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Effects of Ca^{2+} and SO_4^{2-} ions on fluorite flotation

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Abstract: The effects of Ca^{2+} and SO_4^{2-} on the flotation behaviour of fluorite with sodium oleate as a collector and the underlying mechanism by which these effects were investigated via micro-flotation experiments, solution chemistry calculations, and X-ray photoelectron spectroscopy. The results indicated that the addition of SO_4^{2-} and Ca^{2+} inhibited fluorite flotation and the inhibition effect was increased by the addition of pH. This was mainly due to the increase of the sulphate-containing components in the solution and the adsorption of SO_4^{2-} on the surface of fluorite. With the increase of pH, the alkalinity of the solution increases, OH^- and more SO_4^{2-} are further adsorbed on the fluorite surface, thereby reducing the recovery of fluorite flotation.

Keywords: fluorite, flotation, calcium cation, sulphate anion

1. Introduction

Fluorite (CaF_2), a widely distributed mineral, is an important and strategic non-renewable mineral (Foucaud et al., 2018; Tian et al., 2019; Liu et al., 2019). It contains 51.33% calcium and 48.67% fluorine (Zheng et al., 2018). Fluorite is extensively used in various fields such as metallurgy (Zhu et al., 2018), materials science (Chen et al., 2019), pesticides (Liu et al., 2019), and different chemical products (Yang et al., 2020; Jong et al., 2020).

As reserves of high-grade and easily sorted fluorite resources, the development of various resources associated with fluorite such as calcite-type fluorite mine, polymetallic fluorite mine, and barite-fluorite mine has intensified in recent years (Fa et al., 2006). The separation of fluorite and barite (BaSO_4) has always been a difficult task in fluorite beneficiation (Lewandowski et al., 2019; Wang et al., 2020) because both of them have a similar floatability (Tasker, 1980; Marinakis and Shergold, 1985; Liu et al., 2020).

Flotation is the most commonly adopted beneficiation technique for separating fluorite from other gangue minerals (Feng et al., 2015; Foucaud et al., 2018). Flotation can be affected by numerous factors (Marinakis and Shergold, 1985; Filippova et al., 2018) such as pH, various ions in the pulp, and collectors (Sayilgan and Arol, 2004; Chennakesavulu et al., 2008). Conventional collectors such as fatty acids and their salts (Hu and Xu, 2003; Chen et al., 2018; Mielczarski et al., 2020) especially oleic acid and sodium oleate (NaOL) (Li et al., 2017; Foucaud et al., 2019; Mielczarski et al., 2020) are the most typically utilized collectors in fluorite flotation (Fa et al., 2006; Filippova et al., 2018; Filippov et al., 2019). Given that fluorite and barite have a similar floatability, some inhibitors are often added during flotation separation such as inhibitors of mixed aluminium sulphate, sodium hydroxide, and tannin extraction, as well as inhibitors of mixed sodium sulphate, sodium hydroxide, and starch, to separate fluorite from barite (Chen et al., 2017; Zhang et al., 2019; Tian et al., 2019).

Ca^{2+} and SO_4^{2-} are present in solution owing to mineral dissolution (fluorite and barite) and addition of sulphate inhibitors (Flores-Álvarez et al., 2017; Elizondo-Álvarez et al., 2017). Previous studies only have focused on the effects of a single ion such as Mg^{2+} , SO_4^{2-} , CO_3^{2-} , and F^- on minerals (Free and Miller 1996; Sis and Chander, 2003; Filippova et al., 2014; Alroudhan et al., 2016; Filippov et al., 2019). Other studies reported that CaOH^+ and $\text{Ca}(\text{OH})_2$ are formed under the alkaline condition of Ca^+ , which

affects the recovery of fluorite (Chen et al., 2017; Feng et al., 2018; Zhou et al., 2020). However, the effects of the combination of Ca^{2+} and SO_4^{2-} on fluorite flotation have been rarely investigated. This study aimed to evaluate the effects of the addition of Ca^{2+} and SO_4^{2-} on fluorite flotation. The function was observed via micro-flotation experiments, solution chemistry calculations, and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

A single fluorite sample was obtained from Guiyang, Guizhou Province, China. After handpicking, parts of the solid particles were crushed and then ground using a ceramic ball mill. The products were then dry-screened to obtain fractions 106 μm in size for the micro-flotation experiments. The results of X-ray diffraction of fluorite are given in Fig. 1. Chemical analysis revealed that the fluorite sample contained 99.92% CaF_2 .

Chemically pure sodium oleate (NaOL), which was used as a collector in this study, was bought from Shanghai Baisaiqin Chemical Technology Co., Ltd. (Shanghai, China). Anhydrous sodium sulphate (Na_2SO_4) was procured from Hunan Zhuzhou Institute of Chemical Industry (Hunan, China). Anhydrous calcium chloride (CaCl_2) was purchased from China Pharmaceutical Group Chemical Reagents Co., Ltd. (Beijing, China). Hydrochloric acid (HCl) and sodium hydroxide (NaOH), which were used as pH regulators, were acquired from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Other reagents were of analytic grade, and deionized (DI) water (Pure water machine is purchased from Shanghai Hetai Instrument Co., Ltd., model Smart-S15UVF, resistivity 18.2 $\text{M}\Omega\cdot\text{cm}$ @25 $^\circ\text{C}$) was used in all experiments.

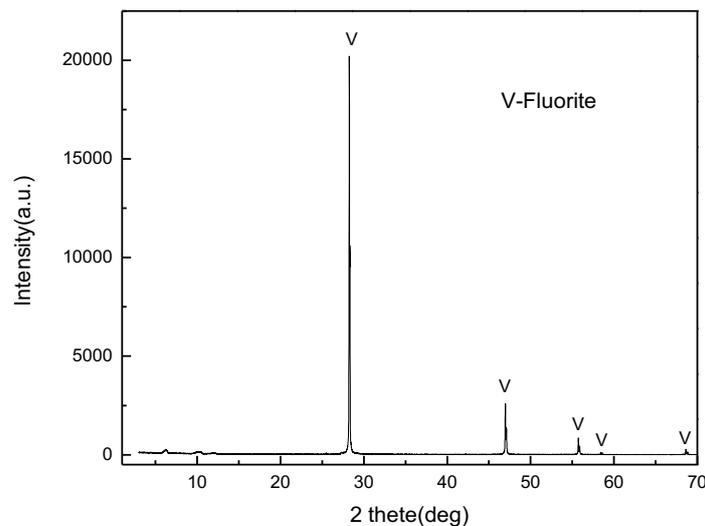


Fig. 1. XRD pattern of fluorite

2.2. Methods

2.2.1. Solution chemistry calculation

Visual MINTEQ (Gustafsson, 2000) is a free chemical equilibrium model for calculating metal speciation, solubility equilibrium, and sorption for natural waters (Chávez and Miguel, 1976). This model combines state-of-the-art descriptions of sorption and complexation reactions. In this study, the ionic component of saturated fluorite dissolved in pure water, the pH of the solution, and ion activity under variable pH conditions were calculated using this software.

2.2.2. Micro-flotation experiments

Micro-flotation experiments were performed in an XFGC II mechanical agitation flotation machine, Jilin Exploration Machinery Plant (Changchun, China). The impeller rotation speed was set at 1992 r/min.

For each experiments, 2.0 g of pure mineral sample was added into a 40 cm³ flotation cell with 35 cm³ deionized (DI) water. After conditioning for 1 min, 10⁻² mol/dm³ CaCl₂ and Na₂SO₄ solution were added successively. The slurry was then adjusted to the desired pH value by using NaOH or HCl for 1 min. The order by which the reagents were added and the conditioning time allotted were as follows: The ions were modified for 3 min and the collector for 2 min. Flotation was conducted for 3 min. The flotation products (both the concentrates and tailings) were collected, filtered, dried, and weighed to calculate mineral recoveries.

2.2.3. Surface analysis

The adsorption of SO₄²⁻ on fluorite surfaces at pH 10 after the addition of Ca²⁺ and SO₄²⁻ was detected via XPS (Zhang et al., 2019). The measurements were performed using a K-ALPHA X-ray photoelectron spectrometer (Thermo Fisher Scientific Inc., USA). For each measurement, 2 g of a mineral sample was prepared each time to prepare the slurry according to the corresponding ions and pH conditions. The slurry was centrifuged (GL-20G-II) at 9000 r/min for 20 min to separate solid and liquid minerals. The solid minerals were washed with distilled water twice and then dried in a vacuum oven at below 25°C (Xu, et al., 2020).

3. Results and discussion

3.2. Micro-flotation experiments

Fluorite recovery initially increased and then tended to stabilize as collector dosage increased (Fig. 2[a]). The highest fluorite recovery was obtained when the collector concentration was 5×10⁻⁵ mol/dm³ (Chen et al., 2017). The addition of chlorine ion and sodium ion did not change the recovery of fluorite flotation whereas the addition of Ca²⁺ had an inhibitory effect on fluorite mainly because the reaction of calcium ion with the collector sodium oleate would form calcium oleate precipitates (Marinakos and Shergold, 1985; Filippova et al., 2014); hence, reducing collector concentration. The addition of SO₄²⁻ can also reduce fluorite flotation recovery. However, its recovery was still higher than when Ca²⁺ was added primarily because SO₄²⁻ easily adsorbs on the surface of fluorite and forms calcium sulphate precipitates, thereby inhibiting the collection of fluorite by sodium oleate (Zhang et al., 2019). Meanwhile, SO₄²⁻ can promote fluorite dissolution and consume the collector by dissolved Ca²⁺. Compared with the absence of ions, the addition of combined ions substantially reduced fluorite flotation recovery (Fig. 2[b]) probably because of the synergistic inhibition of Ca²⁺ and SO₄²⁻.

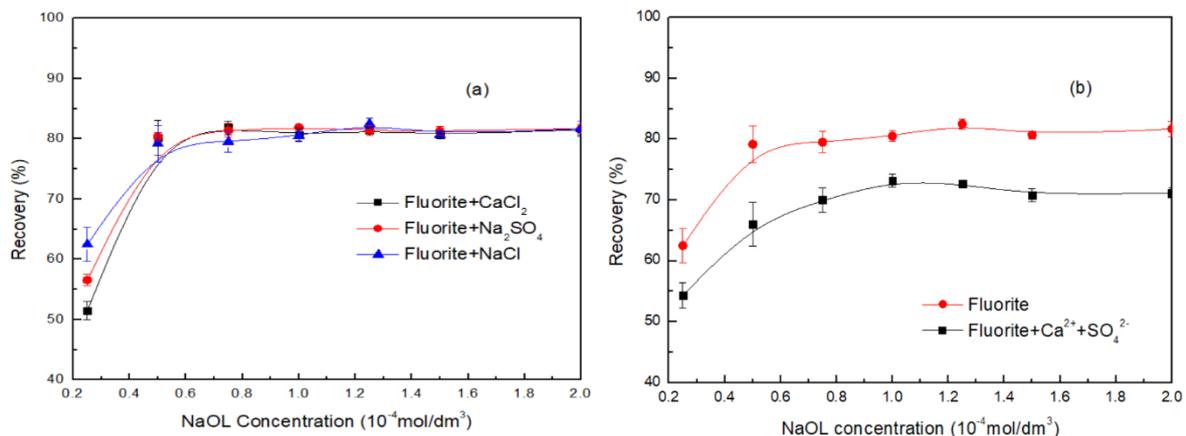


Fig. 2. Recovery of fluorite as a function of NaOL dosage $C_{(ions)} = 1 \times 10^{-2}$ mol/dm³, pH 6.8

Furthermore, the effects of different ions on fluorite flotation under different pH conditions were investigated via micro-flotation experiments. In the absence of the ions, fluorite recovery decreased from 84% to 71.47% at pH 8.5–10.5, indicating that fluorite floatability decreased as pH increased (Fig. 3). When Ca²⁺ alone was added into the solution, fluorite recovery relatively decreased compared with that without ion addition. Compared with the ion-free condition, the addition of SO₄²⁻ almost did not

affect fluorite flotation. When Ca^{2+} and SO_4^{2-} were added, fluorite recovery sharply decreased as pH increased. Thus, under strongly alkaline conditions, the addition of Ca^{2+} and SO_4^{2-} exerted a strong inhibitory effect on fluorite flotation.

Moreover, the effects of ion concentrations on flotation recovery under different pH conditions were examined (Fig. 4). The ions had negligible effects on fluorite flotation as ion concentrations increased at pH 6.8. At pH 9.0, fluorite recovery decreased as ion concentrations further increased. These results indicated that increases in ion concentrations had a considerable effect on fluorite recovery under alkaline conditions.

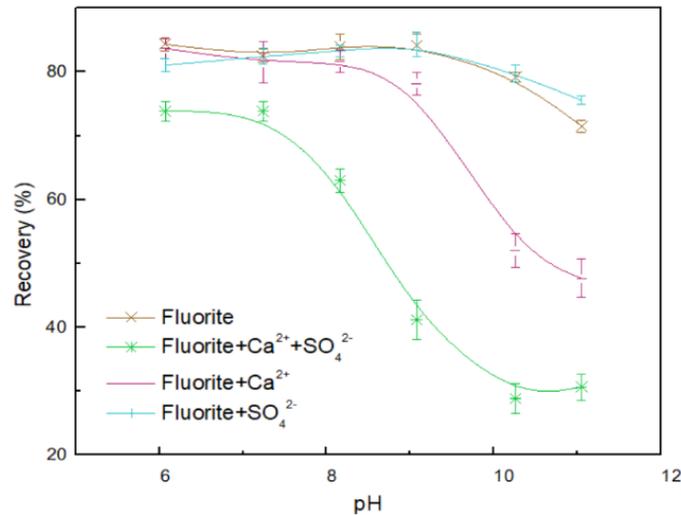


Fig. 3. Recovery of fluorite as a function of pH. $C_{(\text{ions})} = 1 \times 10^{-2} \text{ mol/dm}^3$, $C_{(\text{NaOL})} = 5 \times 10^{-5} \text{ mol/dm}^3$

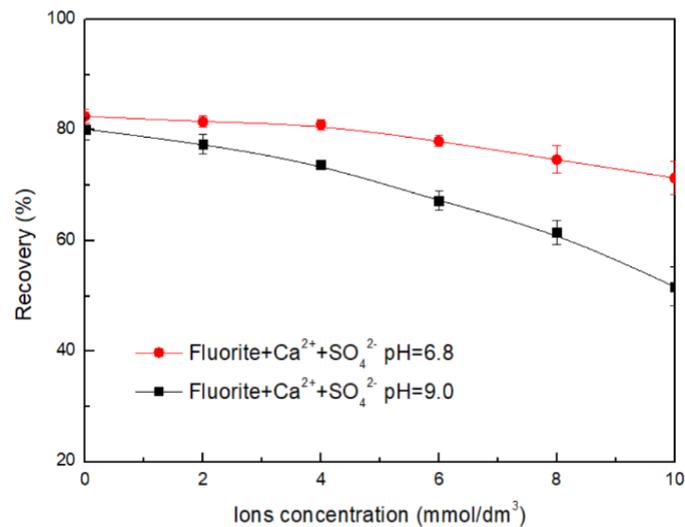
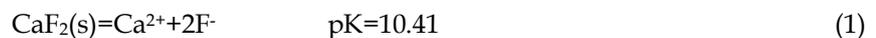


Fig. 4. Recovery of fluorite in different pH as a function of ion concentration. $C_{(\text{NaOL})} = 5 \times 10^{-5} \text{ mol/dm}^3$

3.3. Solution chemical calculation

In flotation solutions, interactions between collectors and fluorite are mainly influenced by charges on mineral surfaces, electrical properties, pH, temperatures, the metal ions added, and ionic strengths. However, these factors are closely related to water chemistry in the flotation process (Sayilgan and Arol, 2004; Foucaud et al., 2018). According to previous studies, the chemical reactions and equilibrium constants of fluorite in an aqueous solution are as follows (Free and Miller 1996):





Changes in various components in the solution under different pH conditions were monitored via solution chemical calculations using Visual MINTEQ 3.0 (Xu et al., 2020). Among these components, Sat index can determine the presence of precipitation in the solution. A Sat index greater than 0 indicates the presence of precipitation, whereas a Sat index less than 0 denotes the absence of precipitation. Herein, the temperature was set at 25°C.

Changes in solution saturation index under different pH and ion conditions are exhibited in Fig. 6. Variations in the concentration of each component in the solution under different pH and ion conditions are shown in Fig. 5. When no ions were added, the concentration of Ca^{2+} , F^- , and CaF^+ remained the same within the pH range of 2–12. Moreover, CaOH^+ concentration increased but HF and HF_2^- concentration decreased as pH increased (Fig. 5[a]). When adding SO_4^{2-} and Ca^{2+} , the solution added sulphate-containing components ($\text{CaSO}_4[\text{aq}]$, SO_4^{2-} , HSO_4^-), the calcium components (Ca^{2+} , CaF^+ , CaOH^+) increased, while fluoride composition (F^- , $\text{HF}[\text{aq}]$, HF_2^-) decreased slightly (Fig. 5 [b]). As the pH (from 2 to 12) increases, the concentration of CaOH^+ increases, while the concentration of HSO_4^- , $\text{HF}(\text{aq})$ and HF_2^- decreases, moreover the concentration of the remaining components remains unchanged (Wang and Hu, 1988).

The saturation index was less than 0, indicating that no precipitation formed in the solution. The

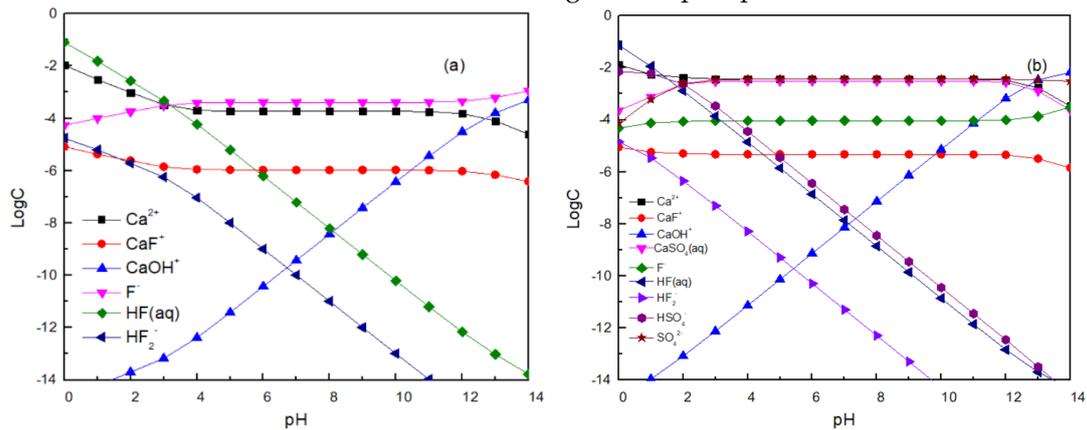


Fig. 5. Ions activity of (a) purity fluorite, and (b) fluorite with combined ion as a function of pH. $C_{(\text{ions})} = 1 \times 10^{-2} \text{ mol/dm}^3$

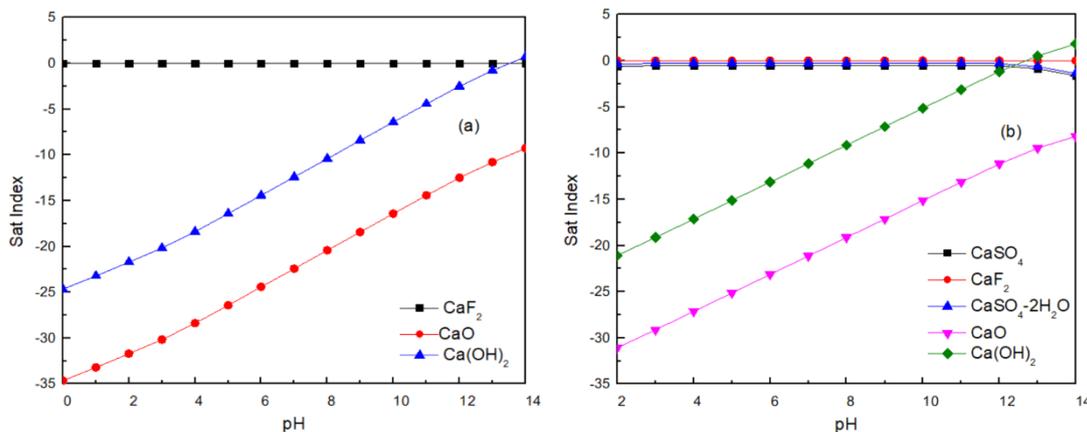


Fig. 6. Sat Index (a) purity fluorite, and (b) fluorite with combined ion added as a function of pH. $C_{(\text{ions})} = 1 \times 10^{-2} \text{ mol/dm}^3$

CaF₂ saturation index remained the same within the range of pH from 2 to 12 (Fig. 6[a]). When the sulphate-containing components were added to the solution, and then the saturation index of Ca(OH)₂ and CaO increased significantly. The saturation index of CaSO₄ and CaSO₄•2H₂O tended toward 0, indicating the presence of large amounts of CaSO₄(aq) (Azimi et al., 2008) in the solution after the addition of the combined ions. With the increase of pH (from 2 to 12), the saturation index of Ca(OH)₂ and CaO showed an increasing trend. (Fig. 6[b]).

In summary, solution chemical calculations revealed that sulphate-containing components were appeared in the solution, the concentration of calcium components (Ca²⁺, CaF⁻, CaOH⁺), especially the saturation indexes of CaSO₄ and CaSO₄•2H₂O approached to 0, when Ca²⁺ and SO₄²⁻ were added. As the pH increases (from 2 to 12), the concentration of CaOH⁺, Ca(OH)₂, and CaO in the solution increases.

3.4. Surface analysis

The surface of fluorite after pre-treatment with 10⁻² mol/dm³ of the ions at pH 6.8 and 10 was examined via XPS (Table 1 and Fig. 7). No sulphur atoms were found on the fluorite surface at pH 6.8 in the absence of Ca²⁺ and SO₄²⁻. After conditioning in the presence of Ca²⁺ and SO₄²⁻, the content of Ca and F on the surface of fluorite decreased by 1.6% and 4.95%, while the content of S and O on the surface of fluorite increased by 1.07% and 2.98%, indicating that SO₄²⁻ were adsorbed on fluorite surface. When the pH was 10, S on the surface of fluorite increased by 0.38%, while O increased by 1.14%, while the content of fluorine and calcium remained unchanged, which indicated that more SO₄²⁻ was adsorbed on the surface of fluorite. The high-resolution spectra of Ca 2P, S 2P, and O 1S are shown in Fig. 7, in the absence of Ca²⁺ and SO₄²⁻, the peak of S cannot be detected on the surface of fluorite at pH 6.8. The binding energies of Ca 2p 2/3 and Ca 2p 1/2 are 347.95 and 351.47 eV, respectively, and the binding energies of O 1s are 531.19 and 532.79 eV, respectively. In the presence of Ca²⁺ and SO₄²⁻, when the pH is 6.8, the Ca2p 2/3 signal shifts by 0.50 eV, while the Ca 2p 1/2 signal shifts by 0.52 eV, the O 1s signal shifts by 0.70 and 1.00 eV (Gao et al., 2019; Tian et al., 2019). Figure 7(e) indicated that S 2p_{3/2} electrons were acquired, the binding energy of S 2p_{3/2}. It is 169.66eV because of the adsorption of SO₄²⁻ on the surface of fluorite (Cui et al., 2020; Wang et al., 2020). When the pH increased to 10, the Ca 2P 2/3, Ca 2P 1/2, and S 2p_{3/2} signals were basically unshifted, and the O 1s signal offset by 0.11 and 1.43eV, respectively, a new peak-to-peak value of 531.31 eV is formed (detected and assigned to Ca(OH)₂) (Vincent, 1999).

Table 1. Concentration (at. %) of elements measured by XPS on the surfaces of fluorite under different reagent conditions C_(ions)=1 × 10⁻² mol/dm³

Reagent conditions	Element analyzed			
	Ca	S	F	O
pH 6.8 Fluorite	34.07	-	48.01	3.96
Fluorite + CaCl ₂ + Na ₂ SO ₄ , pH 6.8	32.47	1.07	43.06	6.94
Fluorite + CaCl ₂ + Na ₂ SO ₄ , pH 10	32.34	1.45	43.28	8.08

4. Conclusions

Under laboratory-scale conditions, the effect of the addition of combined ions under different pH conditions on fluorite flotation was investigated, and reached the following conclusions:

1. After the addition of the ions, the concentration of the calcium-containing components in the solution increases, furthermore the addition of sulphate-containing component, especially the concentrations of CaSO₄ and CaSO₄•2H₂O.
2. The addition of combined ions has an inhibitory effect on the flotation of fluorite, mainly due to the increase of sulphate-containing components in the solution and the adsorption of SO₄²⁻ on the surface of fluorite.
3. Under the conditions of the same ion, the content of Ca(OH)₂, CaOH⁺ and CaO in the solution increased with the increase of pH.
4. The flotation recovery of fluorite decreased significantly with the increase of pH, the main reason is the further adsorption of OH⁻ and SO₄²⁻.

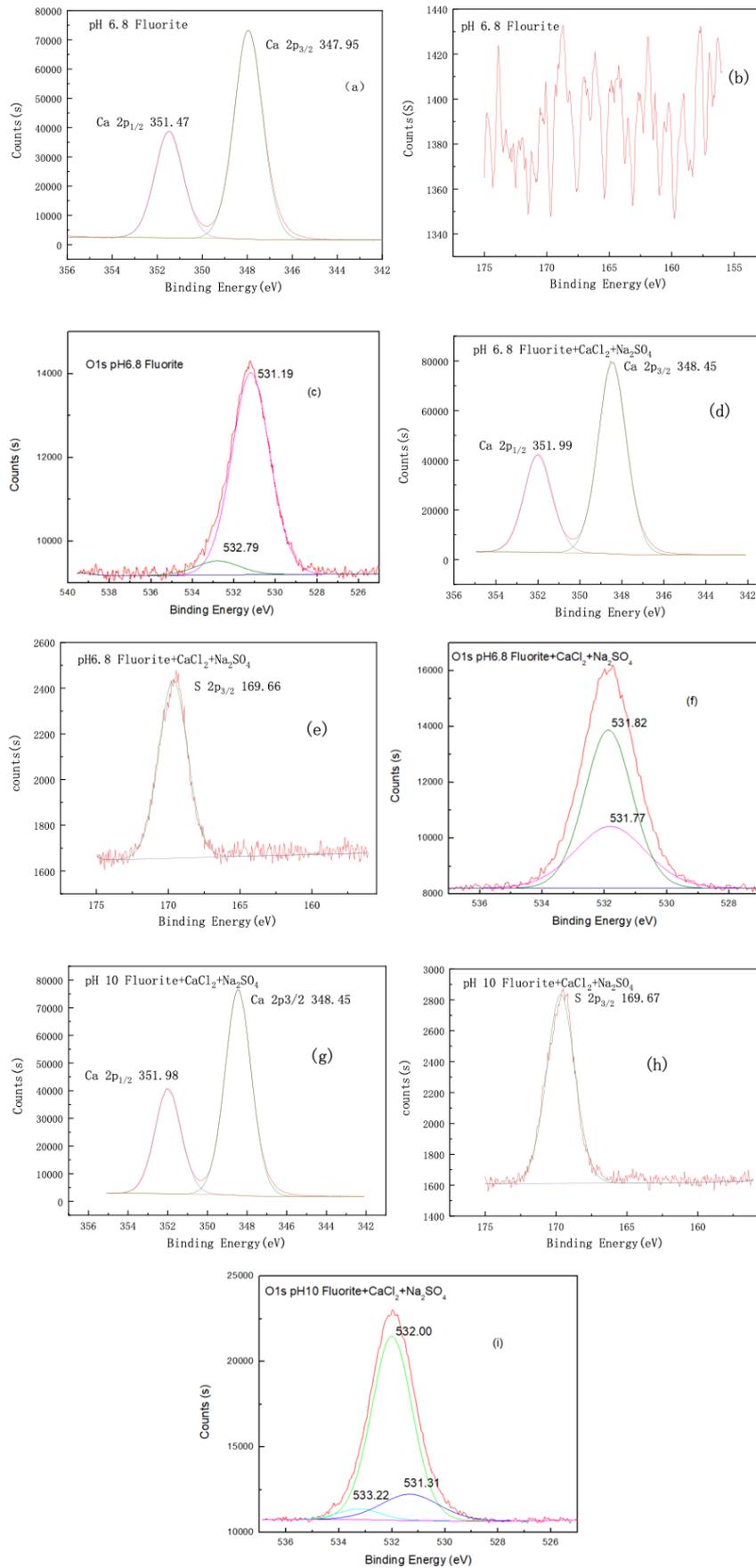


Fig. 7. XPS spectra of Ca 2P, S 2P, O 1S regions for fluorite (a), (b), and (c) fluorite + Ca^{2+} + SO_4^{2-} at pH 6.8 (d), (e) and (f) fluorite + Ca^{2+} + SO_4^{2-} at pH 10 (g), (h), and (i)

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