

Influence and mechanism of Zn^{2+} on fluorite/calcite in sodium hexametaphosphate flotation system

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Abstract: Fluorite and calcite have similar surface properties and natural floatability, so their flotation separation has always been a problem faced by the beneficiation industry. The key to flotation separation is the choice of depressants. Sodium hexametaphosphate (SHMP) has a good effect on fluorite calcite selective inhibition. In this paper, the effects of Zn^{2+} on the selective inhibition of SHMP in the flotation process of fluorite and calcite were studied through single mineral and artificial mixed mineral flotation experiments. Solution chemical calculation, X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared spectroscopy (FT-IR) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analyses investigated the mechanism of action of Zn^{2+} , which had the most significant negative effect on the selective inhibition of SHMP. The results show that the main components of SHMP inhibiting minerals are HPO_4^{2-} and $H_2PO_4^-$, which can react with Ca active sites on the mineral surface to form hydrophilic $Ca(H_2PO_4)_2$ and $CaHPO_4$, while Zn^{2+} The presence of HPO_4^{2-} in solution resulted in the formation of stable $ZnHPO_4$ complexes, thereby weakening the inhibitory effect of SHMP on minerals.

Keywords: fluorite, calcite, sodium hexametaphosphate, flotation, metal ions

1. Introduction

Fluorite (CaF_2) is one of the main sources of fluoride. Fluorine is widely used in special plastics, rubber, refrigeration (Freon), aviation, medicine and other industries (Gagnon et al., 2003; Pérez Muñoz et al., 2020; Tasker, 1980). Fluorite is a non-renewable resource, so most countries have taken protective measures when developing and utilizing fluorite resources (Güleç & Oğuzhanoglu, 2021). With the continuous development of the world economy, the continuous deepening of resource development and the continuous expansion of the application field of fluorine, the demand and consumption of high-quality fluorite are also showing a continuous growth trend, which makes the rational development and utilization of fluorite resources particularly important (Gao et al., 2018; Gao et al., 2021; Tasker, 1980).

Calcite ($CaCO_3$) is a common carbonate gangue mineral, usually associated with fluorite (Gao et al., 2016; Jiang et al., 2018; Pugh & Stenius, 1985). Most of the associated fluorite deposits are calcite type fluorite ore (Sun et al., 2021; Wang et al., 2018). Because calcite has similar surface properties and natural floatability to fluorite, its flotation separation has always been one of the most difficult problems in the mineral processing industry (Grayson, 1956; Sun et al., 2021).

When the calcite content in fluorite ore is high, conventional calcite depressants such as water glass are difficult to effectively separate fluorite and gangue minerals and obtain qualified concentrates due

to poor selectivity. In order to improve the concentrate grade, it is necessary to increase the number of cleaner when designing the flotation process, but this will lead to a decrease in the recovery rate of fluorite. Therefore, the selection of a suitable calcite depressants is the key to obtain a good separation index.

Sodium Hexametaphosphate (SHMP) is a water-soluble inorganic compound, which has a strong selective inhibitory effect on carbonate and silicate gangue minerals (Foucaud et al., 2019; Li et al., 2020; Yao et al., 2020). Gao et al. (2016) used octylhydroxamic acid (HXMA-8) and sodium oleate (NaOL) as collectors and SHMP as a depressant to separate scheelite and calcite by flotation. The recovery rate and grade of the obtained scheelite were up to 83% and 79%, achieving selective separation of scheelite and calcite. Kang et al. (Kang et al., 2019) used NaOL mixed with oleamide at a mole ratio of 2:1 as collectors. And SHMP as a depressant to further enhance the floatability difference of scheelite with calcite. With the absence of SHMP, the recovery of scheelite remained above 85% and the recovery of calcite was reduced to 20%.

Using SHMP as a calcite depressant can achieve better separation results in laboratory tests (Gao et al., 2021; Kang et al., 2019; Wang et al., 2021). However, SHMP has not yet been popularized or applied in the industrial production of calcite-type fluorite ore. The reason is that the slurry environment in industrial production is complex, and the presence of interfering ions is an important factor that cannot be ignored (Shi et al., 2013; Xun et al., 2021). The metal ions in the pulp often affect the effect of the flotation reagents. The metal ions may consume the collectors or depressants in the pulp, making the beneficiation reagents ineffective, thereby affecting the separation results (Sun et al., 2021; Xu et al., 2020; Zhang et al., 2018).

In this paper, fluorite and calcite were used as the research objects, and NaOL was used as the collector to explore the effect of common metal ions Zn^{2+} in industrial pulp on the depression effect of SHMP. Studied by solution chemical calculation, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and time-of-flight ion secondary ion mass spectrometry (ToF-SIMS). The mechanism of action of metal ions provides theoretical guidance and new viewpoints for the flotation separation of fluorite and calcite.

2. Methods

2.1. Materials

The fluorite and calcite used in the test were taken from Yunnan, China. The mineral samples were prepared as follows: first, the minerals were crushed into 2mm particles with a hammer, and the impure particles were manually removed under a microscope. Then the samples were ground using a three-head grinder (XPM- Φ 120 \times 3, China) and graded to obtain two particle size fractions (38~74 μ m and < 38 μ m). Use samples with fractions of 38 to 74 μ m for micro-flotation experiments, and use samples with fractions of < 38 μ m for subsequent detection and analysis.

The prepared single minerals were analyzed by X-ray diffractometer (Empyrean, Malvern Panalytical), and the analysis results are shown in Fig. 1. Fig. 1(a) and (b) show that only the diffraction peaks of fluorite and calcite are detected. The chemical components of the fluorite sample detected by XRF analysis were 99.906% CaF_2 , 0.046% Si, 0.026% Al, 0.019% Fe and 0.002% Sr. The chemical components of the calcite sample detected by XRF analysis were 99.748% $CaCO_3$, 0.160% MgO, 0.032% SiO_2 , 0.020% Fe_2O_3 , 0.019% SrO, 0.015% MnO and 0.006% ZnO. Respectively, indicating that the fluorite single mineral and calcite single mineral have high purity and meet the requirements of experimental research.

The purity of the chemicals used in the experiments were all analytical grades. The collector is NaOL, the depressant is SHMP, the pH adjuster is sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH). zinc sulfate ($ZnSO_4 \cdot 7H_2O$) to simulate the metal ions Zn^{2+} in the actual industrial pulp.

2.2. Micro-flotation experiments

Micro-flotation experiments of the single minerals and artificially mixed ore were carried out using a RK/FGC5-35 flotation machine. The flotation conditions were room temperature, the impeller speed of the flotation machine was 1600r/min, the particle size of the minerals used in the flotation test was - 74+38 μ m, and the pH of the pulp was monitored with a pH meter (PHS-3C, Rex Electric Chemical). The

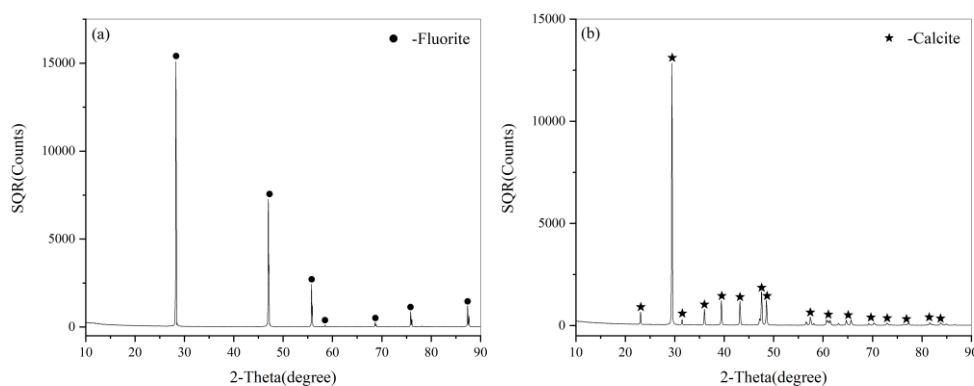


Fig. 1. XRD patterns of (a) pure fluorite and (b) pure calcite sample

test method is as follows: add 2g single mineral sample or artificial mixed mineral sample (1g fluorite + 1g calcite) and 60mL deionized water (18.25M Ω) into the flotation cell, adjust the pH of the pulp with apH adjuster, and then add a depressant to stir 2min, followed by adding collector and stirring for 2min, followed by aeration (flow rate of 15cm³/min) and manual scraping for 3min. After that, the concentrate and tailings were filtered, dried and weighed, and the recovery rates of single minerals and artificial mixed ore were calculated by formulas 1 and 2.

$$\varepsilon = \frac{m_1}{m_1 + m_2} \times 100\% \quad (1)$$

$$\varepsilon = \frac{m_1 \times \beta}{(m_1 + m_2) \times \alpha} \times 100\% \quad (2)$$

where m_1 and m_2 are the masses of the concentrate and tailings, respectively, and α and β are the grades of the feed and concentrate of fluorite, respectively.

2.3. Calculations of solution chemistry

In this paper, the form and content of each component in the binary solution system of metal ions and SHMP under different pH values were calculated by Visual MINTEQ software. Visual MINTEQ is a software developed by the National Environmental Agency of the United States, which has been widely used to simulate the ion and mineral balance in the environmental water balance solution. The software has a powerful database of equilibrium constants, including liquid complexation, dissolution/precipitation, oxidation/reduction, gas-liquid phase equilibrium and adsorption and other equilibrium reactions. It can theoretically calculate the chemical interaction by equilibrium constant, Gibbs free energy and other thermodynamic data, and judge the chemical morphology distribution by mass interaction expression, predict the adsorption of metal ions and metal ion complexes.

2.4. XPS analysis

Samples detected by X-ray photoelectron spectroscopy were prepared as follows: 2 g fluorite or calcite samples were mixed with 60 mL deionized water, and then the pH value was adjusted by sulfuric acid or sodium hydroxide. After stirring for 2 min, depressants were added, and after stirring for another 10min, the pulp was filtered by a funnel. The filtered samples were dried at room temperature and tested by X-ray photoelectron spectroscopy. PHI5000 VersaProbe II (Shanghai Uzong, Shanghai) was used for X-ray photoelectron spectroscopy. The power of the instrument was 50 W, the voltage was 15 kV, and the anode was Al target. The binding energy (EB) was calibrated based on THE C1s of EB[C1s] = 284.8 eV.

2.5. FT-IR analysis

The samples detected by FT-IR were prepared as follows: 2 g fluorite or calcite samples were mixed with 60mL deionized water and their pH values were adjusted. Depressant SHMP was added after

stirring for 2 min, and collector NaOL was added after stirring for another 2min. After stirring for another 30 min, the samples were filtered and dried at room temperature, and then FT-IR was detected. FT-IR detection using ALPHA infrared spectrometer (Bruker, Germany). The range of instrumental analysis was $4000\sim 400\text{cm}^{-1}$, the number of scanning was 16, and the spectral resolution was 4 cm^{-1} .

2.6. ToF-SIMS analysis

The samples detected by the ToF-SIMS were prepared as follows: 2 g fluorite or calcite samples were mixed with 60 mL deionized water and their pH values were adjusted. Depressant SHMP was added after stirring for 2 min, and collector was added after stirring for another 2min. After stirring for another 10 min, the samples were filtered and dried at room temperature, and ToF-SIMS test was performed. Ion beam pulses were applied to the samples using 15 keV Bi^{3+} , and the samples were analyzed using ToF-SIMS V (ION-ToF GmbH, Münster, Germany). The samples were analyzed using delayed extraction mode over the image range of $500\times 500\mu\text{m}$, with a pixel density of 256×256 after 62 s.

3. Results and discussion

3.1. Single mineral micro-flotation experiments

3.1.1. Depression effect of SHMP on flotation of fluorite and calcite

Fig. 2(a) shows the effect of NaOL as a collector at 80mg/L and the depressant SHMP on the recovery of fluorite and calcite in a deionized water system with $\text{pH}=9$. It can be seen from the figure that SHMP has a strong depression effect on the flotation of fluorite and calcite. With the increase of the amount of SHMP, the recovery rate of fluorite and calcite both decrease significantly. When the amount of SHMP is less than 4mg/L , the recovery rate of fluorite is higher than that of calcite. When the amount of SHMP is less than 4 mg/L , the difference between the recovery rate of fluorite and calcite is the largest. The subsequent test will use the amount of SHMP to be 2 mg/L .

Fig. 2(b) shows the effect of different pH values on the recovery of fluorite and calcite when the amount of NaOL as a collector is 80mg/L and SHMP as a depressant is 2mg/L . It can be seen from the figure that with the increase of pH value, the recovery rate of fluorite shows a decreasing trend, while the recovery rate of calcite shows an increasing trend. When $\text{pH}=8$, the difference between the recovery rates of fluorite and calcite reached the maximum value. At this time, the recovery rate of fluorite was 69.09% , and the recovery rate of calcite was 26.69% .

The results show that SHMP has a significantly selectivity for fluorite and calcite without the addition of metal ions.

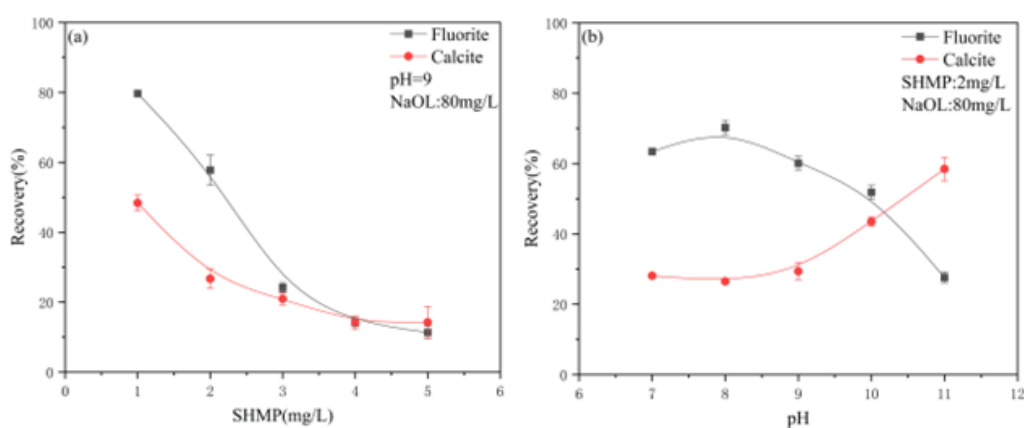


Fig. 2. Effect of the (a) amount of SHMP and (b) pH on the recovery of fluorite and calcite

3.1.2. Effect of Zn^{2+} on SHMP

Fig. 3(a) shows the effect of Zn^{2+} concentration on SHMP when the amount of NaOL as collector at 80 mg/L and SHMP as depressant is 2 mg/L in a deionized water system with $\text{pH} = 8$. It can be seen from the figure that with the increase of Zn^{2+} concentration, the recovery rates of fluorite and calcite both

increased first and then decreased. When Zn^{2+} concentration was low, Zn^{2+} had a certain activation effect on fluorite flotation. However, with the increase of Zn^{2+} concentration, the recovery rate of calcite is closer to fluorite.

Fig. 3(b) shows the influence of pH value on the effect of SHMP when the concentration of Zn^{2+} is 10mg/L, the amount of NaOL as collector is 80mg/L and the amount of SHMP as depressant is 2 mg/L. As can be seen from the figure, with the increase of pH value, the recovery of fluorite showed a downward trend, while the recovery of calcite showed an upward trend. When pH=8, the recovery difference between fluorite and calcite is the largest, and the recovery of fluorite is 77.73% and that of calcite is 59.61%.

The results show that Zn^{2+} has a certain activation effect on fluorite, but seriously interferes with the depression of SHMP on calcite, making the recovery of calcite rise sharply and aggravating the effect of SHMP on fluorite and calcite

3.2. Artificial mixed minerals micro-flotation experiments

In order to verify the negative effects of Zn^{2+} on SHMP, the effects of Zn^{2+} (10 mg/L) SHMP on artificial mixed minerals were investigated when the amount of NaOL as collector was 80 mg/L and the amount of SHMP as depressant was 2 mg/L under the condition of pH=8 in this part. The results are shown in Table 1 and 2.

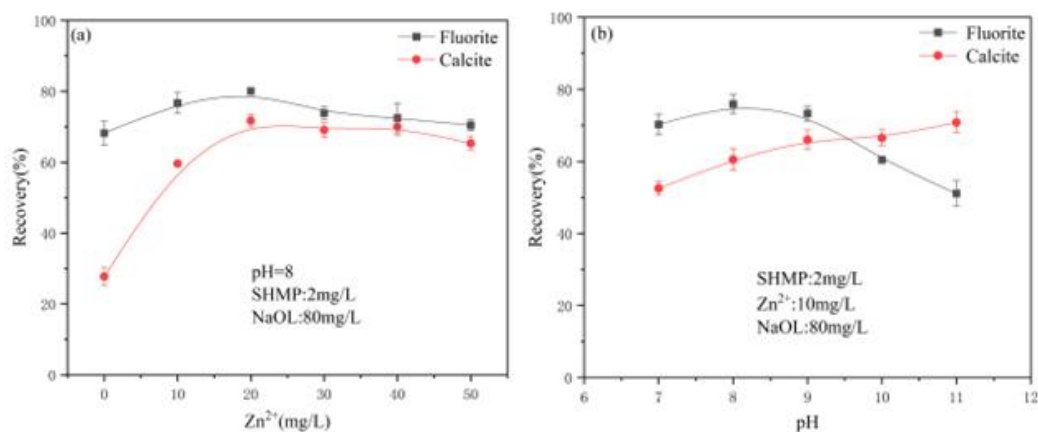


Fig. 3. Effect of the (a) amount of Zn^{2+} and (b) pH on the effect of SHMP

Table 1. Micro-flotation results for the artificial mixed mineral without Zn^{2+} and SHMP

Products	Yield/%	Grade /%		Recovery/%	
		Fluorite	Calcite	Fluorite	Calcite
Concentrate	39.4	64.52	35.48	50.84	27.96
Tailings	60.6	49.04	59.44	49.16	72.04
Artificial mixed	100	50	50	100	100

Table 2. Micro-flotation results for the artificial mixed mineral with Zn^{2+} and SHMP

Products	Yield/%	Grade /%		Recovery/%	
		Fluorite	Calcite	Fluorite	Calcite
Concentrate	47.63	51.87	48.13	49.41	45.85
Tailings	52.37	48.3	51.7	50.59	54.15
Artificial mixed	100	50	50	100	100

With the addition of Zn^{2+} , the grade of fluorite in concentrate decreased from 64.52% to 48.3%, and the recovery rate decreased from 50.84% to 49.41%. The grade of calcite in tailings decreased from 59.44% to 51.7%, and the recovery rate decreased from 72.04% to 54.15%. The results show that Zn^{2+} seriously interferes with the effect of SHMP and worsens the flotation separation effect of fluorite and calcite.

3.3. Calculations of solution chemistry

Visual MINTEQ model is widely used to calculate ion morphology, solubility balance and adsorption in aqueous solution, and the calculated results can reflect ion concentration and potential products in flotation pulp. Fig. 4(a) and (b) show the morphology and content of each component in the binary solution system of Zn^{2+} and SHMP at pH value.

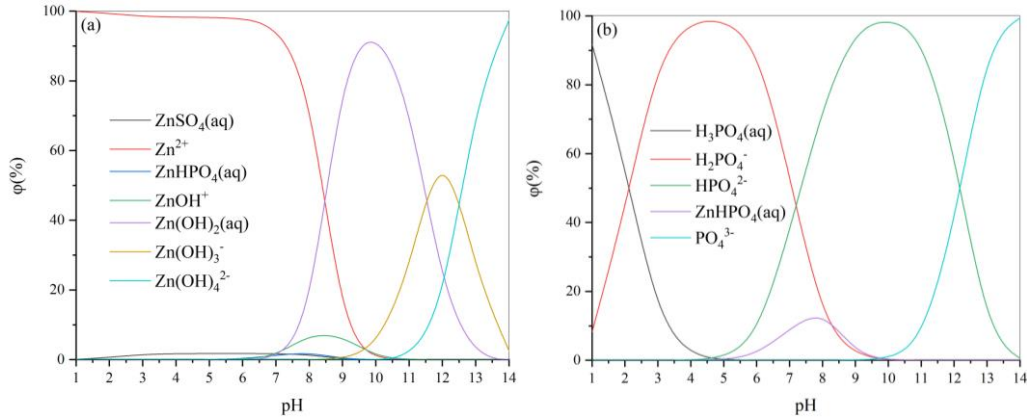


Fig. 4. Effect of pH on the speciation and content of (a) Zn and (b) P in the binary solution system

According to Fig. 4 (a) and (b), the main chemical reactions in binary solution system of Zn^{2+} and SHMP can be inferred as follows:



It can be seen from Fig. 4(a) that Zn^{2+} will hydrolyze gradually in the solution and produce four Zn-containing components such as $Zn(OH)_2$, $ZnOH^+$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$. Zn^{2+} was the dominant component at $pH < 8.5$, and $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ became the dominant component with pH increasing. It can be seen from Fig. 4(b) that there are five phosphorus-containing components in the solution, which are $H_3PO_4(aq)$, $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} generated by the gradual hydrolysis of SHMP, and $ZnHPO_4(aq)$ generated by the reaction of its hydrolysis product HPO_4^{2-} with Zn^{2+} . When $pH < 2.1$, $H_3PO_4(aq)$ was the dominant component; when $2.1 < pH < 7.2$, $H_2PO_4^-$ was the dominant component; when $7.2 < pH < 12.2$, HPO_4^{2-} was the dominant component; when $pH > 12.2$, PO_4^{3-} was the dominant component. When $pH = 8$, the fractions of SHMP in the solution are $HPO_4^{2-} > H_2PO_4^- > ZnHPO_4(aq)$,

PO_4^{3-} and $\text{H}_3\text{PO}_4(\text{aq})$ almost do not exist in the solution, indicating that the main components inhibiting calcite may be HPO_4^{2-} and H_2PO_4^+ . This is consistent with previous research conclusions (Chen et al., 2019), and the addition of Zn^{2+} consumes part of HPO_4^{2-} to produce $\text{ZnHPO}_4(\text{aq})$, which interferes with the depression of SHMP on minerals.

3.4. XPS analysis

In order to further study the effect of Zn^{2+} on SHMP for fluorite and calcite, XPS was used to analyze the relative contents of main elements on the surface of fluorite and calcite treated by SHMP (2 mg/L) with and without Zn^{2+} (10mg/L). The results are shown in Table 3 and 4.

Table 3. Relative content of surface elements of fluorite treated with Zn^{2+}

Elements	Relative content / %		
	Without Zn^{2+}	With Zn^{2+}	Shift
Ca2p	20.25	20.82	+0.57
F1s	23.90	22.17	-1.73
O1s	16.31	15.30	-1.01
C1s	39.20	41.39	+2.19
P2p	0.34	0.13	-0.21
Zn2p	0	0.19	+0.19

Table 4. Relative content of surface elements of calcite treated with Zn^{2+}

Elements	Relative content / %		
	Without Zn^{2+}	With Zn^{2+}	Shift
Ca2p	11.68	12.54	+0.86
O1s	40.35	37.48	-2.87
C1s	47.20	49.65	+2.45
P2p	0.77	0.22	-0.55
Zn2p	0	0.11	+0.11

It can be seen from Table 3 and 4 that after adding Zn^{2+} , the content of Ca2p and Zn2p on the surface of fluorite increased by 0.57% and 0.19%, respectively, and the content of P2p decreased by 0.21%; the content of Ca2p and Zn2p on the surface of calcite increased by 0.86% and 0.11%, respectively, and the content of P2p decreased by 0.55%. The results show that the presence of Zn^{2+} reduces the adsorption of SHMP on the surface of fluorite and calcite, and exposes more calcium active sites to the mineral surface, which may be the main reason for the increased recovery of fluorite and calcite.

Fig. 5 shows the P2p peaks on the surfaces of fluorite and calcite treated with SHMP. The peaks at binding energies of 132.64 eV and 133.47 eV in Fig. 5(a) are attributed to the phosphate species $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaHPO_4 , respectively (Landis & Martin, 1984; Zhang et al., 2021); the signal-to-noise ratio of the P2p spectrum on the fluorite surface in Fig. 5(b) is high, and the peak splitting cannot be performed, indicating that the presence of Zn^{2+} seriously interferes with the adsorption of SHMP on the surface of fluorite, so that the adsorption amount on the surface of fluorite is very low. For calcite, the binding energy peaks at 132.43eV and 133.38eV in Fig. 5(c) are also attributed to $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaHPO_4 , respectively (Landis & Martin, 1984; Zhang et al., 2021); in Fig. 5(d) the peaks of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaHPO_4 were shifted to 132.05 eV and 132.98 eV, respectively, and the intensity of the P2p peak was significantly reduced, indicating that the addition of Zn^{2+} changed the adsorption environment of SHMP on the calcite surface and reduced its adsorption capacity.

According to the results of calculations of solution chemistry and XPS analysis, it can be inferred that the main components of SHMP inhibiting minerals are HPO_4^{2-} and H_2PO_4^+ . These two phosphate ions react with the Ca active sites on the mineral surface to form $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaHPO_4 two calcium

phosphate species, thereby improving the hydrophilicity of the mineral surface; while Zn^{2+} can react with SHMP to generate phosphate species, which consumes part of the SHMP in the solution and reduces the adsorption amount of SHMP on the mineral surface.

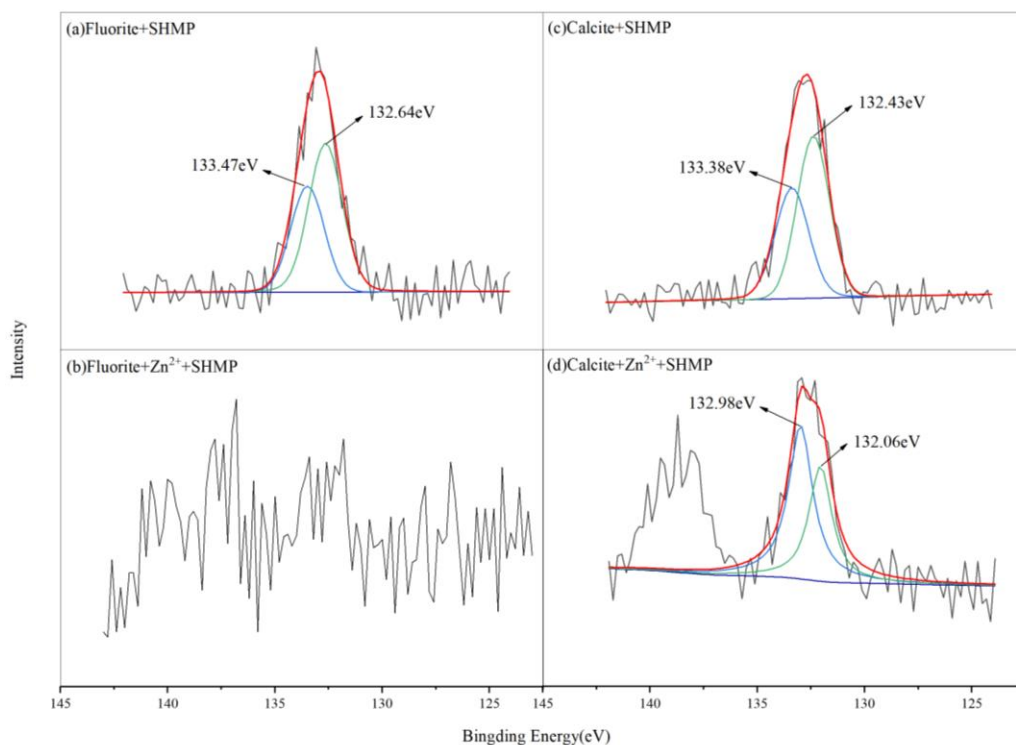


Fig. 5. P2p XPS spectra of (a) SHMP treated fluorite surface, (b) Zn^{2+} , SHMP treated fluorite surface, (c) SHMP treated calcite surface, and (d) Zn^{2+} , SHMP treated calcite surface

3.5. FT-IR analysis

In order to further study the adsorption mode and effect on mineral floatability of SHMP on mineral surface with Zn^{2+} . FT-IR analysis was performed on fluorite and calcite samples treated with depressant SHMP (2mg/L) and collector NaOL (80mg/L) with or without Zn^{2+} (10mg/L), and the results are shown in Fig. 6 and 7.

In Fig. 6(a), characteristic absorption peaks of fluorite can be observed at wave number 3447.03 cm^{-1} , 1638.77 cm^{-1} and 1411.19 cm^{-1} (Zhu et al., 2021). After being treated with SHMP and NaOL, the new absorption peak at wave number 2921.75 cm^{-1} and 2853.73 cm^{-1} in Fig. 6(b) can be attributed to the symmetric and asymmetric stretching vibration of $-CH_2$ in NaOL (Tian et al., 2017; Yang et al., 2019). Characteristic absorption peaks of SHMP can be observed at wave numbers of 1573.39 cm^{-1} , 1538.05 cm^{-1} , 1158.21 cm^{-1} and 1108.21 cm^{-1} (Zhang et al., 2021). After the addition of Zn^{2+} , the absorption peak of NaOL could still be observed at the wave number of 2921.92 cm^{-1} and 2853.73 cm^{-1} in Fig.6 (c), while the characteristic absorption peak of SHMP could only be observed at 1576.12 cm^{-1} and 1538.05 cm^{-1} , and its intensity was significantly weakened. These results indicate that Zn^{2+} interferes with the adsorption of SHMP on fluorite surface.

For calcite, the characteristic absorption peaks of calcite can be observed at wave numbers of 3452.04 cm^{-1} , 2512.52 cm^{-1} and 1414.82 cm^{-1} in Fig. 7(a) (Frost et al., 2008; Tobias, 1979). In Fig. 7(b), the asymmetric stretching vibration of $-CH_2$ with wave number 2922.39 cm^{-1} appears, indicating the chemisorption of NaOL on the calcite surface (Tian et al., 2017; Yang et al., 2019). The characteristic absorption peak of SHMP can be observed at the wave number of 1138.81 cm^{-1} and 1005.22 cm^{-1} (Zhang et al., 2021). In Fig. 7(c), symmetric and asymmetric stretching vibrations of meso- CH_2 were observed at wave numbers 2921.87 cm^{-1} and 2957.46 cm^{-1} , while the characteristic adsorption peak of SHMP disappeared. These results indicate that Zn^{2+} seriously interferes with the adsorption of SHMP on calcite surface.

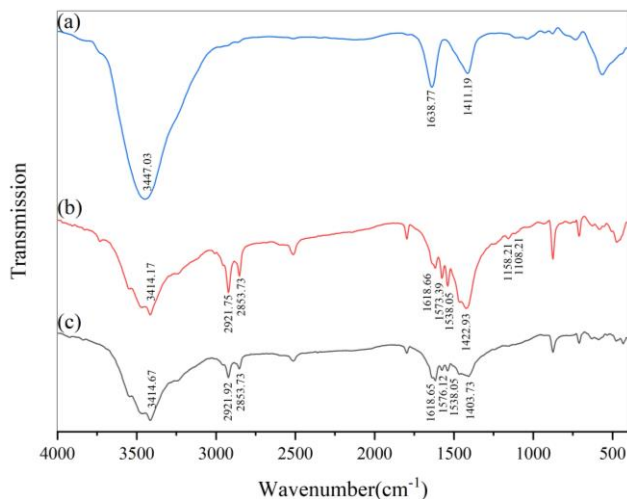


Fig. 6. FT-IR spectra of (a) fluorite, (b) fluorite treated with SHMP and NaOL, (c) fluorite treated with Zn²⁺, SHMP and NaOL

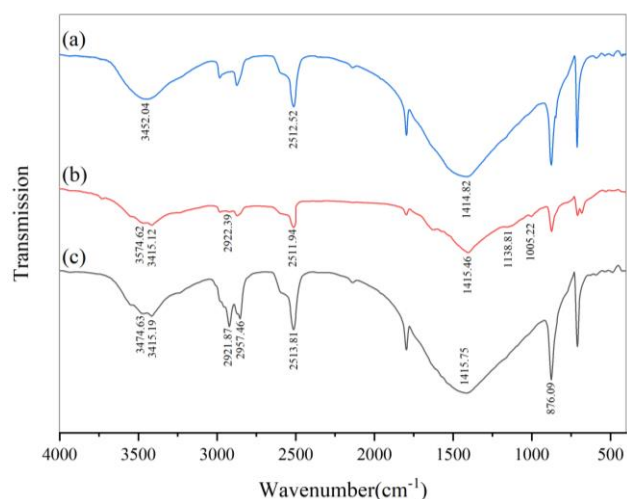


Fig. 7. FT-IR spectra of (a) calcite, (b) calcite treated with SHMP and NaOL, (c) calcite treated with Zn²⁺, SHMP and NaOL

3.6. ToF-SIMS analysis

The adsorption structures of SHMP and NaOL on mineral surfaces were analyzed by TOF-SIMS with and without Zn²⁺ (10mg/L). Images of fluorite and calcite ions treated with SHMP (2 mg/L) and NaOL (80 mg/L) are shown in Fig. 8 and 9. Normalized positive ion intensities on fluorite and calcite surfaces are shown in Fig. 10(a) and (b). Among them, Ca⁺, Zn⁺, HPO₄⁺ and C₂H₂O₂Na⁺ are the representative ion fragments of Ca²⁺, Zn²⁺, sodium hexametaphosphate and sodium oleate on the mineral surface, respectively. In the absence of Zn²⁺ addition, a weak Zn⁺ signal was detected, which is likely to present a very small amount of Zn minerals in the sample that are difficult to remove by physical methods. Fig. 8 shows that the ionic strength of Zn⁺ and C₂H₂O₂Na⁺ on fluorite surface increases significantly with Zn²⁺, while the ionic strength of HPO₄⁺ decreases. The results show that Zn²⁺ can reduce the adsorption capacity of SHMP on fluorite surface, interfere with the depression effect of SHMP, and increase the adsorption capacity of NaOL on fluorite surface. Fig. 9 shows that the changes of ionic strength on calcite surface are consistent with that of fluorite with Zn²⁺, that is, the ionic strength of Zn⁺ and C₂H₂O₂Na⁺ increases, while that of HPO₄⁺ decreases. The results show that Zn²⁺ can reduce the adsorption capacity of SHMP on calcite surface, weaken the depression of SHMP on calcite, and increase the recovery of calcite significantly.

It can be seen from Fig. 10 that the change trend of ionic strength of fluorite and calcite surface with Zn^{2+} is basically the same, that is, the ionic strength of Zn^{2+} and $C_2H_2O_2Na^+$ increases, while that of HPO_4^{2-} decreases, which is consistent with the detection and analysis results of XPS and FT-IR. In addition, the adsorption on the surface of the Zn^{2+} in fluorite and calcite is lower, that Zn^{2+} generated by reaction with SHMP to form $ZnHPO_4$ phosphate species, consuming the depression in the solution, the NaOL collector on the mineral surface adsorption quantity increases, this could be the Zn^{2+} selectivity of SHMP the main cause of a negative impact.

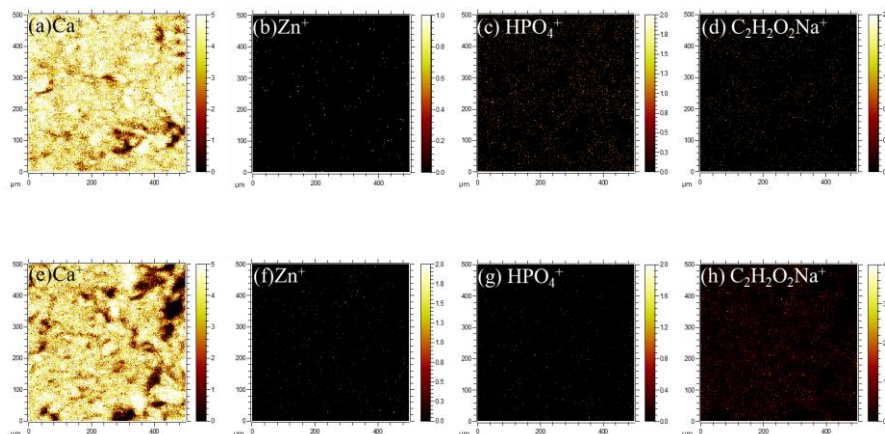


Fig. 8. Positive ion images of (a)-(d) fluorite treated with SHMP and NaOL, and (e)-(h) fluorite treated with Zn^{2+} , SHMP and NaOL

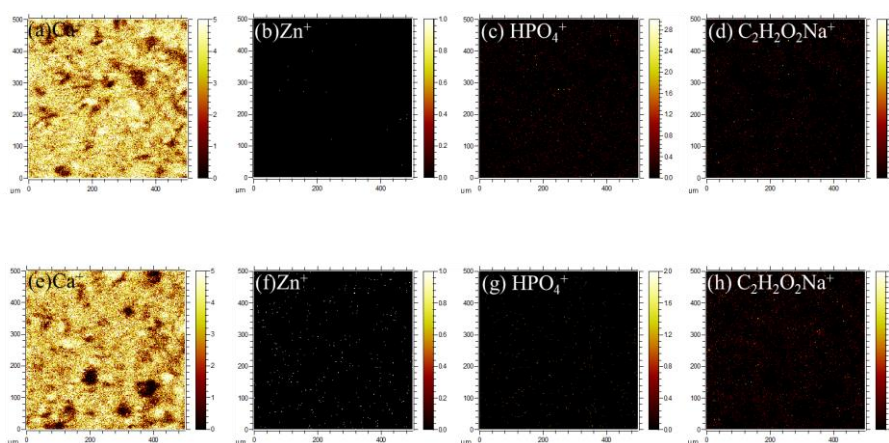


Fig. 9. Positive ion images of (a)-(d) calcite treated with SHMP and NaOL, and (e)-(h) calcite treated with Zn^{2+} , SHMP and NaOL

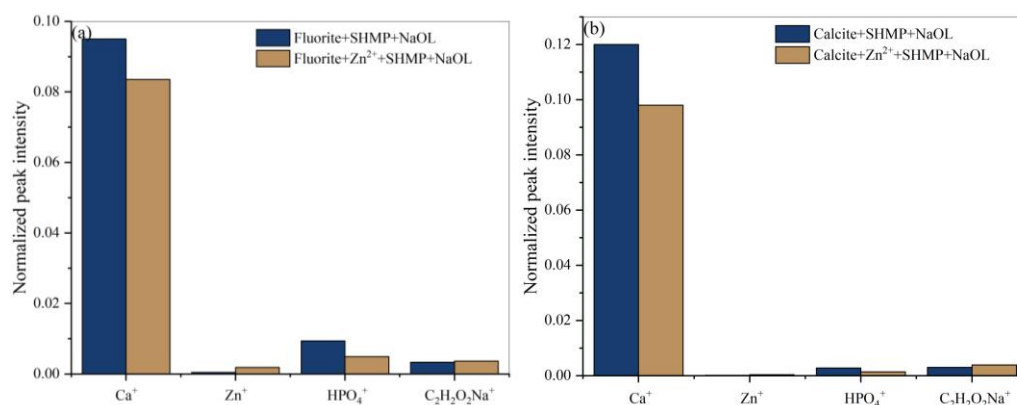


Fig. 10. (a) Peak intensities of positive ion normalization of fluorite with or without Zn^{2+} , and (b) Peak intensities of positive ion normalization of fluorite with or without Zn^{2+}

4. Conclusions

Fluorite and calcite can be effectively separated by flotation when NaOL is used as collector and SHMP is used as depressant. However, Cu^{2+} , Pb^{2+} , Zn^{2+} and Al^{3+} all have negative effects on the selective depression of SHMP, and Zn^{2+} has the most significant effect on the effect of SHMP.

The results of chemical calculation and XPS analysis of flotation solution show that SHMP can depress minerals mainly by HPO_4^{2-} and H_2PO_4^- , and these two phosphate ions can react with the active sites of Ca on mineral surface to form $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaHPO_4 , thus improving the hydrophilicity of mineral surface. However, the addition of Zn^{2+} consumes part of HPO_4^{2-} in the solution to form phosphate species ZnHPO_4 , thus weakening the depression of SHMP on minerals.

FT-IR and ToF-SIMS analysis results show that the addition of Zn^{2+} decreases the adsorption capacity of SHMP on fluorite and calcite, and increases the adsorption capacity of NaOL, which weakens the depression of SHMP, and increases the recovery of both fluorite and calcite greatly.

Selective depression of calcite by SHMP can achieve good results in the laboratory, but the actual depression effect in the production of concentrator is not ideal, so it is difficult to be applied in industry. Therefore, pretreatment of metal ions on the ore surface, strict control of metal ion concentration in the pulp, etc., to avoid the negative impact of metal ions on the selective inhibition of SHMP will become one of the targets of selective depression of calcite by SHMP at the present stage.

References

- CHEN, Z., REN, Z., GAO, H., ZHENG, R., JIN, Y., NIU, C., 2019. *Flotation studies of fluorite and barite with sodium petroleum sulfonate and sodium hexametaphosphate*. Journal of Materials Research and Technology, 8(1), 1267-1273.
- FOUCAUD, Y., BADAWI, M., FILIPPOV, L., 2019. *Comment on: Effects of crystal chemistry on sodium oleate adsorption on fluorite surface investigated by molecular dynamics simulation*: Renji Zheng, Zijie Ren, Huimin Gao, Zhijie Chen, Yupeng Qian, Yubiao Li, Minerals Engineering, vol. 124, pp. 77–85, 2018. Minerals Engineering, 135, 156-159.
- FROST, R. L., MARTENS, W. N., WAIN, D. L., HALES, M. C., 2008. *Infrared and infrared emission spectroscopy of the zinc carbonate mineral smithsonite*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 70(5), 1120-1126.
- GAGNON, J. E., SAMSON, I. M., FRYER, B. J., WILLIAMS-JONES, A. E., 2003. *Compositional heterogeneity in fluorite and the genesis of fluorite deposits: insights from LA-ICP-MS analysis*. The Canadian Mineralogist, 41(2), 365-382.
- GAO, Y., GAO, Z., SUN, W., YIN, Z., WANG, J., HU, Y., 2018. *Adsorption of a novel reagent scheme on scheelite and calcite causing an effective flotation separation*. Journal of colloid and interface science, 512, 39-46.
- GAO, Z., GAO, Y., ZHU, Y., HU, Y., SUN, W., 2016. *Selective flotation of calcite from fluorite: a novel reagent schedule*. Minerals, 6(4), 114.
- GAO, Z., WANG, C., SUN, W., GAO, Y., KOWALCZUK, P. B., 2021. *Froth flotation of fluorite: A review*. Advances in colloid and interface science, 290, 102382.
- GRAYSON, J. F. (1956). *The conversion of calcite to fluorite*. Micropaleontology, 71-78.
- GÜLEÇ, A., & OĞUZHANOĞLU, M. A., 2021. *Fluorite mineral waste as natural aggregate replacement in concrete*. Journal of Building Pathology and Rehabilitation, 6(1), 1-10.
- JIANG, W., GAO, Z., KHOSO, S. A., GAO, J., SUN, W., PU, W., HU, Y., 2018. *Selective adsorption of benzhydroxamic acid on fluorite rendering selective separation of fluorite/calcite*. Applied Surface Science, 435, 752-758.
- KANG, J., HU, Y., SUN, W., GAO, Z., LIU, R., 2019. *Utilization of sodium hexametaphosphate for separating scheelite from calcite and fluorite using an anionic-nonionic collector*. Minerals, 9(11), 705.
- LANDIS, W., & MARTIN, J., 1984. *X-ray photoelectron spectroscopy applied to gold-decorated mineral standards of biological interest*. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 2(2), 1108-1111.
- LI, S., GONG, D., ZHANG, W., LI, G., JUE, K., 2020. *Improving Fluorite Flotation Under Low Temperature and Neutral pH Conditions*. Surface Review and Letters, 27(08), 1950187.
- PÉREZ MUÑOZ, A., CORPAS-MARTÍNEZ, J. R., MARTÍN LARA, M. Á., CALERO DE HOCES, F. M., 2020. *Testing of New Collectors for Concentration of Fluorite by Flotation in Pneumatic (Modified Hallimond Tube) and Mechanical Cells*.
- PUGH, R., STENIUS, P., 1985. *Solution chemistry studies and flotation behaviour of apatite, calcite and fluorite minerals with sodium oleate collector*. International journal of mineral processing, 15(3), 193-218.
- SHI, Q., ZHANG, G., FENG, Q., OU, L., LU, Y., 2013. *Effect of the lattice ions on the calcite flotation in presence of Zn (II)*. Minerals Engineering, 40, 24-29.

- SUN, R., LIU, D., LI, Y., WANG, D., WEN, S., 2021. *Influence of lead ion pretreatment surface modification on reverse flotation separation of fluorite and calcite*. Minerals Engineering, 171, 107077.
- SUN, R., LIU, D., LIU, Y., WANG, D., WEN, S., 2021. *Pb-water glass as a depressant in the flotation separation of fluorite from calcite*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 629, 127447.
- SUN, R., LIU, D., ZHANG, B., LAI, H., WEN, S., 2021. *Homogenization phenomena of surface components of fluorite and calcite*. Physicochemical Problems of Mineral Processing, 57.
- TASKER, P. (1980). *The structure and properties of fluorite crystal surfaces*. Le Journal de Physique Colloques, 41(C6), C6-488-C486-491.
- TIAN, J., XU, L., YANG, Y., LIU, J., ZENG, X., DENG, W., 2017. *Selective flotation separation of ilmenite from titanite using mixed anionic/cationic collectors*. International journal of mineral processing, 166, 102-107.
- TOBIAS, R. S. (1979). *Infrared and Raman spectra of inorganic and coordination compounds* (Nakamoto, Kazuo). In: ACS Publications.
- WANG, J., ZHOU, Z., GAO, Y., SUN, W., HU, Y., GAO, Z., 2018. *Reverse flotation separation of fluorite from calcite: a novel reagent scheme*. Minerals, 8(8), 313.
- WANG, Z.-J., XU, L.-H., WU, H.-Q., HUAN, Z., MENG, J.-P., HUO, X.-M., HUANG, L.-Y., 2021. *Adsorption of octanohydroxamic acid at fluorite surface in presence of calcite species*. Transactions of Nonferrous Metals Society of China, 31(12), 3891-3904.
- XU, Y., XU, L., WU, H., TIAN, J., WANG, Z., GU, X., 2020. *The effect of citric acid in the flotation separation of bastnaesite from fluorite and calcite using mixed collectors*. Applied Surface Science, 529, 147166.
- XUN, L., HU, J., SHI, Q., ZHANG, G., 2021. *Effects of Ca²⁺ and SO₄²⁻ ions on fluorite flotation*. Physicochemical Problems of Mineral Processing, 57.
- YANG, Z., TENG, Q., LIU, J., YANG, W., HU, D., LIU, S., 2019. *Use of NaOL and CTAB mixture as collector in selective flotation separation of enstatite and magnetite*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 570, 481-486.
- YAO, W., LI, M., ZHANG, M., QIAN, G., CUI, R., NING, J., 2020. *Effect of grinding media on the flotation behavior of fluorite using sodium oleate as a collector*. Physicochemical Problems of Mineral Processing, 56.
- ZHANG, C., WEI, S., HU, Y., TANG, H., GAO, J., YIN, Z., GUAN, Q., 2018. *Selective adsorption of tannic acid on calcite and implications for separation of fluorite minerals*. Journal of colloid and interface science, 512, 55-63.
- ZHANG, H., ZHOU, F., YU, H., LIU, M. (2021). *Double roles of sodium hexametaphosphate in the flotation of dolomite from apatite*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 626, 127080.
- ZHU, W., PAN, J., YU, X., HE, G., LIU, C., YANG, S., . . . LIU, T., 2021. *The flotation separation of fluorite from calcite using hydroxypropyl starch as a depressant*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 616, 126168.