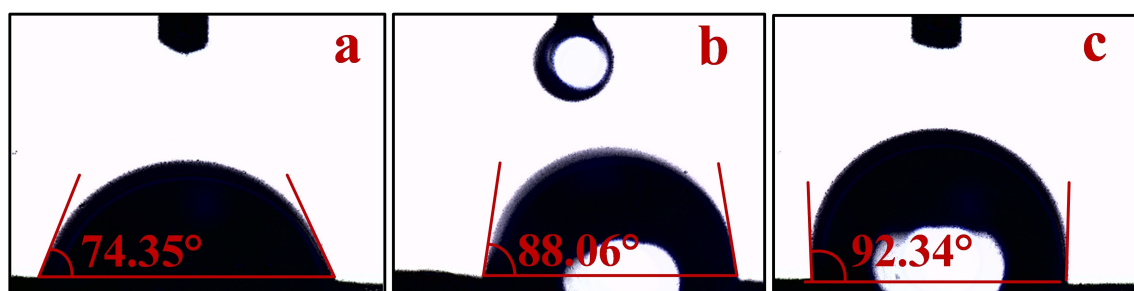


Figure 8. Contact angles of fluorite (a), fluorite + OA (b), fluorite + OA:SPE (c).

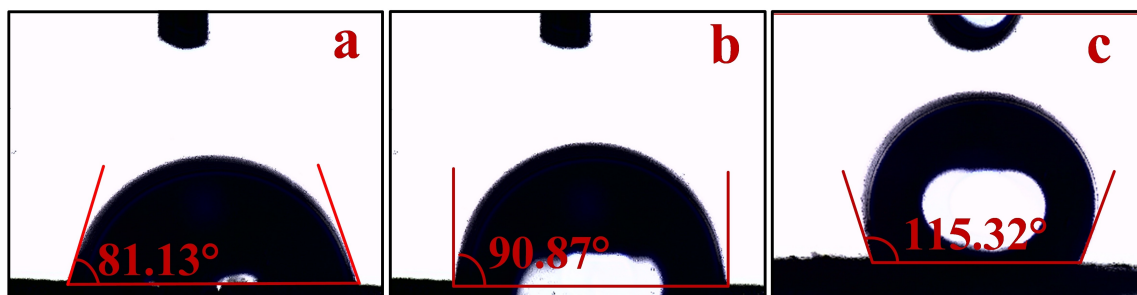


Figure 9. Contact angles of dolomite (a), dolomite + OA (b), dolomite + OA:SPE (c).

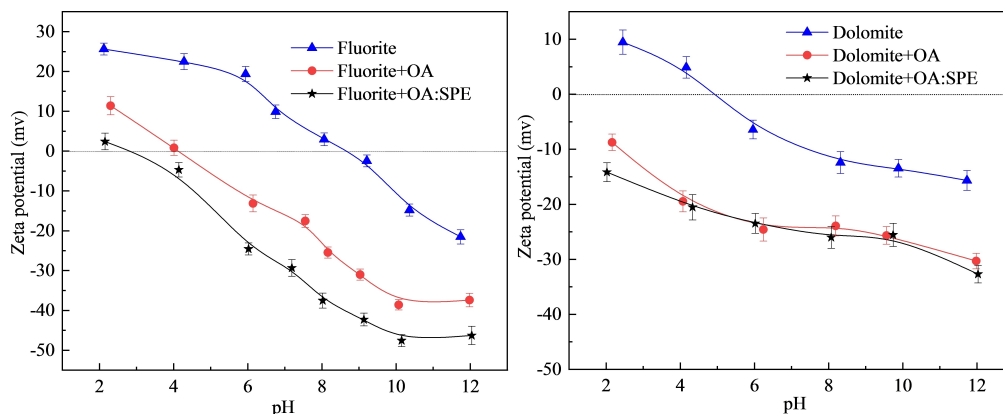


Figure 10. Effect of pH on the zeta potential of fluorite and dolomite in the absence and presence of different flotation agents.

als and flotation reagents, zeta potential measurements of fluorite and dolomite were carried out before and after the addition of collectors. As shown in Figure 10, in the absence of any collector, the isoelectric points of fluorite and dolomite were at pH 8.2 and pH 4.8, respectively, which was in line with previous studies.<sup>[22–24]</sup>

The addition of OA causes the zeta potential of fluorite and dolomite to significantly shift towards the negative direction, indicating that OA strongly adsorbed on the surfaces of the two minerals. When SPE-emulsified OA was added, compared to the addition of OA alone, although both fluorite and dolomite underwent negative shifts in zeta potential, although to different degrees as the addition of SPE-emulsified OA decreased the zeta potential of fluorite much more than that of dolomite. At pH 9 ± 0.2, the zeta potential of dolomite decreased from −25.02 mV to −26.14 mV while a more negative shift from −30.83 mV to −41.66 mV was observed in the zeta potential of fluorite, implying the greater affinity of SPE towards the surface of fluorite than to that of dolomite. That is to say, the adsorption of SPE onto fluorite was stronger than that onto dolomite, which is in agreement with the high flotation recovery of fluorite in the presence of SPE-emulsified OA.

### FTIR Analysis

FTIR mainly studies the composition and structure of material molecules based on the absorption of different wavelengths of

infrared light.<sup>[25]</sup> The FTIR tests were conducted to study the adsorption of different reagents at pH 9 ± 0.2 on the two mineral surfaces. The results of the measurements are depicted in Figures 11 and 12. As presented in Figure 11, the peaks at 3432.16 cm<sup>−1</sup>, 1644.68 cm<sup>−1</sup>, 1085 cm<sup>−1</sup> and 797 cm<sup>−1</sup> in the IR spectrum of natural fluorite are the characteristic absorption peaks of fluorite.<sup>[26]</sup> After treated with OA, two new bands at 2922.23 cm<sup>−1</sup> and 2859.54 cm<sup>−1</sup> appeared which were attributed to the symmetrical vibration absorption peaks of −C−H in the −CH<sub>2</sub> and −CH<sub>3</sub> moieties.<sup>[27]</sup> Moreover, the most representa-

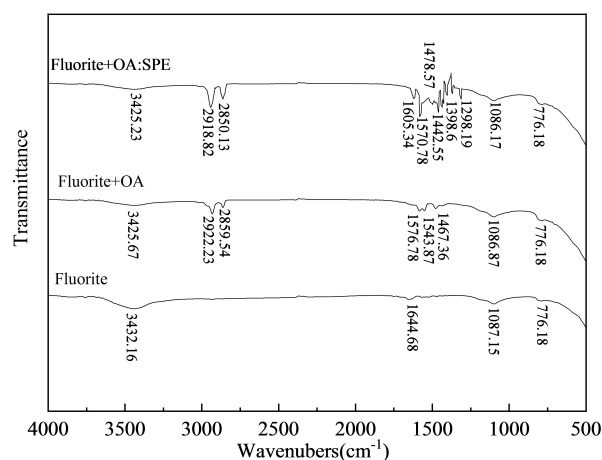


Figure 11. FTIR spectra of fluorite with and without different reagents.



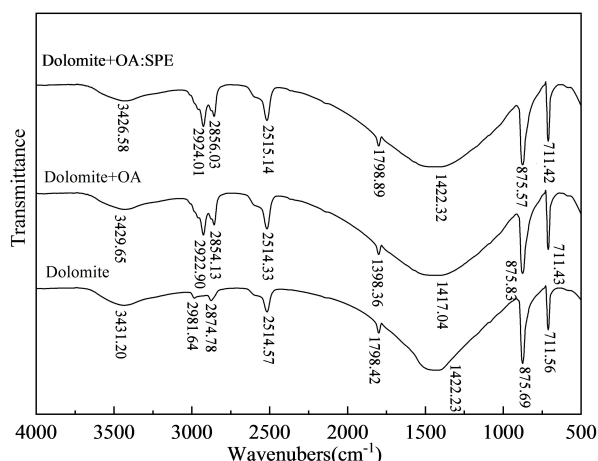


Figure 12. FTIR spectra of dolomite with and without different reagents.

tive characteristic peaks were located at  $1543.87\text{ cm}^{-1}$  and  $1467.36\text{ cm}^{-1}$ . The former was attributed to the adsorption peak of C=O asymmetric stretching in  $\text{-COO}^-$ , and the latter was due to the symmetric vibration of  $\text{-COO}^-$ ,<sup>[28–29]</sup> indicating the chemical adsorption of OA on the fluorite surface. When fluorite was treated with SPE-emulsified OA, the  $\text{-CH}_2$  and  $\text{-CH}_3$  absorption peaks of the infrared spectrum shifted to  $2916.88\text{ cm}^{-1}$  and  $2841.90\text{ cm}^{-1}$ , and the absorption peaks were significantly enhanced. At the same time, the skeleton characteristic peaks of the benzene ring also shifted to  $1570.78\text{ cm}^{-1}$ ,  $1478.57\text{ cm}^{-1}$  and  $1442.55\text{ cm}^{-1}$ , respectively. Two distinct peaks appeared at  $2916.88\text{ cm}^{-1}$  and  $2841.90\text{ cm}^{-1}$ , which were attributed to the vibration absorption peaks of C=C and C–O–C, respectively. Due to the strong skeleton characteristic peak of the benzene ring, the asymmetric and symmetric stretching peak of  $\text{-COO}^-$  were obstructed. This was indicated that under the emulsified OA system of SPE, SPE and OA had co-adsorbed on the surface of fluorite, and the adsorption of OA was strengthened.

Figure 12 illustrates that after dolomite was treated with OA, the  $\text{-CH}_2$  and  $\text{-CH}_3$  absorption peaks of the infrared spectrum shifted to  $2916.88\text{ cm}^{-1}$  and  $2841.90\text{ cm}^{-1}$ , and the absorption peaks were significantly enhanced. After dolomite was treated with SPE-emulsified OA, there no new remarkable absorption peak appeared in the FTIR spectrum of treated dolomite, indicating that SPE was adsorbed weakly on the dolomite surface. Therefore, it was proved that the SPE-emulsified OA greatly enhanced the adsorption capacity and hydrophobicity of the agent on the surface of fluorite, but had only a small impact on dolomite.

## Conclusion

SPE was used as the emulsifier in the separation of fluorite and dolomite and the mechanism was studied. The micro-flotation results showed that SPE could improve the recovery of fluorite and reduce dosage of collector. Contact angle measurements demonstrated that SPE increased the hydrophobicity of fluorite.

Zeta potential measurements and IR analyses illustrated that SPE was selectively absorbed on the fluorite surface. Nevertheless, SPE has a little effect on the flotation of dolomite. Therefore, the shortcomings of poor OA selectivity in the separation flotation of fluorite and dolomite can be effectively improved by using SPE as an emulsifier.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

**Keywords:** dolomite · flotation · fluorite · selective adsorption · separation

- [1] C. Liu, S. Song, H. Li, *Miner. Eng.* **2019**, *134*, 390–393.
- [2] Z. Gao, Y. Gao, Y. Zhu, Y. Hu, W. Sun, *Miner.* **2016**, *114*, 1–8.
- [3] H. Zhu, W. Qin, C. Chen, L. Chai, F. Jiao, W. Jia, *Miner. Eng.* **2018**, *120*, 80–86.
- [4] W. Chen, Y. Chen, X. Bu, T. Long, G. Zhang, F. Chen, R. Liu, K. Jia, Y. Song, *Powder Technol.* **2019**, *354*, 423–431.
- [5] Y. Foucaud, I. V. Filippova, L. O. Filippov, *Powder Technol.* **2019**, *352*, 501–512.
- [6] A. S. Ślaczka, *Int. J. Miner. Process.* **1987**, *20*, 193–210.
- [7] H. Lin, X. Fu, F. Zhang, *Fine and Speciality Chemicals*. **2010**, *18*, 39–43.
- [8] Z. Liang, *Functional Surfactants*, Light Industry Press, China, **2002**, p.113.
- [9] M. Zhao, F. Huang, H. Jing, Y. Liu, *Coal Conversion*. **1998**, *1*, 94–96.
- [10] D. Shi, *Flotation of Lead-Zinc Oxide Ore*, Yunnan Science and Technology Press, China, **1996**, p.22.
- [11] J. Rubio, X. Zhang, C. Li, *J. Metallic Miner. Process.* **2008**, *6*, 32–38.
- [12] L. Guo, *Met. Miner. Rev.* **2007**, *313*, 26–28.
- [13] D. Sun, J. Zhang, L. Zhu, *J. Heilongjiang Min. Inst. China* **1998**, *8*, 1–5.
- [14] G. He, *J. Guangdong Nonferrous Met. China*. **2000**, *10*, 92–95.
- [15] Y. Cui, F. Jiao, Q. Wei, X. Wang, L. Dong, *Sep. Purif. Technol.* **2020**, *242*, 116698.
- [16] Z. Wang, H. Wu, Y. Xu, K. Shu, J. Yang, L. Luo, L. Xu, *Sep. Purif. Technol.* **2020**, *237*, 116387.
- [17] B. Yang, Z. Zhu, H. Sun, W. Yin, J. Hong, S. Cao, Y. Tang, C. Zhao, J. Yao, *Miner. Eng.* **2020**, *156*, 106492.
- [18] C. Chen, Y. Hu, H. Zhu, W. Sun, W. Qin, R. Liu, Z. Gao, *Miner. Eng.* **2019**, *133*, 60–68.
- [19] Y. Ma, Y. Han, Y. Zhu, Y. Li, H. Liu, *J. Trans. Nonferr. Metals Soc. China*. **2016**, *26*, 3245–3252.
- [20] D. Fuerstenau, W. Pradip, R. Herrera-Urbina, *Colloids Surf.* **1992**, *68*, 95–102.
- [21] A. Jordens, C. Marion, O. Kuzmina, K. E. Waters, *Miner. Eng.* **2014**, *66*, 119–129.
- [22] Z. Gao, D. Bai, W. Sun, X. Cao, Y. Hu, *Miner. Eng.* **2015**, *72*, 23–26.
- [23] E. R. L. Espiritu, S. Naseri, K. E. Waters, *Colloids Surf. A* **2018**, *546*, 254–265.

- [24] E. R. L. Espiritu, G. R. da Silva, D. Azizi, F. Larachi, K. E. Waters, *Colloids Surf. A* **2018**, 539, 319–334.
- [25] X. Guan, S. Yan, Z. Xu, H. Fan, *J. Environ. Chem. Eng.* **2017**, 5, 479–487.
- [26] W. Yin, H. Sun, J. Hong, S. Cao, B. Yang, C. Won, M. Song, *Miner. Eng.* **2019**, 144, 106050.
- [27] W. Yin, B. Yang, Y. Fu, F. Chu, J. Yao, S. Cao, Z. Zhu, *Powder Technol.* **2019**, 343, 578–585.
- [28] P. Boguta, V. D'Orazio, N. Senesi, Z. Sokołowska, K. Szewczuk-Karpisz, *J. Environ. Manage.* **2019**, 245, 367–374.
- [29] D. Yuan, K. Cadien, Q. Liu, H. Zeng, *Miner. Eng.* **2019**, 133, 43–47.

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