

Effective flotation separation of scheelite and calcite by applying methylene phosphonic acid sodium as a novel and green depressant

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Abstract: It is known that the flotation separation of scheelite and calcite is quite difficult due to their similar surface properties. To solve the problem, ethylenediaminetetra (methylene phosphonic acid) sodium (EDTMPS), an environmentally friendly reagent, was employed as an efficient depressant for flotation separation of calcite for the first time. In flotation experiments, it demonstrates that EDTMPS could strongly inhibit the flotation of calcite but barely affect the flotation behavior of scheelite, showing excellent depress ability and selectivity. Based on a series of measurements including contact angle analysis, zeta potential, and XPS analysis, it was found that large amount of EDTMPS could be absorbed on the surface of calcite through strong chemical chelation reaction and thus inhibiting the further adsorption of NaOL. On the contrary, little EDTMPS was absorbed on that of scheelite owing to the negatively charged tungstate ions on the surface in relative terms. All in all, these results exhibit EDTMPS has excellent selective inhibition ability on calcite, which can be potentially applied in actual scheelite and calcite flotation separation process.

Keywords: scheelite, calcite, ethylenediamine tetra (methylene phosphonic acid) sodium, inhibition mechanism, flotation separation

1. Introduction

Scheelite (CaWO₄), a typical tungstate mineral, is diffusely applied in the production of high-tech products (Feng et al., 2018; Guan et al., 2022). However, in natural, scheelite usually is associated with calcite (CaCO₃) due to its low grade, the presence of multifarious trace elements, and complex mineral composition (Wang et al., 2021; Dong et al., 2021). Froth flotation is the principal exploitation technique in the field of mineral processing (Yao et al., 2022; Wang et al., 2021). However, the flotation separation of scheelite and calcite is highly difficult due to their same surface calcium ion site (Dong et al., 2021; Shi et al., 2014). Fatty acids are the most commonly used collectors in flotation recovery of scheelite, which are difficult to separate scheelite from calcite by flotation owing to their similar surface properties (Feng et al., 2018; Wang et al., 2021). Consequently, the addition of depressant, an important flotation separation step, plays an extremely important role in scheelite beneficiation using these traditional fatty acids (Chen et al., 2021).

All the time there have been many researches on depressants in the beneficiation technology of scheelite and calcium gangue minerals. Kang et al. found that 1-Hydroxyethylidene-1, 1-diphosphonic acid (HEDP) has a strong adsorption effect on calcium-bearing veinstone minerals, which can reduce the floatability of calcite and fluorite (Kang et al., 2019). Liu et al. found that the addition of amino trimethylene phosphonic acid (ATMP) could reduce the recovery of calcite to less than 15% (Liu et al., 2022). Ethylenediaminetetraacetic acid (EDTA) was used by Tian et al. to reduce the separation difficulty of diatomite from fluorite and calcite (Tian et al., 2019). Zhang et al. tried the polyacrylic acid

(PAA) as an environmental inhibitor to flotation of fluorite, which could hinder the adsorption of sodium oleate on calcite (Zhang et al., 2018). These studies all used scale inhibitors with good chelating effect as inhibitors and showed significant separation of useful and calcium-bearing minerals for flotation.

The molecular structure of ethylenediamine tetra(methylene phosphonic acid) sodium (EDTMPS) is shown in Fig. 1. EDTMPS is a non-toxic, water-soluble phosphate and is used in medical drugs (Sepini et al., 2016; Das et al., 2017). Moreover, EDTMPS is often used as a scale inhibitor in water treatment because it readily chelates with metal ions to form reticulate complexes (Feng et al., 2020; Han et al., 2019). Therefore, it is likely that EDTMPS has potential as an effective inhibitor for the flotation separation of scheelite and calcite. In this paper, in order to investigate the important role of depressant EDTMPS in scheelite flotation, micro flotation experiments, contact angle test, zeta potential detection, and X-ray photoelectron spectroscopy (XPS) were used to verify the separation mechanism of EDTMPS on flotation.

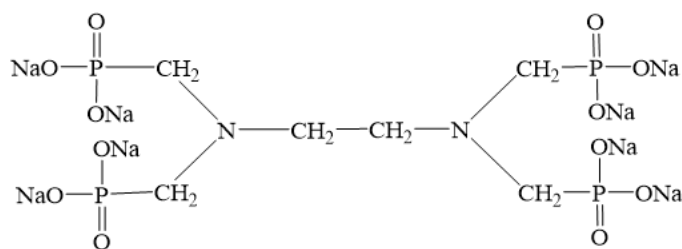


Fig. 1. Molecular structure of EDTMPS

2. Materials and methods

2.1. Pure minerals and reagents

Guangdong Province and Hunan Province, China, were the sampling sites for scheelite and calcite samples used in the experimental study. In order to obtain high quality ore samples, these lumpy minerals were manually crushed and selected. Some selected lumpy samples were hand-ground and polished to make the light sheets required for the contact angle analysis experiments. The high-quality ore samples were ground and sieved separately to obtain products of different particle sizes using a porcelain ball mill. The $-74+38\ \mu\text{m}$ particle size was used for flotation experiments and XPS analysis, while the $-38\ \mu\text{m}$ particle size could be used for XRD analysis experiments and zeta potential analysis. Fig. 2 showed the results of XRD analysis, which proved that the purity of the experimental ore samples is suitable for pure mineral flotation experiments.

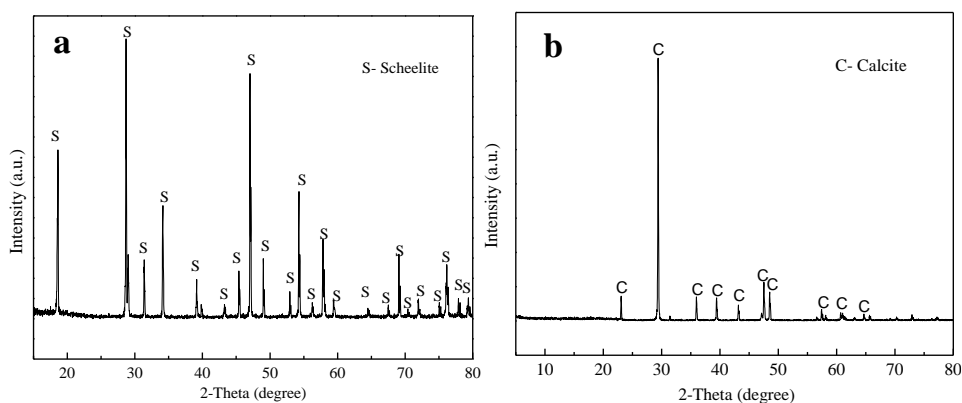


Fig. 2. X-ray diffraction patterns of (a) scheelite and (b) calcite

The ultrapure water consumed during the experiments was prepared using deionized water from the UPK-1-5T ultrapure water machine produced by Sichuan Youpu Ultrapure Technology Co. The industrial grade drug EDTMPS was used as an inhibitor. The collector sodium oleate (NaOl) was

obtained from Aladdin Chemical Technology Co., Ltd. A solution of HCl and NaOH at a concentration of 1% was used as the pH adjuster for the experiments.

2.2. Micro-flotation experiments

The micro-flotation behavior was verified all using the XFG-type flotation machine with the spindle speed of 1800 r/min. The experimental procedure of micro-flotation is presented in Fig.3. During each the single mineral flotation test, 2 g pure mineral powders were recommended into 40 mL flotation cell, then mixed into 35 mL deionized water. Adjust the pH value after stirring for 1 min. Then, a certain concentration of EDTMPS and NaOl solutions were added in turn and acted in the pulp for 3 min respectively. The flotation recovery was calculated after weighing the dry weight of the concentrate and tailings. The ore sample for the artificial mixed ore flotation experiment was composed of scheelite and calcite in a mass ratio of 1:1. The mixed ore flotation process was consistent with Fig. 3.

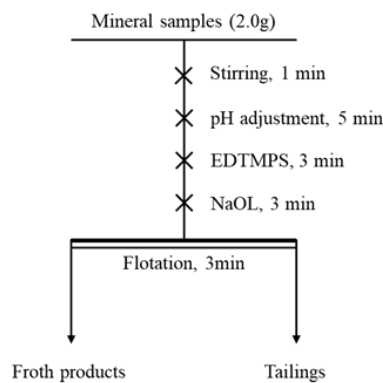


Fig. 3. Flow chart of flotation experiment

The mixed ore flotation products were collected, the dry weight data were retained and chemically analyzed for WO₃ content. The recovery of scheelite can be calculated according to WO₃ grade of concentrate and feed. For all the flotation tests, they were repeated for 3 times. The average of the tests was reported as the final value, and error bars represented one standard deviation around the average value.

2.3. Contact angle experiments

The contact angle experimental analysis instrument is the SL200C contact angle meter made in Shanghai, China. The sample of good quality was selected, and the surface of the sample was polished with sandpaper of different fineness, and the surface of the sample was cleaned with ultrasonic after polishing. Then the prepared mineral samples were immersed in a solution of EDTMPS at a concentration of 10 mg/L or a beaker containing 10 mg/L EDTMPS and 7×10^{-5} mol/L NaOL solution for 30 min, and the samples were removed and dried naturally. Finally, the samples were tested on the test bench and the average value was taken three times.

2.4. Zeta potential experiments

The samples were prepared as follows: 0.2 g of ore powder with a particle size of $-38 \mu\text{m}$ was weighed and immersed in a beaker containing 120 mL of deionized water. Then the sample was stirred with a magnetic stirrer at 150 r/min to make the sample better dispersed. Finally, the pH was adjusted and flotation chemicals were added sequentially according to the requirements of the micro-flotation experiment. The instrument used for the zeta potential experiments was a ZetaProbe (Colloidal Dynamics LLC, USA).

2.5. X-ray photoelectron spectroscopy experiments (XPS)

XPS analytical means were used to detect the surface characteristics of minerals under the influence of different chemical agents (Wang et al., 2022; Zhang et al., 2022). The instrument model used for the

assay was Thermo SCIENTIFIC ESCALAB Xi+. The source type of the analyzer was a monochromated Al target ($E=1486.68$ eV). The vacuum pressure in the analytical chamber was kept below 1×10^{-7} Pa. The means of sample preparation for the XPS experiments was the same as the flotation experimental procedure. The prepared samples were placed in a constant temperature (50°C) oven to remove excess water. The results were analyzed using the software Thermo Avantage and the spectra were calibrated with the C1s peak at a binding energy of 284.8 eV.

3. Results and discussion

3.1. Flotation test analyses

The results of studying the flotation performance of scheelite and calcite at different NaOL concentrations around $\text{pH}=8.0$ were shown and displayed in Fig. 4. In Fig. 4, the natural floatability of calcite is significantly better than that of scheelite. As the amount of NaOL solution increased to 7×10^{-5} mol/L, the flotation recoveries of both scheelite and calcite reached more than 90%. Even if the dosage of NaOL was further increased, the flotation results of the two minerals are not very different. This indicated that the agent NaOL lacked selectivity and had difficulty acting in the flotation separation process of both minerals.

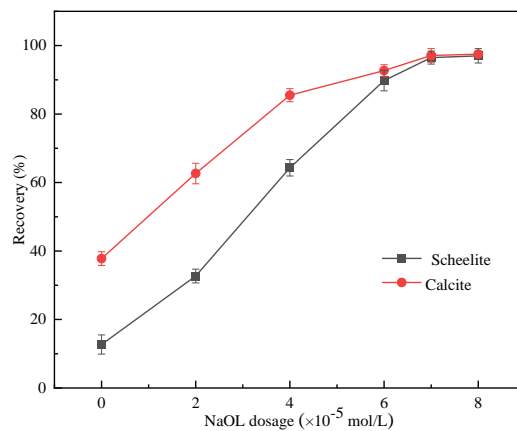


Fig. 4. Effects of NaOL concentration on the floatability of scheelite and calcite at pH 8.0

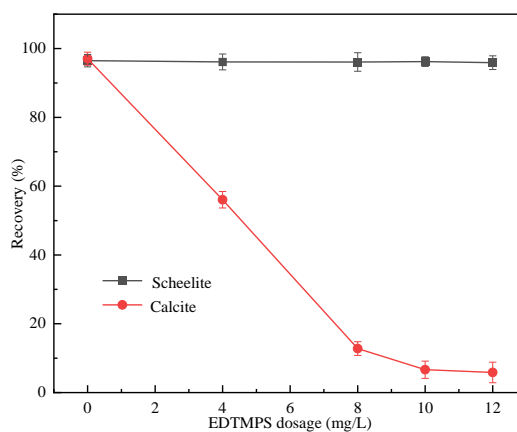


Fig. 5. Effects of EDTMPS dosage on the floatability of scheelite and calcite (conditions: pH 8.0; $c(\text{NaOL}): 7 \times 10^{-5}$ mol/L)

Fig. 5 investigates the effect of EDTMPS dosage on the flotation of the two minerals. According to Fig. 5, it can be seen that the trend of scheelite recovery was very smooth and remained around 95% when the pH and NaOL concentration were fixed values, even though the amount of EDTMPS gradually increased. However, with the increase of the depressant dosage, the recovery of calcite plummeted. Until the concentration of EDTMPS was 10 mg/L, the graph line went flat and the recoveries were all below 10%.

In order to study the optimal conditions of EDTMPS in the experiment, the effects of addition and absence of the depressant EDTMP of scheelite and calcite on the flotation effect of collector NaOL at different pH conditions were studied, and the results were shown in Fig. 6. The concentration of NaOL was controlled at 7×10^{-5} mol/L and the agent concentration of EDTMPS was maintained at 10mg/L. The data in Fig. 6 presented that both scheelite and calcite exhibited good floatability in the pH range of 6-11 absence the depressant EDTMPS, and the recoveries of both minerals were able to exceed 90%. As mentioned above, the flotation processes of scheelite and calcite were not significantly affected by pH without the involvement of EDTMPS. In the presence of EDTMPS, the recovery of calcite gradually decreased with increasing pH value. In the pH range of 7-11, the recovery of calcite dropped to the lowest point and all remained below 10%. The recovery of scheelite was above 90% at pH 7-10 for both. This experimental result indicated that EDTMPS was beneficial to the flotation separation of scheelite and calcite as a depressant.

Based on the results of the single mineral flotation experiments, the artificial mixed ore experiments were used to continue the study of the suppression performance of EDTMPS. The experimental conditions and flotation results of the artificial mixed mineral flotation were recorded in Table 1. As can be seen from the figure, the flotation results under NaOL-only conditions were suppressed with the micro-flotation experiment, and the floatability of both minerals was so similar that most of the minerals went into the concentrate product. In contrast, the separation of the mixed ore was greatly enhanced after containing 10 mg/L EDTMPS in the slurry. The taste of scheelite in the concentrate product was increased from 41.65% to 66.30%. At the same time, the reagent can also ensure the recovery rate of scheelite. Combined with the experiment, it can be seen that EDTMPS can better achieve the flotation separation between scheelite and calcite.

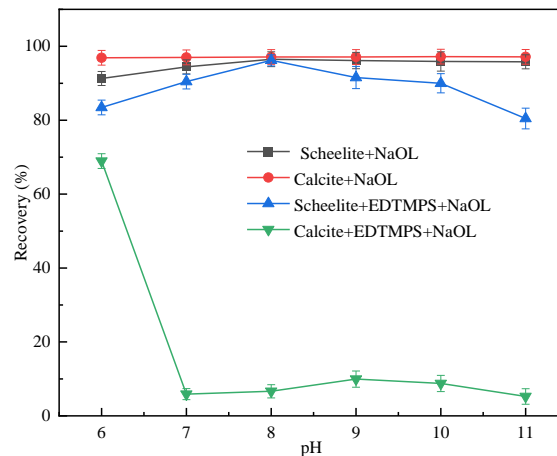


Fig. 6. Effects of pH on the flotation behavior of scheelite and calcite ($c(\text{NaOL}):7 \times 10^{-5}$ mol/L; $c(\text{EDTMPS}):10$ mg/L)

Table 1. The results of artificial mixed ore flotation tests (pH=8.0)

EDTMPS dosage (mg/L)	product	Yield (%)	WO ₃ grade (%)	WO ₃ recovery (%)
0	Concentrate	90.91	41.65	93.96
	Tailing	9.09	26.80	6.04
	Feed	100.00	40.30	100.00
10	Concentrate	51.35	66.30	84.48
	Tailing	48.65	12.86	15.52
	Feed	100.00	40.30	100.00

3.2. Contact angle analyses

Contact angle experiments are used to characterize the surface wettability of minerals under different experimental conditions (Zhu et al., 2022; Wang et al., 2020).

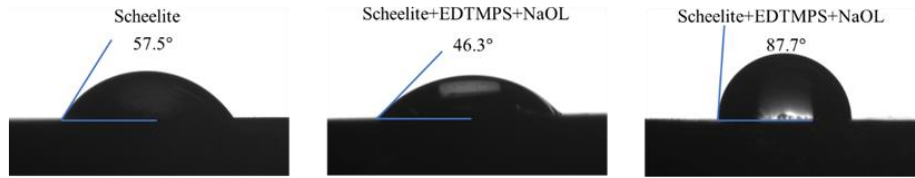


Fig. 7. Contact angles of scheelite before and after treatment with various reagents

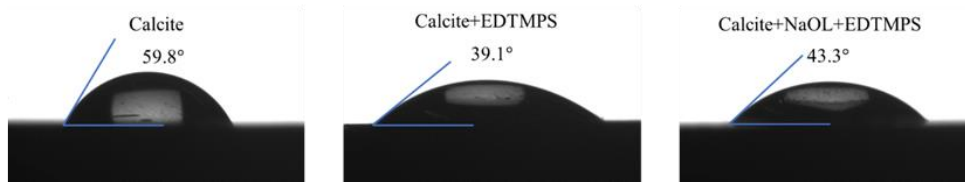


Fig. 8. Contact angles of calcite before and after treatment with various reagents

After being reacted with EDTMPS, the angles of both scheelite and calcite decreased, with the angle of calcite decreasing most significantly, which means the hydrophobicity of the mineral surface is weakened. Immediately following the action of NaOL on the mineral surface, a very significant increase in the angle of scheelite can be seen in the figure, from 46.3° to 87.7°. However, there was no significant change in the angle of calcite. It can be shown that NaOL can enhance the hydrophobicity of scheelite even in the presence of EDTMPS. On the contrary, EDTMPS hindered the interaction of NaOL on the calcite surface thus acting to increase the hydrophilicity of the calcite surface.

3.3. Zeta potential test analyses

Zeta potential analysis intuitively visualizes the change in surface charge during mineral flotation thus showing the adsorption mechanism on the mineral surface (Liu et al., 2016; Chen et al., 2017; Zhang et al., 2023). Fig. 9 showed the variation of zeta potential versus pH for calcite and scheelite under different reagent conditions, respectively. In Fig. 9, it was obvious that the zeta potential of scheelite and calcite decreases with increasing pH, which was due to the large amount of hydroxyl groups adsorbed on the surface of the original minerals, and the zeta potential of scheelite was always negative, which was consistent with the description of the findings in the literature (Liu et al., 2016; Deng et al., 2018; Zhu et al., 2022). The structure of EDTMPS contains a large number of phosphate groups, and the solution of EDTMPS is negatively charged (Liu et al., 2018). The zeta potential of calcite decreased dramatically after the addition of EDTMPS in Fig. 9(a), which indicated that EDTMPS had a great effect on the surface charge energy of calcite. In addition to this, the zeta potential after sequential treatment with EDTMPS and NaOL was very close to the charge in the presence of EDTMPS alone. These results indicated that EDTMPS was heavily adsorbed on the calcite surface, which affected the adsorption of NaOL on the calcite surface. As shown in Fig. 9(b), the effect of NaOL addition on the zeta potential of scheelite was

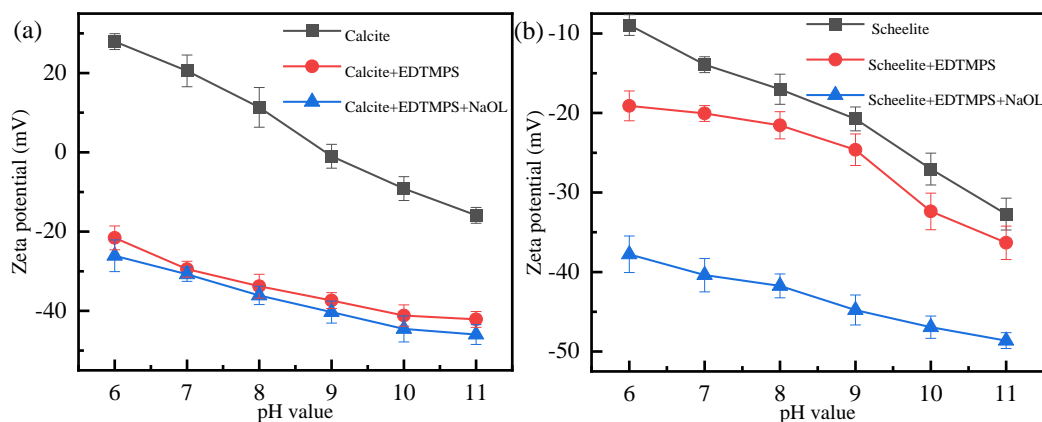


Fig. 9. Zeta potentials of (a) calcite and (b) scheelite as a function of pH under different conditions

much greater than that of EDTMPS. In conclusion, the adsorption effect between EDTMPS and calcite was much greater than that of scheelite. In addition, this result also illustrated the phenomenon that the effect of EDTMPS on the interaction between scheelite and NaOL was extremely small.

3.4. X-ray photoelectron spectroscopy analyses

XPS analysis is usually used to show the change state of chemical elements before and after the reaction between minerals and agents (Pan et al., 2022). XPS analysis was used to probe more deeply into the mechanism of action between EDTMPS and calcite.

Fig. 10 showed the XPS measurement results of calcite. Fig. 10(a) showed the spectra of Ca2p on the calcite surface before and after treatment with the reagent. The double peaks with binding energies of 346.97 eV and 350.52 eV in the figure correspond to Ca2p_{3/2} and Ca2p_{1/2} of calcite, respectively (Deng et al., 2018; Yao et al., 2022). In the environment of EDTMPS addition, there was a small decrease in the binding energy of both peaks, both by 0.06 eV. This indicated that the O1s spectrum of calcite was shown in Fig. 10(b). For pristine calcite, the double peaks with bond energies of 532.00 eV and 531.43 eV were generated due to the Ca-O of C-O, respectively (Wei et al., 2018). After EDTMPS treatment, where the peak with a binding energy of 513.36 eV in O1s was attributed to the phosphate group of EDTMPS. The binding energy of 532.00 eV decreased by 0.11 eV, and the larger change was likely due to the chelation of EDTMPS at the Ca²⁺ site on the calcite surface (Kang et al., 2019). In Fig. 10(c), no peak of P2p was detected in the original calcite. However, after the addition of EDTMPS, two distinct peaks with binding energies of 134.40 eV and 132.69 eV appeared in the spectrum. One of the peaks was due to the phosphate group of EDTMPS, and the other was a Ca-O-P group formed on the calcite surface (Chen and Tang, 2020). The high-resolution spectra of N1s depicted in Fig 10(d). The N1s after EDTMPS treatment were much more pronounced than those of the pristine calcite. This result demonstrates that EDTMPS produced adsorption on the calcite surface (Liu et al., 2018).

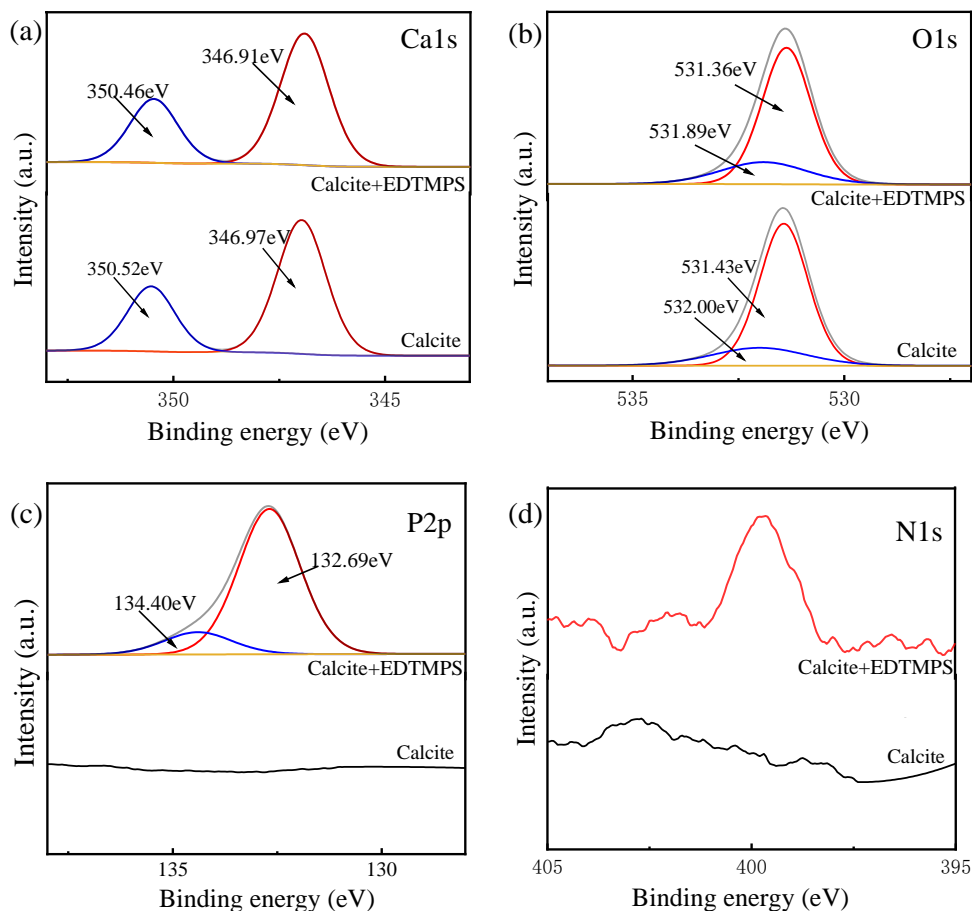


Fig. 10. The XPS spectra of calcite before and after interaction with EDTMPS: (a) Ca 2p; (b) O 1s; (c) P 2p; (d) N 1s

Besides, the XPS experiments also obtained the high-resolution spectra of Ca2p, W4f, P2p, and N1s of scheelite in the presence and absence of EDTMPS, as shown in Fig. 12. The adsorption of EDTMPS on scheelite can be understood by Fig. 12, which further confirms the experimental value of EDTMPS as a depressant. According to Fig. 12(a) and Fig. 12(b), the binding energies of Ca2p and W4f spectra of scheelite were not significantly shifted after the chemical treatment. From Fig. 12(c) and Fig. 12(d), it can be seen that no significant absorption peaks were produced on the P2p and N1s spectra. This result illustrated the absence of chemisorption between EDTMPS and scheelite.

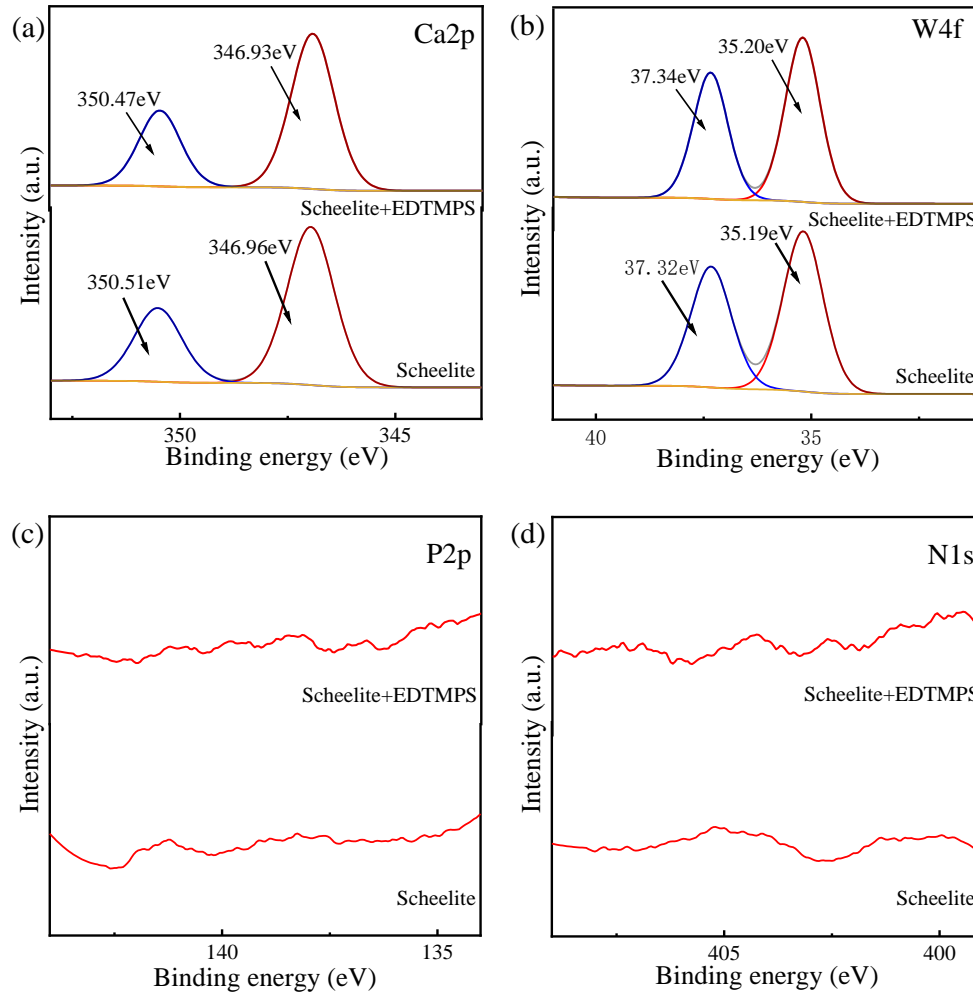


Fig. 11. The XPS spectra of scheelite before and after interaction with EDTMPS: (a) Ca 2p; (b) W 4f; (c) P 2p; (d) N 1s

3.5. Depression mechanism of EDTMPS

Fig. 12 combined the analytical results of the characterization experiments to compile a mechanism diagram for the selective depression of calcite by EDTMPS. It is well documented that NaOL can form calcium dicarboxylate by chemical adsorption at the Ca ion site on the surface of calcium-containing minerals to realize the flotation recovery of useful minerals (Zhou et al., 2021; Pugh and Stenius, 1985; Chen et al., 2017). In combination with the literature, the usual presentation of calcium ion sites on calcite surfaces is in the form of CaCO_3 and $\text{Ca}(\text{OH})^+/\text{Ca}(\text{OH})_2$ (Chen and Tang, 2020; Chen et al., 2022). According to the analytical results of the flotation and characterization experiments used, EDTMPS can effectively adsorb on the Ca^{2+} sites on the calcite surface as a depressant, resulting in a strong chemical chelation reaction and the formation of stable Ca-EDTMPS chelates (Chen and Tang, 2020; Sun et al., 2021). Hence, EDTMPS will cover a large amount of calcite surface, which hinders the action of NaOL on calcite. Ultimately, the surface of calcite is hydrophilic. Meanwhile, the main adsorption species of EDTMPS at weak alkalinity are H_2L_6^- and H_3L_5^- , which can interact with each

other to adsorb on metal ions making the calcite surface less susceptible to adsorption with NaOL (Sun et al., 2021). On the other hand, literature shows that the surface of scheelite is mainly composed of negatively charged tungstate ions (Jiao et al., 2019). Zeta potential analysis suggested that there would be a large number of phosphate ions when EDTMPS was added into the solution. The negatively charged phosphate ion is difficult to combine with the equally negatively charged tungstate ion. Therefore, tungstate ion hinders the adsorption of EDTMPS on scheelite surface, and it is difficult to influence the interaction between NaOL and scheelite. Secondly, the literature showed that the calcite (104) plane was the main dissociation plane which interacted with flotation reagents (Kuang et al., 2022). The Ca-Ca distance on the commonly cleavage plane (104) of calcite (4.050 Å (crosswise), 4.990 Å (lengthways)) is very close to the O-O distance of EDTMPS structure (Liu et al., 2019). Obviously, the O-O distance in the phosphate group of EDTMPS can well match the Ca-Ca distance in calcite. This statement may also be the reason that prompted EDTMPS to suppress calcite. This result further illustrates that EDTMPS has a much greater inhibitory effect on calcite than scheelite. In conclusion, EDTMPS has the potential to replace conventional calcite inhibitors.

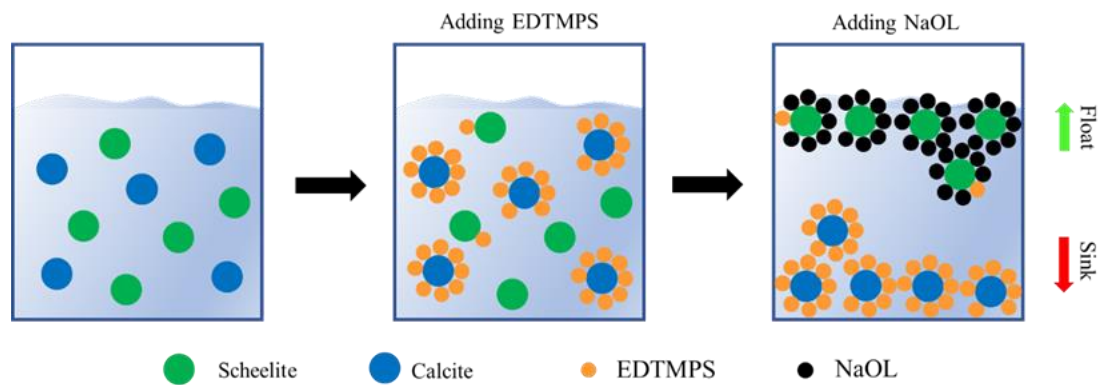


Fig. 12. Mechanism diagram of selective separation of calcite by EDTMPS

4. Conclusions

EDTMPS has the potential to act as an efficient inhibitor of calcite. Combined with the results of single mineral flotation experiments, EDTMPS was able to maintain good separation of scheelite and calcite in the pH range of 7-11, and also significantly inhibited calcite in the mixed ore flotation experiments. The best flotation conditions for the separation of scheelite and calcite were learned from micro-flotation experiments with EDTMPS (10 mg/L) and NaOL (7×10^{-5} mol/L) and pH of 8.0. After contact angle test, zeta potential and XPS analysis, the inhibition mechanism of EDTMPS on calcite was analyzed. The depressant EDTMPS can effectively and stably separate calcite with only a small dose. The phosphate group dissociated by EDTMPS can well adsorb on the Ca^{2+} sites on the calcite surface, thus inhibiting the adsorption of NaOL on calcite and ensuring the good floatability of scheelite. Moreover, it is difficult for the tungstate ions on the surface of scheelite to match the phosphate groups in EDTMPS, so EDTMPS has little effect on scheelite.

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