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Application of diethylenetriaminepenta pentasodium salt as an eco-friendly depressant to effectively improve the flotation separation of scheelite and calcite

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Abstract: Diethylenetriaminepenta (methylene-phosphonic acid) pentasodium salt (DTPMPA), an eco-friendly reagent, was tried for the first time as a depressant for flotation separation of scheelite from calcite. Micro-flotation tests show that DTPMPA can selectively depress the floatability of calcite. In contrast, DTPMPA barely affects the flotation behavior of scheelite. Based on the selective depress effect, floatation separation of scheelite and calcite can be effectively achieved by using DTPMPA as depressant in artificially mixed minerals flotation tests. Based on a series of measurements, it found the surface of calcite was positively charged due to the existence of Ca ion site, which can be chelated with -PO_3H- functional group on the surface of DTPMPA. In the flotation process, DTPMPA can be chemically absorbed on the surface of calcite to inhibit further collector adsorption. On contrast, little DTPMPA was adsorbed on the surface of scheelite due to the spatial site resistance and electrostatic repulsion induced by surface WO_4^{2+}. All in all, these results exhibit DTPMPA has excellent selective depression ability on calcite, which can be potentially applied in the actual scheelite flotation process.

***Keywords*:** flotation, scheelite, calcite, diethylenetriaminepenta pentasodium salt, depressant, adsorption

1. Introduction

Tungsten, a crucial metallic element, is widely applied in high-tech product manufacturing areas due to its special properties of high melting point, low-sputter erosion rate, high density and good radiation resistance (Faramarzpour et al., 2022; Guan et al., 2022). Among numerous tungsten-bearing minerals, only wolframite [(Fe, Mn)WO_4] and scheelite ($CaWO_4$) have utilization value in industry (Wang et al., 2021). In recent years, scheelite resource has become increasingly important due to the exhaustion of wolframite resource.

In mine development industry, for wolframite resource, it can be recovered from ore deposits by simple gravity and eco-friendly beneficiation method. While, for recovery of scheelite, the most prevalent method is froth flotation due to its low grade, disseminated grain size and complex mineral composition (Dong et al., 2019; Dong et al., 2021). In scheelite flotation process, fatty acids reagents (e.g. sodium oleate, tall oil and oxidized paraffinum sodium salt) are often applied as collectors to effectively enhance the floatability of scheelite, which can be adsorbed on its surface via exposed Ca^{2+} active site (Guan et al., 2022; Chen et al., 2020). However, in natural ore deposits, calcite ($CaCO_3$), a typical calcium-containing mineral, is the most common gangue mineral densely associated with scheelite. (Guan et al., 2022). When using fatty acids as collector, calcite exhibits almost the same flotation behavior with that of scheelite due to their similar surface Ca^{2+} active site (Dong et al., 2021). Thus, the separation of scheelite and calcite is always a difficult problem in flotation area.

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In flotation process, depressant should be added in ore pulp is indispensable to selectively reduce the floatability of calcite, which plays a vital role in scheelite beneficiation (Chen et al., 2020; Wang et al., 2020; Cai et al., 2021; Cai et al., 2023). The common depressants used for calcite fall into two categories, inorganic depressants and organic depressants. Water glass, a typical inorganic depressant, is the most widely used depressant for calcite in industry (Faramarzpour et al., 2022). Water glass can be selectively adsorbed on the surface of calcite minerals to inhibit the further adsorption of the collector (Kupka et al., 2018). However, water glass has some negative effects, such as limited selectivity, high dosage of required chemicals and chemical pollution (Jiao et al., 2019). Currently, organic depressants are commonly macromolecular compounds, e.g. dextrin, fenugreek gum, starch and tannins (Chen et al., 2022; Liu et al., 2021; Yang et al., 2020). These organic depressants usually have functional groups such as -OH and -COO- in their molecular structures, which can react with Ca^{2+} active sites on the surface of calcite (Zhou et al., 2022; Zhu et al., 2021). Although they have the advantages of non-toxicity and degradability, some fatal defects, including low adsorption ability and weak depressant effect, greatly limit their wide application (Deng et al., 2019; Pan et al., 2020). Thus, there are still enormous opportunities and challenges to develop comprehensive depressants with high selectivity and excellent depress effect for calcite (Wei et al., 2023; Wei et al., 2024).

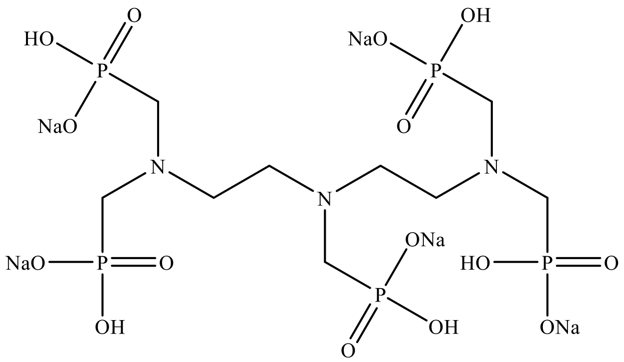

Fig. 1. The molecular structural formula of DTPMPA

Diethylenetriaminepenta (methylene-phosphonic acid) pentasodium salt (DTPMPA) is a non-toxic and hydrophilic neutral product with formula $C_9H_{28}O_{15}N_3P_5$ (molecular weight: 573.2). The molecular structure of DTPMPA is presented in Fig. 1. DTPMPA has excellent chelating ability, which can be easily reacted with various metal ions, especially for that of calcium and magnesium ions (E. Oddo et al., 1990). For example, DTPMPA can prevent the formation of calcium carbonate ($CaCO_3$) in Ca^{2+} containing water through chelating with Ca^{2+} to form Ca- DTPMPA chelate compound. For a long time, based on this ability, DTPMPA is widely applied as the antiscalant in many industrial areas, e.g. circulating cooling water systems and water treatment (Zeino et al., 2018). Since wide industrial applications have shown the excellent chelating ability of DTPMPA with calcium ions, DTPMPA can probably be employed as an efficient depressant for calcite.

Motivated by the above summary, in the current research, DTPMPA was applied as a selective depressant to promote the separation of scheelite and calcite. The feasibility of the flotation separation of scheelite and calcite by DTPMPA was studied by single mineral flotation and artificially mixed mineral flotation. Measurements, including Zeta potential, contact angle and X-ray photoelectron spectroscopy (XPS), were carried out to understand the underlying interaction between minerals and reagents (collector and depressant).

2. Materials and methods

2.1 Materials and reagents

The pure scheelite and calcite minerals used in this study were commercially obtained from Guangdong Province, China and Hunan Province, China, respectively. The samples with higher purity were hand crushed and then agate ground. All the ground samples were respectively classified by a sieve set and the particle size fraction of -74+38 μm was collected for micro-flotation tests. X-ray diffraction (XRD) analysis was performed to characterize the crystalline structures of the as-prepared samples, the results are presented in Fig. 2. As marked in Fig. 2, the diffraction peaks in the XRD pattern can be indexed to the scheelite and calcite. Moreover, little trace of impurity phase can be observed in the spectra, indicating the as-prepared samples are of high purity.

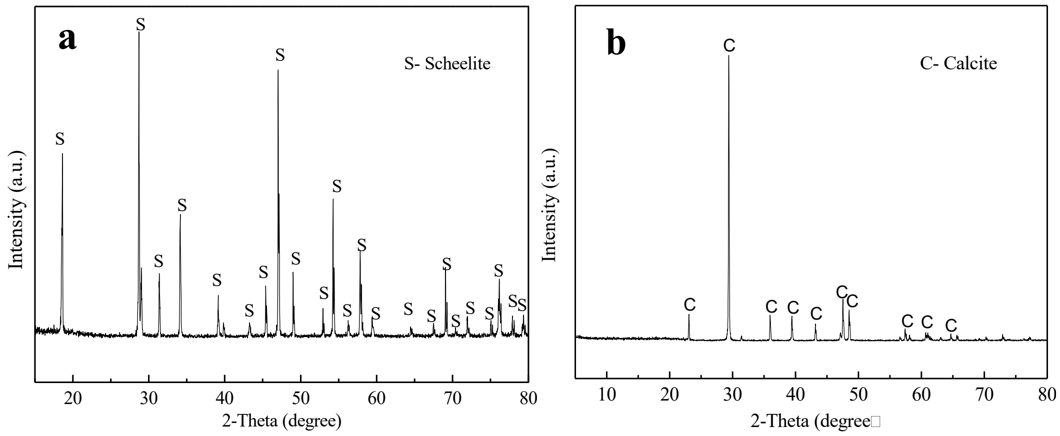

Fig. 2. XRD patterns of as-prepared samples: (a) scheelite; (b) calcite

In the current research, commercially available reagents, including Sodium oleate (NaOl, analytical pure), DTPMPA (technical grade) and water glass (technical grade) were used as collector and depressants, respectively. These reagents were used as received without further purification. De-ionized water was used in all the flotation tests and measurements.

2.2. Flotation experiments

Micro-flotation tests were performed to research the flotation behavior of the as-prepared mineral samples under different conditions. The tests were carried out in an XFG-type mechanical agitation flotation machine equipped with a plexiglass cell whose effective volume is 40 mL (Changchun, Jilin Province, China). The impeller speed of the machine was fixed at 1900r/min during the whole flotation process. In each flotation test, 2 g of the ultrasonically cleaned mineral samples and 35 mL distilled water were successively added into the flotation cell to form uniform ore pulp after being continuously agitated for 2min. The pH of the pulp was then regulated to designed value by addition of hydrochloric acid or sodium hydroxide solution (0.1 mol/L). After 5 min agitation, specified dosage of depressant and collector (NaOl) were successively added in the pulp at a regular interval of 3 min. In quick succession, flotation was carried out and the floated froth product was manually collected for 5 minutes. At the end of the flotation test, the froth product and tailings were successively filtered, dried and weighed. Each conditional test was measured 3 times, and the measured results were average.

For the single ore micro-flotation test, the recovery rate can be calculated based on the weight distributions between the froth product and tailings. For artificially mixed ore flotation test, the mineral samples are mixed according to the weight ratio of 1:1. The flotation concentrate was used to detect the grade of WO_3, and used along with the output to calculate the recovery rate of scheelite and calcite. All micro-flotation tests were repeated 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. Zeta potential analysis

The measurement of Zeta potential is carried out by using Zeta potential analyzer. Colloidal Dynamics LLC, USA was the origin of instruments. ZetaProbe was the model of the machine. 0.2 g -38 μm scheelite or calcite mineral specimen and 120 ml deionized water were added into a beaker, and stirred by a magnetic stirrer with a stirring speed of 150rpm. According to the flotation requirements, the pH value of the pulp was adjusted with a certain dose of HCl and NaOH, and stirred continuously for 5 minutes. Then, a specified dose of flotation reagent DTPMPA solution and NaOl solution were added in turn and stirred for 2 minutes respectively. Each group of conditional tests was measured 3 times, and the measured results were average.

2.4. Contact angle measurement

The influence of mineral surface wettability on different flotation reagents was usually characterized by a contact angle test. The experimental equipment was SL200C type contact angle measuring instrument made in Shanghai, China. First, chose a relatively flat lump ore and polished it with sandpaper of different specifications, and then burnished it. Put water containing 80 mg/L DTPMPA solution or both 80 mg/L DTPMPA and 20 mg/L NaOl solution into a beaker, and soaked the polished sample in the beaker for 30min. Took out the soaked sample and air dry it naturally. After each sample was measured three times, the average value was taken as the test measurement result.

2.5. X-ray photoelectron spectroscopy analysis

XPS analysis was performed on an X-ray photoelectron spectroscopy, and Al Ka sputtering source was used in the experiment. All binding energies were calibrated using the standard C(1s) binding energy at 284.80eV. Thermo Advantage software was used for peak fitting and data analysis. The preparation method of the test sample was as follows: Add 2.0g of mineral sample with a particle size of -74+37 μm to 40 mL of DTPMPA solution with or without 80 mg/L. The pH of the aqueous solution was maintained at 9.0 and stirred continuously in a beaker for 30 min, filtered, rinsed with deionized water, and then dried under vacuum at 40 °C for 24 hours.

3. Results and discussion

3.1. Micro-flotation test results

Micro-flotation tests were performed to evaluate the effect of DTPMPA on flotation behavior of scheelite and calcite. Fig. 3 illustrates the recovery of scheelite and calcite as a function of NaOl dosage (Flotation condition: pH value= 9.0; Without addition of depressant). As seen, the flotation recovery of scheelite and calcite were about 23% and 38% without the addition of collector, implying that the natural floatability of scheelite is even worse than that of calcite. When the NaOl dosage was 20 mg/L, the recoveries of scheelite and calcite dramatically increase to 90%. The flotation recovery of the two minerals was barely changed by further increasing the dosage of NaOl. This indicated that the scheelite and calcite have similar flotation behavior when using NaOl as collector, confirming the flotation separation of scheelite and calcite can't be achieved without the addition of depressant. Moreover, this implies that the optimum NaOl dosage for flotation recovery of the scheelite and calcite samples should be 20 mg/L.

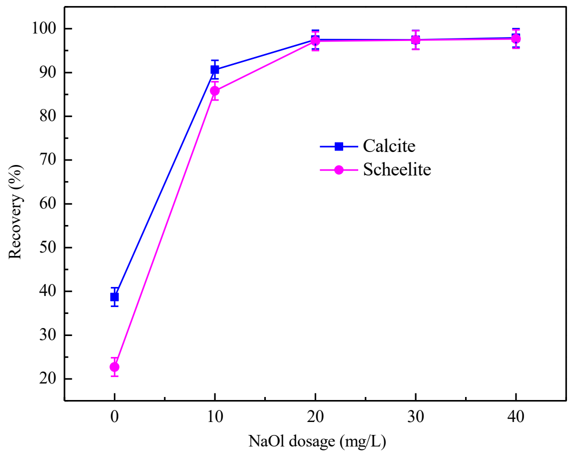

Fig. 3. Flotation recovery of scheelite and calcite as a function of NaOl dosage

Fig. 4 presented the flotation recoveries of scheelite and calcite varying with pH values in the presence and absence of the depressant DTPMPA (Flotation condition: NaOl dosage= 20 mg/L; DTPMPA dosage= 80 mg/L). It can be seen in Fig. 4 that the variation of pH value from 6 to 11 barely affects the floatation behavior of scheelite and calcite. After the addition of 80 mg/L DTPMPA, for calcite, the flotation recovery of calcite shows a decrease, from 97.41% to 78.10%. When the pH value reaches 7, the flotation recovery of calcite sharply decreased to 1.83%. This variation tendency is almost unchanged as the further increase of pH value to 11. Clearly, the flotation of calcite was strongly depressed by the addition of DTPMPA at the pH value range of 7-11. In comparison, for scheelite, the flotation recovery is minor decreased and maintains above 90% at the pH value range of 7~9. When pH value above 9, the falling range of the flotation recovery is significantly increased. This implies the floatation recovery of scheelite was barely affected by the presence of DTPMPA at the pH range of 7~9.

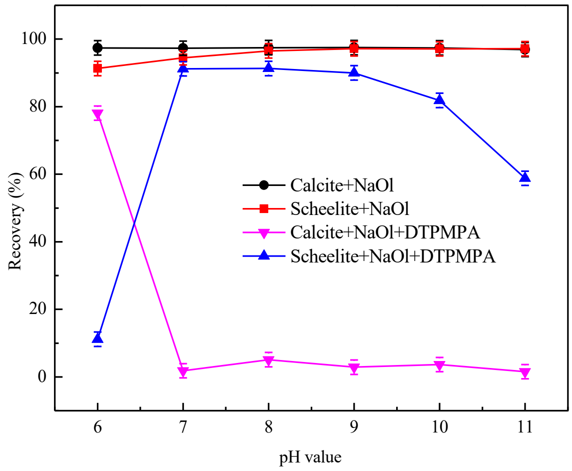

Fig. 4. Flotation recovery of scheelite and calcite as a function of pH values under different reagent conditions

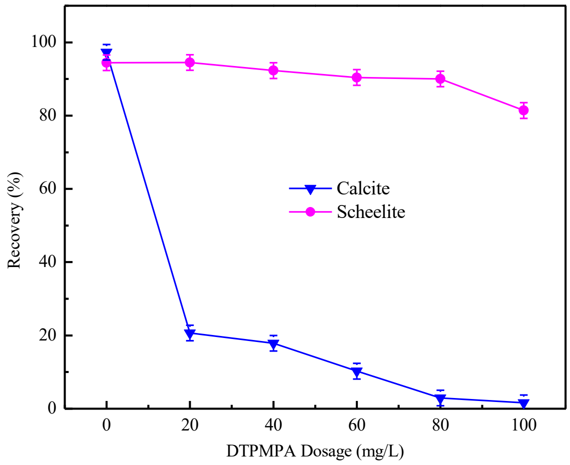

Fig. 5. Flotation recovery of scheelite and calcite as a function of DTPMPA dosage

The flotation recoveries of scheelite and calcite with different DTPMPA dosages were shown in Fig. 5 (Flotation condition: NaOl dosage= 20 mg/L; pH value=9.0). As seen, the flotation recovery of calcite sharply decreased with the increase of DTPMPA dosage. While, the flotation recovery barely changed when DTPMPA dosage increased from 80 mg/L to 100 mg/L. In comparison, for scheelite, the flotation recovery minor decreased from 94.52% to 90.27% when the DTPMPA dosage increased from 20 mg/L to 80 mg/L. However, the flotation recovery significantly decreased to 81.43% with the further increase of DTPMPA dosage to 100 mg/L. It serves to show the optimum DTPMPA dosage for flotation separation of calcite and scheelite should be 80 mg/L.

In industrial flotation recovery of scheelite, water glass is the mostly applied depressant for calcite and the other calcium-containing gangue minerals (Zhong et al., 2021). Thus, for comparative purposes, water glass was also tested as depressant for flotation separation of calcite and scheelite in the current research. The test results are shown in Fig. 6 (Flotation condition: NaOl dosage= 20 mg/L; pH value=9.0). As seen, similar to DTPMPA, the flotation recovery of calcite was decreased with the increase of water glass. While, unlike that of DTPMPA, the recovery of calcite still remains at 19.13% even when the dosage of water glass reaches 2000 mg/L. At the same condition, the recovery of scheelite is 81.81%. This confirms the high dosage of water glass in industrial applications. The high concentration of water glass in pulp would bring the problem of water pollution and filtration difficulty (Wang et al., 2020). Clearly, compared with water glass, DTPMPA has much better depress ability, selectivity and environmental protection for using as depressant in flotation separation of scheelite and calcite.

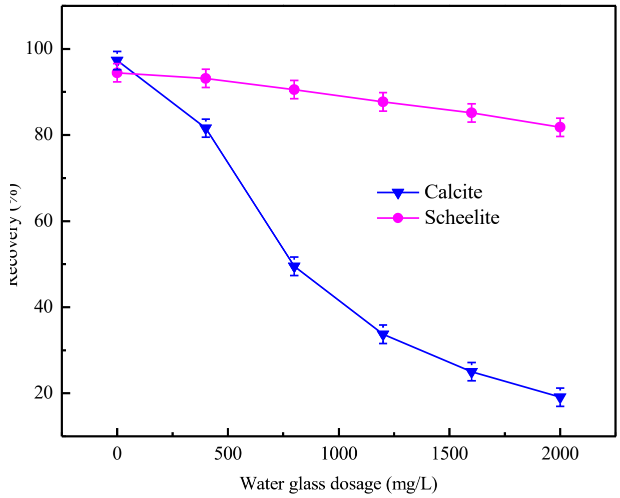

Fig. 6. Flotation recovery of scheelite and calcite as a function of water glass dosage

Since the excellent depress effect of DTPMPA in single mineral flotation test, flotation tests on artificially mixed ore (calcite: scheelite=1: 1) were carried out to further evaluate the ability of DTPMPA on flotation separation of scheelite and calcite. The tests were conducted in the absence & presence of DTPMPA and the results are presented in Table 1 (other flotation condition: NaOl = 20 mg/L; pH = 9.0). It can be seen that above 90% of the mineral is entered in concentrate. This confirming the separation of scheelite and calcite is impossible in the absence of depressant. When applying 80 mg/L DTPMPA as depressant, the flotation separation of the calcite and scheelite is well achieved by obtaining a concentrate with WO_3 grade of 69.84% and WO_3 recovery of 83.90%.

Table 1. The flotation results of artificially mixed ore.

DTPMPA dosage (mg/L)	product	Yield (%)	WO_3 grade (%)	WO_3 recovery (%)
0	Concentrate	91.65	41.77	94.99
	Tailing	8.35	24.17	5.01
	Feed	100.00	40.30	100.00
80	Concentrate	50.91	69.84	88.23
	Tailing	49.09	9.66	11.77
	Feed	100.00	40.30	100.00

In the whole, the above micro-flotation test results manifest the excellent depression ability of DTPMPA on calcite. On the contrary, in the flotation process, DTPMPA has minor effect on that of scheelite. Thus, DTPMPA is a potential depressant that can be applied for efficient flotation separation of scheelite and calcite in industry.

3.2. Zeta potential analysis

Zeta potential analysis was carried out to elucidate the adsorption behavior of reagent on calcite and scheelite in the flotation process (Liu et al., 2022; Huang et al., 2022). Fig. 7 presents the zeta potentials of scheelite and calcite as a function of pH under different reagent conditions. As seen, for scheelite, the zeta potential of scheelite is negative at the whole pH range. This can be attributed to the localized ions on the surface of scheelite are mainly negatively charged tungstate (WO_4^{2-}) (Wang et al., 2021). The isoelectric point (IEP) of pure calcite was about pH 8.9. The information was consistent with the results reported in former research (Chen et al., 2021). With the addition of DTPMPA, the zeta potentials of scheelite and calcite were negatively shifted in the whole pH range. This implies that the adsorption of DTPMPA was taken place on both scheelite and calcite. It is worth noting the negatively shifted level calcite's zeta potential is much greater than that of scheelite. This difference manifests that the adsorption capacity of DTPMPA on the calcite is much higher than that of scheelite. With the further addition of NaOl, the zeta potential of scheelite is significantly deceased. While, for calcite under the same condition, the decreasing amplitude is much smaller than that of scheelite. Clearly, the existence of DTPMPA in the pulp inhibits the adsorption of NaOl on the calcite's surface.

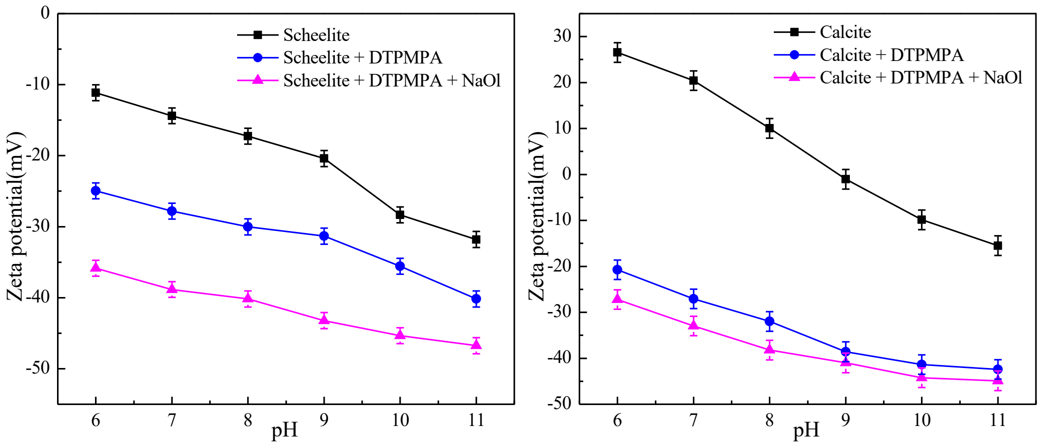

Fig. 7. Zeta potentials of (a) scheelite and (b) calcite as a function of pH under different reagent conditions

3.3. Contact angle measurement

Fig. 8 display the variations of contact angles of scheelite and calcite after being treated with different reagent. As seen, the contact angle of initial scheelite and calcite is 52.2° and 54.9°, respectively. After being treated with DTPMPA, the contact angles decreased to 42.1° and 38.6°, respectively, indicating the adsorption of DTPMPA on both mineral. After being treated with DTPMPA. The contact angle of scheelite increases to 92.9° by further being treated with NaOl. In contrast, for calcite, it slightly increased to 40.1°. It is known that the smaller contact angle represents the stronger hydrophilicity and the worse floatability of the mineral, and vice versa (Cui et al., 2020). Obviously, the existence of DTPMPA can greatly inhibit the adsorption of NaOl on the calcite's surface. On the contrary, it barely affects the adsorption of NaOl on the scheelite's surface, which is in accordance with the zeta potential measurement results.

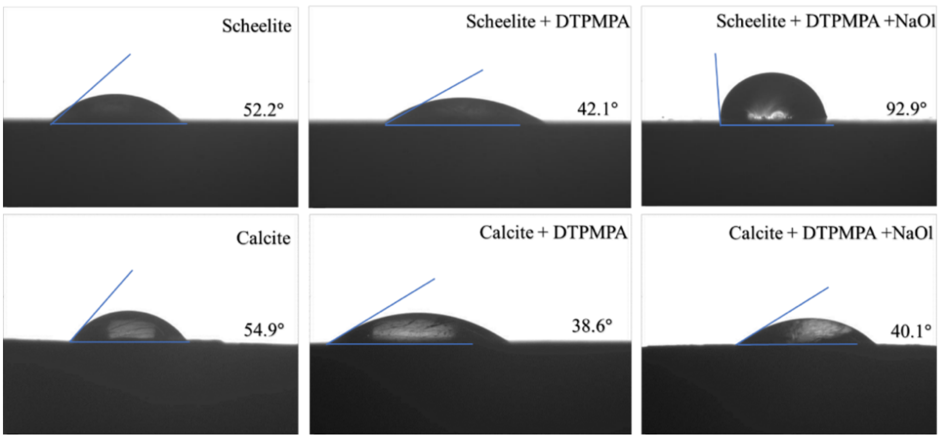

Fig. 8. Contact angles of scheelite and calcite before and after being treated with different reagent

3.4. XPS analysis results

The elemental composition and chemical state of the surface of the sample before and after the interaction (pH=9.0) with DTMPA were analyzed by XPS (Wang et al., 2020). The results are shown in Fig. 9 and Fig. 10, presenting high-resolution spectra (C 1s and O 1s) of calcite and scheelite. The binding energies of each peak were derived using the relevant literature as a reference (Zhou et al., 2021).

As shown in Fig. 9a, for calcite, the peaks centered at binding energy of 284.80 eV and 285.86 eV are respectively assigned to hydrocarbons and carbon oxides (Chen et al., 2022; Chen et al., 2018). The peak with a binding energy of 289.47 eV is attributed to CO_3^{2-} in $CaCO_3$ (Zhou et al., 2021; Zhang et al., 2018). Obviously, after being treated with DTMPA, the peak centered at binding energy of 285.86 eV is greatly increased in intensity. This possibly induced by the adsorption of DTMPA on the surface of calcite. For scheelite, as presented in Fig. 9b, three peaks centered at 284.80 eV, 286.29 eV and 288.53 eV can be attributed to C-H, C-O and C=O bonds (Kang et al., 2019). After scheelite being treated with DTMPA, All the peaks are little changed in intensity.

In Fig. 10a, the peak of O 1s bond energy of 531.51 eV is belonging to $CaCO_3$ of calcite (Zhong et al., 2022). After being interacted with DTPMPA, a new peak appeared at the bond energy of 532.79 eV, which can be assigned to the separation peak of $-PO_3H-$ (Liu et al., 2022). The generation of the new peak indicated that DTPMPA generated chemisorption on the calcite surface. In addition, the peak of O 1s of scheelite is slightly shifted from 530.70 eV to 530.56 eV, as presented in Fig. 10b, which confirms the minor adsorption of DTPMPA on the surface of scheelite.

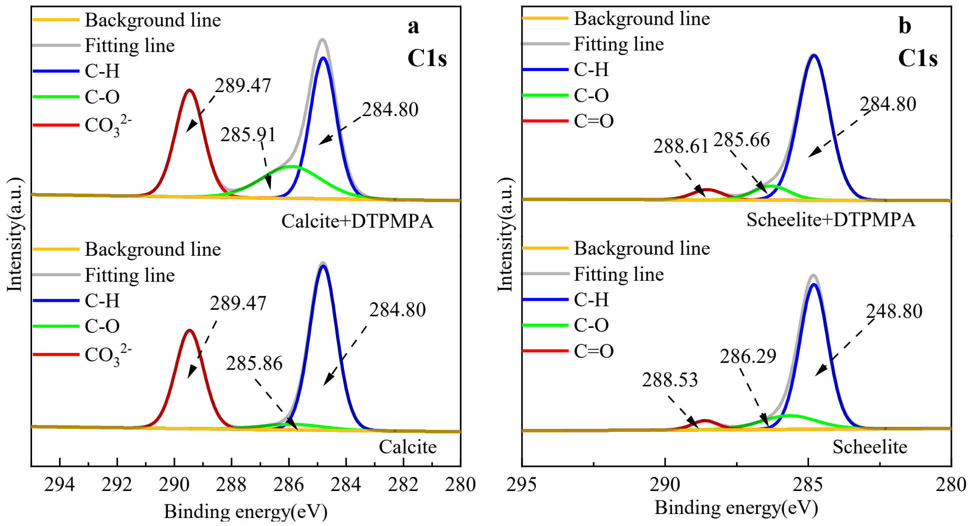

Fig. 9. C 1s spectrum of mineral surface before and after DTPMPA treatment

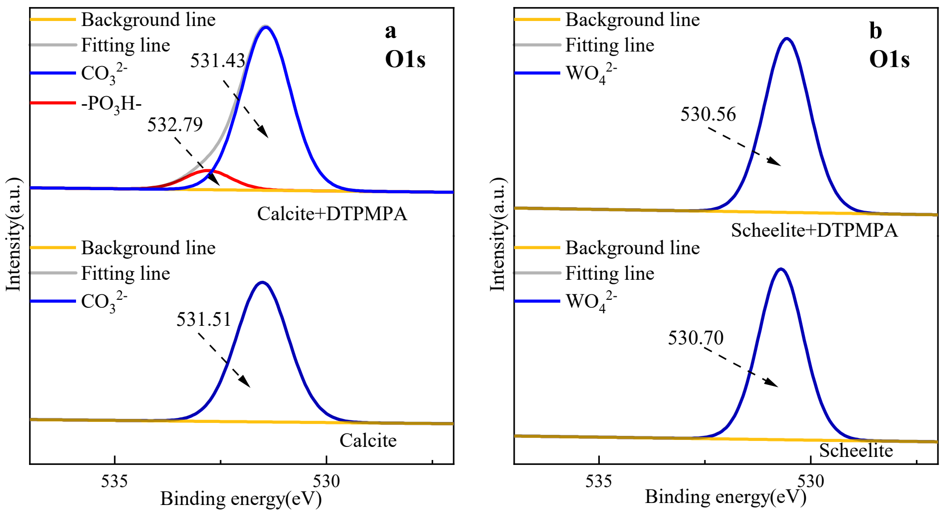

Fig. 10. O 1s spectrum of mineral surface before and after DTPMPA treatment

3.5. Conceivable depression mechanism of DTPMPA

Based on the micro-flotation test results and measurement results, a model is presented in Fig. 11 to show the effect of DTPMPA on the flotation separation of scheelite and calcite. $-PO_3H-$ is the main group in DTPMPA (as presented in Fig .1), making it a highly anionic character and hydrophilicity (Liu et al., 2019; Wang et al., 2021; Zhu et al., 2021). Base on the group with great ability on chelating Ca^{2+}, it can be absorbed the surface of many calcareous material (e.g. $CaCO_3$, $CaSO_4$). Base on the property, it can inhibit the formation of calcium scale formation, which enable its utilization as scale inhibitors. In addition, recent researches had been reported that DTPMPA can be efficiently absorbed on the surface of $CaCO_3$ to form a hydrophilic coating (Zhu et al., 2021; Kiaei et al., 2014; Zhu et al., 2022). Thus, since measurement results (Zeta and XPS) have proved the adsorption of DTPMPA on calcite, DTPMPA would also be coating on the surface of calcite via adsorption to form the hydrophilic layer (as presented in Fig. 11). Under the case, on one hand, the DTPMPA coatings can greatly increase the hydrophilic of calcite. On the other hand, it can prevent the adsorption of collector on the surface of calcite. Thus, in this way, the flotation of calcite is depressed by DTPMPA.

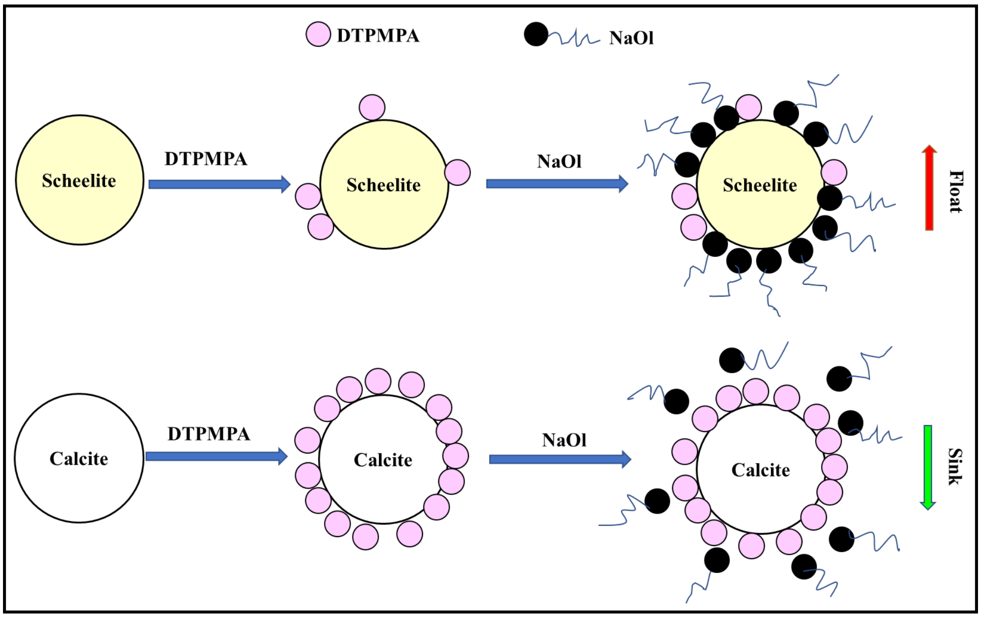

Fig. 11. The possible mechanism of separating scheelite from calcite by DTPMPA

In comparison, the flotation behavior of scheelite were barely affected by the presence of DTPMPA, as presented in micro-flotation tests result. The reason is that much fewer DTPMPA were absorbed on the scheelite than that of calcite, as concluded in zeta potential and XPS measurement results. Although calcite and scheelite have the same surface cations, the anions of the two minerals are different. The much larger volume of WO_4^{2-} ion makes it has higher negative charge than that of CO_3^{2-}. In pulp, the preferential dissociation of the calcium ions on the surface of scheelite leads to excess WO2- 4 on the surface (Liu et al., 2019; Gao et al., 2013; Wei et al., 2020). Thus, compared to that of calcite, the electrostatic repulsion and steric hindrance between scheelite and DTPMPA is much stronger (Wei et al., 2020). In addition, the different adjacent calcium atoms distance in calcite and scheelite possibly be another explication (Liu et al., 2019; Wei et al., 2020). For calcite, the Ca-Ca distance is 4.050 Å (crosswise) and 4.990 Å (lengthways). While, for scheelite, it is 3.867 Å. Attribute to this difference, the -PO_3H- group of DTPMPA possibly matches with Ca-Ca on the calcite surface better than that of scheelite (Liu et al., 2019). The analysis should be part of the reason that the adsorption of DTPMPA on calcite is much higher than on scheelite. More investigations are required to be performed to in-depth reveal the selective interaction mechanism of DTPMPA with calcite or scheelite.

4. Conclusions

DTPMPA, an eco-friendly reagent, was tried for the first time as a depressant for flotation separation of scheelite and calcite. The presence of DTPMPA in the pulp can effectively depress the flotation of calcite. On contrast, DTPMPA barely affects the flotation recovery of scheelite. It was also found that the depressing effect and selectivity of DTPMPA is much better than that of traditional glass water depressant via comparative experiments. Flotation separation of artificially mixed calcite and scheelite can be well achieved by using DTPMPA as depressant and NaOl as collector at pH 9.0. Zeta potential, contact angle test analysis and XPS analysis results indicate that the adsorption of DTPMPA on the surface calcite is much higher than that of scheelite. The possible reason for the difference in adsorption behavior is the different adjacent calcium atoms distance and different surface anions in calcite and scheelite.

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References

CHEN, Y., TANG, X., 2020. *Selective flotation separation of smithsonite from calcite by application of amino trimethylene phosphonic acid as depressant*. Appl. Surf. Sci. 512, 145663.

CHEN, Y., FENG, B., YAN, H., ZHANG, L., ZHONG, C., WANG, T., WANG, H., XU, L., 2022. *Adsorption and depression mechanism of an eco-friendly depressant dextrin onto fluorite and calcite for the efficiency flotation separation.* Colloids Surf., A. 635, 127987.

CHEN, C., SUN, W., ZHU, H., LIU, R., 2021. *A novel green depressant for flotation separation of scheelite from calcite.* Trans. Nonferrous Met. Soc. China. 31, 2493-2500.

CHEN, W., FENG, Q., ZHANG, G., LIU, D., LI, L., 2018. *Selective flotation of scheelite from calcite using calcium lignosulphonate as depressant.* Miner. Eng. 119, 73-75.

CUI, Y., JIAO, F., WEI, Q., WANG, X., DONG, L., 2020. *Flotation separation of fluorite from calcite using sulfonated ligniteas depressant*. Sep. Purif. Technol. 242, 116698.

CAI J., SHEN P., LIU D., ZHANG X., FANG J., SU C., YU X., LI J., WANG H., 2021. *Growth of covellite crystal onto azurite surface during sulfurization and its response to flotation behavior*. Int. J. Min. Sci. Techno., 31, 1003-1012.

CAI J., MA Y., SU C., LAI H., SHEN P., LIU D., PEI B., 2023. *New insight into enhancing sulfurization of azurite with ethylenediamine and its response to xanthate adsorption*. J. Mol. Liq., 389, 122865.

DONG, L., JIAO, F., QIN, W., LIU, W., 2019. *Selective flotation of scheelite from calcite using xanthan gum as depressant*. Miner. Eng. 138, 14-23.

DONG, L., JIAO, F., QIN, W., WEI, Q., 2021. *New insights into the depressive mechanism of citric acid in the selective flotation of scheelite from fluorite.* Miner. Eng. 171, 107117.

DONG, L., JIAO, F., QIN, W., WEI, Q., 2021. *Utilization of iron ions to improve the depressive efficiency of tartaric acid on the flotation separation of scheelite from calcite*. Miner. Eng. 168, 106925.

DENG, J., LIU, C., YANG, S., LI, H., LIU, Y., 2019. *Flotation separation of barite from calcite using acidified water glass as the depressant*. Colloids Surf., A. 579, 123605.

FARAMARZPOUR, A., YAZDI, M., MOHAMMADI, B., CHELGANI, S., 2022. *Calcite in froth flotation - A review.* J. Mater. Res. Technol. 19, 1231-1241.

GUAN, Z., LU, K., ZHANG, Y., YANG, H., LI, X., 2022. *Mechanism of manganese ion interaction with the surface of scheelite and calcite and its effect on flotation separation*. Colloids Surf., A. 648, 129397.

GAO, Z., SUN, W., HU, Y., LIU, X., 2013. *Surface energies and appearances of commonly exposed surfaces of scheelite crystal.* Trans. Nonferrous Met. Soc. China 23, 2147−2152.

HUANG, Z., SHUAI, S., BUROV, V. E., POILOV, V. Z., LI, F., WANG, H., LIU, R., ZHANG, S., CHENG, C., LI, W., YU, X., HE, G., FU, W., 2022. *Application of a new amidoxime surfactant in flotation separation of scheelite and calcite: Adsorption mechanism and DFT calculation*. J. Mol. Liq. 364, 120036.

JIAO, F., DONG, L., QIN, W., LIU. W., HU, C., 2019. F*lotation separation of scheelite from calcite using pectin as depressant*. Miner. Eng. 136, 120-128.

KUPKA, N., RUDOLPH, M., 2018. *Froth flotation of scheelite – A review*. Int. J. Min. Sci. Technol. 28, 373-384.

KANG, J., KHOSO, S, A., HU, Y., SUN, W., GAO, Z., LIU, R., 2019. *Utilisation of 1-Hydroxyethylidene-1, 1-diphosphonicacid as a selective depressant for the separation of scheelite from calcite and fluorite.* Colloids Surf., A. 582, 123888.

KIAEI, Z., HAGHTALAB, A., 2014. *Experimental study of using Ca-DTPMP nanoparticles in inhibition of $CaCO_3$ scaling in a bulk water process.* Desalination. 338, 84-92.

Liu, D., Zhang, G., Chen, Y., 2021. *Investigations on the selective depression of fenugreek gum towards galena and its role in chalcopyrite-galena flotation separation*. Miner. Eng. 166, 106886.

LIU, J., WANG, K., ZHU, Y., HAN, Y., 2022. *Flotation separation of scheelite from fluorite by using DTPA as a depressant.* Miner. Eng. 175, 107311.

LIU, C., ZHU, L., FU, W., CHI, R., LI, H., YANG, S., 2022. *Investigations of amino trimethylene phosphonic acid as a green and efficient depressant for the flotation separation of apatite from calcite*. Miner. Eng. 181, 107552.

LIU, C., ZHANG, W., SONG, S., LI, H., LIU, Y., 2019. *Flotation separation of smithsonite from calcite using 2-phosphonobutane-1,2,4-tricarboxylic acid as a depressant*. Powder Technol. 352, 11–15.

ODDO, J.E., TOMSON, M.B., 1990. *The solubility and stoichiometry of calcium-diethylenetriaminepenta (methylene phosphonate) at 70° in brine solutions at 4.7 and 5.0 pH*. Appl. Geochem. 5, 527-532.

PAN, Z., WANG, Y., WEI, Q., CHEN, X., JIAO, F., QIN, W., 2020. *Effect of sodium pyrophosphate on the flotation separation of calcite from apatite*. Sep. Purif. Technol. 242, 116408.

WANG, X., JIA, W., YANG, C., HE, R., JIAO, F., QIN, W., CUI, Y., ZHANG, Z., LI, W., SONG, H., 2021. *Innovative application of sodium tripolyphosphate for the flotation separation of scheelite from calcite*. Miner. Eng. 170, 106981.

WANG, X., JIAO, F., QIN, W., YANG, C., CUI, Y., WANG, Y., ZHANG, Z., SONG, H., 2020. *Sulfonated brown coal: A novel depressant for the selective flotation of scheelite from calcite.* Colloids Surf., A. 602, 125006.

WANG, C., LIU, R., SUN, W., JING, N., XIE, F., ZHAI, Q., HE, D., 2021. *Selective depressive effect of pectin on sphalerite flotation and its mechanisms of adsorption onto galena and sphalerite surfaces*. Miner. Eng. 170, 106989.

WANG, T., FENG, B., GUO, Y., ZHANG, W., RAO, Y., ZHONG, C., ZHANG, L., CHENG, C., WANG, H., LUO, X., 2020. *The flotation separation behavior of apatite from calcite using carboxymethyl chitosan as depressant*. Miner. Eng. 159, 106635.

WANG, M., HUANG, G., ZHANG, G., CHEN, Y., LIU, D., LI, C., 2021. *Selective flotation separation of fluorite from calcite by application of flaxseed gum as depressant.* Miner. Eng. 168, 106938.

WEI, Z., FU, J., HAN, H., SUN, W., YUE, T., WANG, L., SUN, L., 2020. *A Highly Selective Reagent Scheme for Scheelite Flotation: Polyaspartic Acid and Pb–BHA Complexes*, Minerals 10, 561.

WEI, Z., SUN, W., WANG, P., HAN, H., LIU, D. 2023. *The structure analysis of metal–organic complex collector: From single crystal, liquid phase, to solid/liquid interface*. J. Mol. Liq., 382.

WEI, Z., SUN, W., HAN, H., XING, Y., GUI, X. 2024. *Molecular design of multiple ligand metal–organic framework (ML-MOF) collectors for efficient flotation separation of minerals*. Sep. Purif. Technol., 328.

YANG, S., XU, Y., LIU, C., HUANG, L., HUANG, Z., LI, H., 2020. *The anionic flotation of fluorite from barite using gelatinized starch as the depressant*. Colloids Surf., A. 597, 124794.

ZHOU, H., ZHANG, Y., TANG, X., CAO, Y., LUO, X., 2022. *Flotation separation of fluorite from calcite by using psyllium seed gum as depressant.* Miner. Eng. 159, 106514.

ZHU, W., PAN, J., YU, X., HE, G., LIU, C., YANG, S., ZENG, Y., ZENG, A., LIU, T., 2021. *The flotation separation of fluorite from calcite using hydroxypropyl starch as a depressant*. Colloids Surf., A. 616, 126168.

ZEINO, A., ALBAKRI, M., KHALED, M., ZARZOUR, M., 2018. *Comparative study of the synergistic effect of ATMP and DTPMPA on CaSO4 scale inhibition and evaluation of induction time effect*. J. Water Process. Eng. 21, 1-8.

Zhong, C., Wang, H., Feng, B., Zhang, L., Chen, Y., GAO, Z., 2021. *Flotation separation of scheelite and apatite by polysaccharide depressant xanthan gum.* Miner. Eng. 170, 107045.

ZHOU, H., YANG, Z., TANG, X., SUN, W., GAO, Z., LUO, X., 2021. *Enhancing flotation separation effect of fluorite and calcite with polysaccharide depressant tamarind seed gum.* Colloids Surf., A. 624, 126784.

ZHANG, C., SUN, W., 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.* J. Colloid Interface Sci. 512, 55-63.

ZHONG, C., FENG, B., ZHANG, L., ZHANG, W., WANG, H., GAO, Z., 2022. *Flotation separation of apatite and calcite using gum arabic as a depressant.* Colloids Surf., A. 632, 127723.

ZHU, Y., LI, H., ZHU, M., WANG, H., LI, Z., 2021. *Dynamic and active antiscaling via scale inhibitor pre-stored superhydrophobic coating*. Chem. Eng. J. 403, 126467.

ZHU, M., QIAN, H., FAN, W., WANG, C., YUAN, R., GAO, Q. WANG H., 2022. *Surface lurking and interfacial ion release strategy for fabricating a superhydrophobic coating with scaling inhibition*. Pet. Sci. 19(6), 3068-3079.