Improvement Effect of FeSO₄·7H₂O on Flotation Separation of Scheelite from Fluorite

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ABSTRACT: In this study, FeSO₄·7H₂O was used as an auxiliary depressant to improve the selective depression effect on fluorite. Microflotation tests using oleic acid as the collector showed that the pre-addition of FeSO₄·7H₂O and subsequent addition of sodium silicate (SS) resulted in a stronger selective depression effect on fluorite compared with SS alone. Addition of FeSO₄·7H₂O reduced the required dosage of SS and had little negative effects on scheelite recovery. The selective depression mechanism of FeSO₄·7H₂O was investigated in detail. X-ray photoelectron spectroscopy indicated that the difference in the number of surface active sites was the mechanism for improved differential flotation of scheelite from fluorite. The improved depression of fluorite was attributed to both ferrous and sulphate ions. The pre-adsorption of ferrous species increased the number of active sites, enhancing the adsorption of silicate species on the fluorite surface. Simultaneously, sulfate ions were selectively adsorbed on the fluorite surface to form hydrophilic calcium sulfate, reducing the floatability of fluorite.

1. INTRODUCTION

Scheelite (CaWO₄) is an important mineral for extracting tungsten and usually associated with fluorite in Chinese scheelite deposits. The utilization of refractory scheelite deposits—wolframite resources that can be easily separated via the gravity method and are almost depleted—has become important. Conventional flotation practice for separating scheelite from fluorite utilizes sodium silicate (SS) (water glass) to depress fluorite followed by a fatty oil collector such as oleic acid to float scheelite. Similar surface reactivity of these two minerals requires the use of a depressant to enhance flotation selectivity. Therefore, these materials are almost impossible to separate without a selective depressant.

Recently, depressants such as organic colloids, sodium phosphates, quebracho, and hydroxols have been used to separate scheelite from fluorite. Water glass is the most widely used and cheapest among these depressants. In practice, it is found that a high water glass dosage is required to effectively depress fluorite. However, this frequently results in simultaneous depression of scheelite. A more selective depressant, featuring low cost and dosage, is needed for the separation of scheelite from fluorite. The depressant mixture is a good choice for this specific goal. To enhance the separation efficiency, a mixture of water glass with metal ions (such as Al³⁺, Fe²⁺, Pb²⁺, and Ca²⁺) have been used in scheelite flotation. The depressant effect of the joint addition of SS and other salts was first studied by Belash and a number of studies have since been done. The original study indicated that these ions could promote the depression capability of water glass in scheelite flotation systems. Oliveira and Sampaio first used FeSO₄·7H₂O as a depressant in scheelite flotation. The authors investigated the effect of a mixture of SS with FeSO₄·7H₂O on the bench scale for a scheelite ore from Brazil. The addition of SS and FeSO₄·7H₂O at a ratio of 5/1 resulted in substantially increased selectivity. Recently, Deng et al. used this mixture depressant to separate scheelite and calcite. The authors attributed the improved depression effect to Fe²⁺, which facilitated the formation of polymeric silicate species.

Although there have been many studies on the effects of metal ions on scheelite flotation, the underlying mechanisms are still unclear and some even incompatible. In addition, the aforementioned studies focused on only cations (Fe²⁺), ignoring the role of anions (SO₄²⁻) on the separation of scheelite from fluorite. In this study, FeSO₄·7H₂O was used as an assistant depressant in an attempt to selectively separate scheelite from fluorite. The depression mechanism was revealed by microflotation, zeta-potential measurements, and X-ray photoelectron spectroscopy (XPS) analysis. To the best
of our knowledge, this is the first report on the effect of \( \text{SO}_4^{2-} \) on the flotation separation of scheelite from fluorite.

2. MATERIALS AND METHODS

2.1. Materials and Reagents. High-quality scheelite and fluorite samples were collected from Yunnan Province, China. The pure samples were crushed by hand, ground using an agate mortar, and sieved using Tyler screens. A sample of 38–90 \( \mu \text{m} \) fraction was used in the flotation tests and XPS analysis. The <5 \( \mu \text{m} \) fraction was used for zeta-potential measurements. Chemical analyses and X-ray powder diffraction (XRD) indicated that the purities of the scheelite and fluorite particles exceeded 97%. The results of the XRD analyses are shown in Figure 1. The water for all experiments was ultrapure water with a resistivity of 18.2 M\( \Omega \) cm. The reagents used in this study are shown in Table 1.

Table 1. Reagents Used in the Experiments

| chemical       | conc. | supplier | role            |
|----------------|-------|----------|-----------------|
| HCl            | 96    | Merck    | pH adjuster    |
| NaOH           | 96    | Merck    | pH adjuster    |
| Na\(_2\)SO\(_4\) | 99.5   | Aladdin | depressant      |
| FeCl\(_2\)     | 99.6   | Aladdin | depressant      |
| SS             | 97    | Merck    | depressant      |
| FeSO\(_4\)\(_7\)\text{H}_2\text{O} | 98   | Akzo Nobel | depressant |
| NaCl           | 99    | Aladdin | depressant      |
| oleic acid     | 99    | Merck    | collector       |

2.2. Micro flotation. Micro flotation experiments were performed at room temperature in an XFG flotation machine assembled with a 40 mL plexiglass cell at an impeller speed of 1800 rpm. A mineral suspension was prepared by adding 2 g of the mineral sample (1.0 g of scheelite and 1.0 g of fluorite for artificially mixed minerals) into the plexiglass cell with 30 mL of ultrapure water. A survey scan for the analyzed sample was conducted in the XPS tests. Subsequently, a dilute HCl or NaOH solution was used to adjust the pH of the mixture. The resultant suspensions were allowed to stand still for 1 min, and the supernatant of the suspension was transferred to a measuring vessel using a plastic dropper for zeta-potential measurements at ambient temperature. The tests were repeated three times and the average values were calculated.

2.3. Zeta-Potential Measurement. The zeta potentials of the minerals were measured using a Brookhaven ZetaPlus zeta-potential analyzer (USA). The measurements were performed using a PHIs000 Versa Probe II (PHIs000, ULVAC-PHI, Japan) with an Al \( \text{K}\alpha \) X-ray source. The conditioning times of \( \text{FeSO}_4\cdot 7\text{H}_2\text{O} \) and SS were both 5 min. The solid phase was washed three times by ultrapure water then vacuum dried at 40 \( ^\circ \text{C} \) for 24 h. A survey scan for the analyzed sample was conducted in the first place to detect elemental substances, and then a precise scan was performed to obtain the XPS spectrum of each specific element. MultiPak Spectrum software was used to analyze the XPS data, including peak fitting and semi-quantitative estimation. The carbon 1s spectral peak at 284.8 eV was obtained to calibrate all of the measured spectra as an internal standard for charge compensation.

For the single mineral flotation, the flotation recovery was calculated based on the mass ratios. For the flotation of the mixed minerals, the WO\(_3\) grades of the concentrates and tailings were analyzed, and their recoveries were calculated.

2.4. X-ray Photoelectron Spectroscopy. The scheelite and fluorite samples treated with different depressants were analyzed by XPS. The measurements were performed using a PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) with an Al \( \text{K}\alpha \) X-ray source. The conditioning times of \( \text{FeSO}_4\cdot 7\text{H}_2\text{O} \) and SS were both 5 min. The solid phase was washed three times by ultrapure water then vacuum dried at 40 \( ^\circ \text{C} \) for 24 h.

Figure 1. XRD patterns of scheelite and fluorite.

Figure 2. Flowsheet of the micro flotation experimental procedure.

![Image of XRD patterns](image-url)

![Image of Flowsheet](image-url)
3. RESULTS AND DISCUSSION

3.1. Depression Behavior of FeSO₄·7H₂O

3.1.1. Flotation Behavior of Scheelite and Fluorite. The flotation behavior of scheelite and fluorite at different pH values in the presence or absence of FeSO₄·7H₂O is shown in Figure 3.

![Figure 3](image)

Figure 3. Effect of pH on the floatability of scheelite and fluorite with or without the addition of FeSO₄·7H₂O. (FeSO₄·7H₂O and SS were added at the same time; SS concentration: 400 mg/L; FeSO₄·7H₂O concentration: 100 mg/L; oleic acid concentration: 1.8 × 10⁻⁴ mol/L).

In this experiment, FeSO₄·7H₂O and SS were added simultaneously, and the conditioning times for SS, FeSO₄·7H₂O, and oleic acid were 2, 5, and 2 min, respectively. Figure 3 shows that the alkaline solution was beneficial for the inhibition of fluorite. However, when SS (400 mg/L) was used as a depressant alone, the depression effect towards fluorite was weak, and the recovery of fluorite was >47%. After the addition of FeSO₄·7H₂O, the recovery of fluorite significantly decreased, reaching an optimum value at a pH of 9, where the recovery decreased from 48 to 35%. Thus, it is clear that FeSO₄·7H₂O is beneficial for the inhibition of fluorite, which is consistent with the findings of Oliveira and Sampaio. Another benefit of the addition of FeSO₄·7H₂O is its negligible effect on the scheelite floatability. The addition of FeSO₄·7H₂O had almost no influence on the scheelite flotation with the pH varying from 6 to 9. However, when the pH exceeded 10, the recovery of scheelite rapidly decreased. Thus, the flotation separation of scheelite and fluorite can be achieved at a pH of 9–10.

The flotation results can be affected by the addition order of the flotation reagents. In this study, three different methods of FeSO₄·7H₂O addition were considered: adding FeSO₄·7H₂O prior to the addition of NaOH and SS; simultaneous addition of FeSO₄·7H₂O and SS; and adding FeSO₄·7H₂O after the addition of SS. The tests of single mineral flotation were performed to determine the effects of the addition order on the flotation results with respect to the depressant dosage.

Figure 4 shows that the flotation recovery of scheelite remained unchanged when different reagents addition order were used; however, it was markedly affected by the FeSO₄·7H₂O concentration. Scheelite recovery remained relatively constant with increasing ferrous sulphate addition up to 150 mg/L, above which it decreased notably. Correspondingly, the consequence of fluorite flotation was dramatically changed by the addition method of FeSO₄·7H₂O, and the best depression effect for fluorite was obtained when FeSO₄·7H₂O was added prior to NaOH and SS (point 1 in Figure 2). The depression effect of FeSO₄·7H₂O on fluorite manifested at low FeSO₄·7H₂O dosages, and the recovery decreased with increasing the dosage. The flotation recovery of fluorite was only 33.2% at a FeSO₄·7H₂O dosage of 150 mg/L. Although a larger FeSO₄·7H₂O dosage could increase the depression effect towards fluorite, it also reduced scheelite recovery.

3.1.2. Flotation separation of scheelite and fluorite mineral mixtures. Flotation separation tests of artificially mixed minerals (with a scheelite-to-fluorite mass ratio of 1:1) were performed to further investigate the effect of FeSO₄·7H₂O on the separation performance with respect to the SS dosage. Figure 5 shows that the flotation performance was significantly affected by the SS dosage. Numerous studies have shown that the addition of SS improves the grade of scheelite concentrate but considerably reduces the recovery. In the absence of FeSO₄·7H₂O, the optimum SS dosage for separation was 500 mg/L, at which the recovery and grade of the produced scheelite were only 87.4% and 62.5%, respectively. In the presence of FeSO₄·7H₂O, the separation of scheelite and fluorite was achieved with a SS dosage of only 400 mg/L, and the recovery and grade of scheelite increased to

![Figure 4](image)

Figure 4. Effect of the FeSO₄·7H₂O dosage on the floatability of scheelite and fluorite: FeSO₄·7H₂O added prior to NaOH and SS (a,d), FeSO₄·7H₂O and SS added simultaneously (b,e), FeSO₄·7H₂O added after SS (c,f). (pH 9.5; SS concentration: 400 mg/L; oleic acid concentration: 1.8 × 10⁻⁴ mol/L).

![Figure 5](image)

Figure 5. Flotation performance of scheelite in the artificially mixed mineral samples with respect to the SS dosage in the presence or absence of FeSO₄·7H₂O. (pH 9.5; FeSO₄·7H₂O added prior to NaOH and SS; FeSO₄·7H₂O concentration: 130 mg/L; oleic acid concentration: 1.8 × 10⁻⁴ mol/L).
91.2 and 64.3%, respectively. Clearly, this improved separation was due to the addition of FeSO₄·7H₂O, which reduced the consumption of SS and increased fluorite inhibition.

3.1.3. Determining Active Ingredients in FeSO₄·7H₂O. In previous studies, the inhibition of FeSO₄·7H₂O was attributed to cations in the scheelite flotation mixture, but the role of anions was largely ignored. To investigate the role of SO₄²⁻ in the flotation separation of scheelite and fluorite, microflotation tests were performed using various reagents. Fe²⁺ from FeCl₂, SO₄²⁻ from Na₂SO₄, and NaCl as a control were used in this study. The results presented in Figure 6 show that FeCl₂ exhibited the strongest inhibition effect on fluorite, followed by Na₂SO₄, and NaCl showed no depression effect. This indicated that the depression effect of FeSO₄·7H₂O is mainly due to the iron ions. However, SO₄²⁻ could reduce the floatability of fluorite too, although this inhibition was not significant at Na₂SO₄ dosages below 100 mg/L. This finding is important for flotation of scheelite.

3.2. Depression Mechanism of FeSO₄·7H₂O. 3.2.1. Zeta-Potential Measurements. Zeta-potential measurement is an in situ method that can be used to explore the interactions of ionic species with minerals. To investigate the mechanism of the FeSO₄·7H₂O depressant on the mineral surfaces, zeta-potential measurements were determined as a function of pH, as shown in Figure 7. From Figure 7, the zeta potential of scheelite was negative and decreased along with the increase of the pH either with or without a depressant. The isoelectric point of fluorite occurred at pH 8.1, which is in accordance with the previous literature. After separate treatments with FeCl₂ and Na₂SO₄, the zeta potentials of fluorite showed a pronounced shift towards more positive values and a slight shift towards more negative values, respectively, indicating that both Fe²⁺ and SO₄²⁻ were adsorbed on the fluorite surface.

The SS is soluble in water, and numerous silicate species can form in the solution. Si(OH)₄, SiO(OH)₃⁻, and SiO₂(OH)₂⁻ are the dominant monomeric species with protons transferred between different species as the pH changed. The balanced equations and equilibrium constants of the silicate species are presented in eqs 1−3 and their distribution diagrams are shown in Figure 8. At pH values of <9.4, 9.4−12.6, and >12.6, the main components in the solution were Si(OH)₄, SiO(OH)₃⁻, and SiO₂(OH)₂⁻, respectively.

Figure 6. Effects of different ions on the fluorite floatability. The ions were added prior to NaOH and SS (pH 9.5; oleic acid concentration: 1.8 × 10⁻⁴ mol/L).

Figure 7. Zeta potentials of scheelite (a) and fluorite (b) with respect to the pH (FeSO₄·7H₂O concentration: 130 mg/L; SS concentration: 400 mg/L).

Figure 8. Species distribution diagrams for SS with respect to the pH.

\[ \text{SiO}_2(\text{amorph}) + 2\text{H}_2\text{O} = \text{SiO(OH)}_4, \log K = -2.7 \]  
\[ \text{Si(OH)}_4 = \text{SiO(OH)}_3^- + \text{H}^+, \log K = -9.43 \]  
\[ \text{SiO(OH)}_3^- = \text{SiO}_2(\text{OH})_2^- + \text{H}^+, \log K = -12.56 \]  

Figure 7 shows that the zeta potential of both scheelite and fluorite shifted to a more negative value after the addition of 400 mg/L SS, and the fluorite potential shift was more significant than that of scheelite. This indicates that the number of silicate species adsorbed on the fluorite surface is much more than that of scheelite. Figure 8 shows that the main...
species involved in the flotation separation of scheelite from fluorite were Si(OH)$_3$ and SiO(OH)$_2$ at a pH of 9–10, where both the zeta potentials of fluorite and scheelite showed negative values. This indicates that the adsorption mechanisms of Si(OH)$_3$ and SiO(OH)$_2$ on the surface of scheelite and fluorite maybe dominated by chemisorption (in eqs 4 and 5, \( ≡ \) is the mineral surface).\(^{23}
\[
\text{Ca(OH)}_2 + \text{Si(OH)}_2 \rightarrow \text{CaO} \cdot \text{Si(OH)}_3 + \text{H}_2\text{O} \quad (4)
\]
\[
\text{Ca(OH)}_2 + \text{SiO(OH)}_3^- \rightarrow \text{CaO} \cdot \text{Si(OH)}_3 + \text{OH}^- \quad (5)
\]

After the reaction with silicate species, the number of active sites (\(≡\text{Ca(OH)}_2\)) on the fluorite surface was significantly reduced, while those on the scheelite surface demonstrated a reduced effect. This difference led to the flotation separation of the two minerals.\(^{23}\) After the addition of FeSO$_4$·7H$_2$O, the zeta potential of scheelite was unaffected compared with the case of the addition of SS alone (Figure 7a). However, a significant decrease in the zeta potential of fluorite was observed after the simultaneous accretion of FeSO$_4$·7H$_2$O and SS (Figure 7b). This suggests that FeSO$_4$·7H$_2$O facilitated the adsorption of negative species on the fluorite surface but not the scheelite surface. This phenomenon is beneficial for the separation of scheelite from fluorite. During the addition of FeSO$_4$·7H$_2$O, another negative species (SO$_4^{2−}$) was introduced to the solution. To investigate the relationship between the decreased zeta potential and SO$_4^{2−}$, FeCl$_2$, and Na$_2$SO$_4$ were used as depressants for the zeta-potential tests in the presence of SS (Figure 7b). The zeta potential of fluorite + Na$_2$SO$_4$ + SS was nearly identical to that of fluorite + SS, indicating that Fe$^{3+}$ and not SO$_4^{2−}$ in FeSO$_4$·7H$_2$O promotes the adsorption of SS on the surface of fluorite.

3.2.3. XPS analysis of fluorite with depressants. The XPS was used to detect the properties of mineral surface species, including the elemental composition and chemical states of a mineral surface, according to the distinctive binding energies of the inner electrons of each element.\(^3,34\) The changes of atomic concentrations and chemical states on the mineral surface of the two samples are shown in Table 2. As shown in Table 2, the atomic concentration of Si was only 0.65% which made clear that a small amount of SS was adsorbed on the surface of scheelite when SS, put alone, was used at a 400 mg/L dosage. This is consistent with the zeta potential results. With the FeSO$_4$·7H$_2$O + SS treatment, Fe was detected on the scheelite surface at a low atomic concentration of 0.16%, and the atomic concentration of Si rose by 0.27%, indicating that the Fe$^{3+}$ slightly promoted the adsorption of SS on the scheelite surface. However, the microlotation results indicate that such a small increase did not significantly change the scheelite floatability. The high-resolution XPS spectra of Fe 2p peaks on the fluorite surface. It demonstrated that, in the absence of FeSO$_4$·7H$_2$O, there was no signal of Fe 2p on the fluorite surface. However, after treated with FeSO$_4$·7H$_2$O, significant Fe 2p (with the atom concentration of 1.93%) characteristic peaks appeared on the surface. It indicated that the Fe$^{3+}$ could adsorb on the fluorite surface. In the presence of both FeSO$_4$·7H$_2$O and SS, the Fe atom concentration increased by only a small amount (0.12%). Thus, the adsorption mechanism of Fe$^{3+}$ and SS is mainly that Fe$^{3+}$ was first adsorbed on the fluorite surface, and then the silicate species were adsorbed at the Fe$^{3+}$ site. Table 3 lists the changes of atomic concentrations on the fluorite surface with SS or FeSO$_4$·7H$_2$O + SS treatments. Because of the addition of FeSO$_4$·7H$_2$O, the concentrations of calcium and silicon changed by $−4.64\%$ and $+2.42\%$, respectively. Combined with the zeta-potential results, it can be concluded

![](image)

**Table 2. Atomic Concentrations and Binding Energies of Scheelite with or without FeSO$_4$·7H$_2$O, pH 9.5 (FeSO$_4$·7H$_2$O Concentration: 130 mg/L, SS Concentration: 400 mg/L)**

| elements | with SS | with FeSO$_4$·7H$_2$O + SS | shift |
|----------|--------|--------------------------|-------|
| concentration (%) |        |                          |       |
| O 1s     | 72.02  | 73.65                   | +1.63 |
| Ca 2p    | 10.82  | 9.13                    | −1.69 |
| W 4f     | 17.32  | 16.14                   | −1.18 |
| Si 2p    | 0.65   | 0.92                    | +0.27 |
| S 2p     | 0.00   | +0.00                   |       |
| Fe 2p    | 0.16   | +0.16                   |       |
| binding energy (eV) |        |                          |       |
| O 1s     | 530.14 | 530.24                  | +0.10 |
| Ca 2p    | 346.64 | 346.71                  | +0.07 |
| W 4f     | 34.95  | 34.95                   | +0.00 |
| Si 2p    | 102.02 | 102.17                  | +0.15 |

| elements | with SS | with FeSO$_4$·7H$_2$O + SS | shift |
|----------|--------|--------------------------|-------|
| concentration (%) |        |                          |       |
| O 1s     | 48.87  | 39.51                   | −9.36 |
| Ca 2p    | 28.92  | 24.28                   | −4.64 |
| W 4f     | 18.11  | 26.71                   | +8.61 |
| Si 2p    | 4.10   | 6.52                    | +2.42 |
| Fe 2p    | 2.05   | +2.05                   |       |
| S 2p     | 0.93   | +0.93                   |       |

**Table 3. Atomic Concentrations on the Fluorite Surface with Depressants at pH 9.5 (FeSO$_4$·7H$_2$O Concentration: 130 mg/L, SS Concentration: 400 mg/L)**
that the adsorbed Fe$^{2+}$ provided an abundance of reaction sites and promoted the subsequent adsorption of silicate species on the fluorspar surface. The more silicate species is adsorbed on the fluorspar surface, the more hydrophilic it is. Thus, the FeSO$_4$$\cdot$7H$_2$O + SS exhibited a more significant depression effect on fluorspar than SS functioning solely, which is consistent with the results of the flotation tests.

The binding energy peaks of calcium, fluorine, oxygen, and silicon were measured on the fluorspar surface. Figure 10 shows the Ca 2p, F 1s, O 1s, and Si 2p XPS spectra for fluorspar treated with FeSO$_4$$\cdot$7H$_2$O + SS or SS alone. Figure 10(1) shows the high-resolution XPS spectra of the Ca 2p peaks for fluorspar reacted with different depressants. Two peaks appear at 347.42 and 351.02 eV, which were assigned to Ca 2p$_{3/2}$ and 2p$_{1/2}$, respectively, indicating that fluorspar consisted of pure calcium fluoride (CaF$_2$). After treatment with SS alone, the binding energy of Ca 2p$_{3/2}$ increased to 347.80 eV, indicating that the environment of the calcium ions changed. This is attributed to the fluoride ions, which were coordinated with the calcium ions and replaced by silicate ions, forming calcium silicate on the fluorspar surface. With FeSO$_4$$\cdot$7H$_2$O + SS treatment, the binding energy of Ca 2p$_{3/2}$ increased by 0.25 eV. Although this change is small, it suggests that more silicate species combined with calcium ions on the fluorspar surface under this treatment regime.

The F 1s spectrum of the original fluorspar in Figure 10(2) exhibits only one well-fitted peak at 684.93 eV. After treatment with SS or FeSO$_4$$\cdot$7H$_2$O + SS, the binding energy of fluorine 1s shifted by <0.2 eV, which is similar to the instrumental error, illustrating that the electron density of fluorine witnessed no significant change. All the results presented herein indicated that the fluoride ions in the fluorspar did not react with the depressants.

For O 1s spectra, in Figure 10(3), only one spectral peak at 531.96 eV was fitted reasonably well for the fluorspar sample treated with SS alone. This peak was assigned to the O 1s from the SS. After treatment with FeSO$_4$$\cdot$7H$_2$O + SS, the binding energy of O 1s in the SS increased a rise of 0.24 eV, likely owing to the reaction between the silicate species and Fe$^{2+}$. Moreover, a new peak emerged at 530.12 eV, which was attributed to the O 1s in the sulfate group of CaSO$_4$. Figure 6 indicates that the addition of Na$_2$SO$_4$ helps to depress fluorspar. Thus, it can be inferred that the formation of CaSO$_4$ on the fluorspar surface is the reason for the depression (in eq 6), and the same conclusion was obtained by Zhang et al.

\[
\text{Ca}^+ + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4^{-} \quad (6)
\]

For Si 2p, distinct peaks were witnessed in each spectrum (Figure 10(4)). When SS alone was used as the depressant, the peak at 102.14 eV was attributed to Si 2p in CaSiO$_3$. After the addition of FeSO$_4$$\cdot$7H$_2$O, a new peak appeared at 101.37 eV, which was ascribed to the reaction product of the ferrous ions and silicate species.23

3.3. Discussion. Both scheelite and fluorspar are highly soluble salt minerals but exhibit differences in their dissolution mechanisms. For scheelite, the Ca$^{2+}$ preferentially transferred into the solution over WO$_4^{2-}$, resulting in the scheelite surface lacking Ca$^{2+}$ with excess WO$_4^{2-}$, imparting an overall negative charge. The dissociation of fluorspar in the aqueous solution occurs in the opposite manner to that of scheelite. Fluorine anions preferentially transferred into the solution over Ca$^{2+}$, resulting in excess Ca$^{2+}$ on the surface and an overall positive charge. According to the XPS analysis results, $\equiv$CaOH represents the most important active sites, which react with...
silicate species on the fluorite and scheelite surfaces. However, Tables 2 and 3 display that the atomic concentrations of calcium on scheelite and fluorite surfaces were 10.82 and 28.92%, respectively. Remarkably, this difference may be the theoretical basis for the flotation separation of scheelite from fluorite.

Tables 2 and 3 show the adsorption of Fe$^{2+}$ and SO$_4^{2-}$ on the fluorite and scheelite surfaces in the presence of FeSO$_4$·7H$_2$O + SS. The results indicate that only a small amount of Fe$^{2+}$ adsorbed on the scheelite surface. By contrast, a considerable amount of Fe$^{2+}$ was detected on the fluorite surface. Hydroxyl groups are abundant on the fluorite surface with silicate to form hydrophilic metal-silicate chelate complexes, which were responsible for improving the depression of fluorite. A possible mechanism for the silicate species onto the Fe-modified fluorite surface is schematically suggested in Figure 12.

4. CONCLUSIONS

This study examined the effect of FeSO$_4$·7H$_2$O on the flotation separation of scheelite from fluorite with SS as a depressant. The interaction of Fe$^{2+}$, SO$_4^{2-}$, and silicate species with scheelite and fluorite surfaces was studied using microflotation tests, zeta-potential tests, and XPS analysis to understand the underlying mechanism. According to the aforementioned results, the following conclusions can be drawn.

- The auxiliary depressant FeSO$_4$·7H$_2$O, which was added prior to the addition of NaOH and SS, exhibited improved selective depression for fluorite compared with the case of SS alone. With the addition of FeSO$_4$·7H$_2$O, the separation of scheelite and fluorite was completed at a SS dosage of 400 mg/L, and the recovery and grade of scheelite were increased by 4.3 and 2.7%, respectively.
- The XPS results indicate that the difference in the number of active sites is the basis for the flotation separation of scheelite from fluorite. The Fe$^{2+}$ is preferentially adsorbed on the surface of fluorite and increases the number of active sites which can react with silicate species.
- Sulfate ions are selectively adsorbed on the surface of fluorite with the formation of hydrophilic calcium sulfate, which reduces the floatability of fluorite.

Figure 11. Mechanism for the adsorption of FeSO$_4$ onto the fluorite surface.

![Figure 11](https://example.com/figure11.png)

From Figure 4, the addition orders of FeSO$_4$·7H$_2$O and SS are crucial for flotation separation. The pre-addition of FeSO$_4$·7H$_2$O is conducive to the formation of active sites containing iron species. It is likely that the ferrous species were first adsorbed onto the fluorite surface and subsequently reacted with silicate to form hydrophilic metal-silicate chelate complexes, which were responsible for improving the depression of fluorite. A possible mechanism for the silicate species onto the Fe-modified fluorite surface is schematically suggested in Figure 12.

Figure 12. Mechanism for the adsorption of silicate species onto the fluorite surface.

![Figure 12](https://example.com/figure12.png)
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