



# Camphor leaf extract as neoteric and environmentally friendly depressant in flotation separation of scheelite and calcite

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**Abstract:** Camphor leaves were directly extracted as depressants by using simple physical methods. The active ingredients and depression mechanism were studied through contact angle measurements, Fourier transform infrared spectroscopy (FTIR), and atomic force microscopy (AFM). The flotation experiment showed that camphor leaf extract (CLE) had a strong depression effect on calcite but minimal effect on scheelite. The adsorption morphology detected using AFM confirmed the existence of active ingredients on calcite. FTIR results indicated that the adsorbed components on the surface of calcite contained a large number of hydroxyl groups that made calcite hydrophobic. Zeta potential measurements and FTIR revealed a much higher adsorption amount of CLE on the calcite surface than on the scheelite surface. The CLE has potential application value in the flotation separation of scheelite and calcite.

**Key words:** scheelite; calcite; flotation; camphor leaf extract; depressant

## 1 Introduction

Scheelite ( $\text{CaWO}_4$ ) is one of the primary sources of tungsten used in the tool industry to produce hard and wear-resistant materials [1]. Flotation is a common method to separate scheelite from calcium-bearing gangue minerals such as calcite and fluorite by utilising the difference in the wettability between valuable and gangue minerals [2–4]. Fatty acids are the most commonly used collectors for calciferous minerals [5–7]. Owing to the poor selectivity of fatty acids, the separation of scheelite from calcium-bearing gangue minerals is usually achieved using depressants to modify the wettability.

Sodium silicate is a vital depressant of calcite in industrial scheelite flotation [8,9]. However, the required dosage is high, and its selectivity is limited [10]. Sodium silicate will depress scheelite

when its dosage exceeds a certain amount [11]. Polyphosphates are useful depressants for calcite but cause the eutrophication of water bodies [12]. Plant gums, which are macromolecular organisms such as starch [13], seed gum [14,15], and cellulose [16], are effective inhibitors of calcite and have been applied in the industry. The gums are chemisorbed on the calcite surface by reacting with  $\text{Ca}^{2+}$  site and thus preventing sodium oleate adsorption [15,17]. However, the synthesis of these agents requires a complex chemical treatment, complicated process, and harsh conditions [18–20]. In addition, the synthesis of flotation reagents may cause environmental pollution [21]. A reagent that is easy to prepare, widely available, and environmentally friendly is a good choice. Therefore, this work aimed to directly extract useful substances from plants leaf for use as depressants.

The camphor tree is an evergreen tree belonging to genus *Cinnamomum* of *Lauraceae* [22]

and is widespread in the south of China, including the south area of Yangtze River and southwest provinces [23]. The camphor tree is widely utilised in the wood industry, and its bark, leaf and fruit can be used to extract essential substances [24–28]. CHEN et al [29] has indicated that the Camphor leaf extract exhibits an excellent anti-corrosion property of Q235 steel in HCl medium owing to the adsorption onto the Q235 steel surface. However, studies on using camphor leaves for flotation are limited.

In this study, camphor leaves to be used as a calcite depressant were directly extracted by using unprecedented physical methods. The possibility of flotation separation of calcite and scheelite was explored. The morphology of active ingredients was imaged by atom force microscopy, and infrared spectrum was obtained. This work is useful for separating scheelite from calcite and paves the way for the direct use of plants in flotation. The plant kingdom is the key to the great mineral treasure provided by the lithosphere.

## 2 Experimental

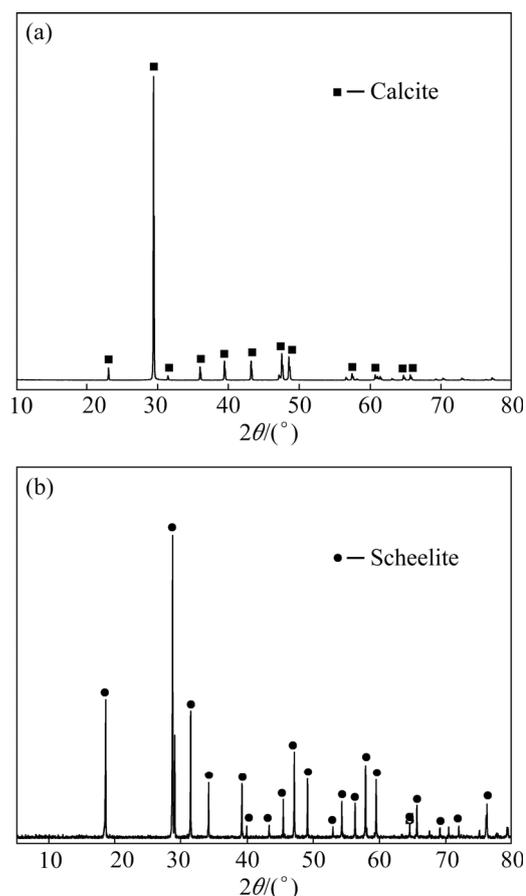
### 2.1 Materials

The resistivity of deionized (DI) water used in the experiment was over  $17 \text{ M}\Omega \cdot \text{cm}$ . The AR-grade sodium oleate (NaOL), HCl, and NaOH (Sinopharm Chemical Reagent Co., Ltd.) were used. HCl and NaOH were used to adjust pulp pH, and methyl alcohol (HPLC grade, evaporation residue less than  $5 \text{ mg/L}$ ) was applied as solvent.

Figure 1 shows the X-ray diffraction patterns of calcite and scheelite samples. The purities of natural calcite ( $\text{CaCO}_3$ ) and scheelite ( $\text{CaWO}_4$ ) were 98.0% and 98.7%, respectively, as determined by chemical analysis. The pure minerals were crushed, hand-selected, ground, and screened. A sample of  $37\text{--}74 \mu\text{m}$  was used in the flotation and Fourier transform infrared spectroscopy (FTIR) tests. The whole process was free from metal contamination.

### 2.2 Preparation method of depressant

Fresh green leaves were picked from the camphor tree and washed by ethyl alcohol first and then with water to remove the organic pollutants and dust. 50 g of cleaned leaves were crushed with 50 mL of DI water by a juicer (BG-JS4, Midea

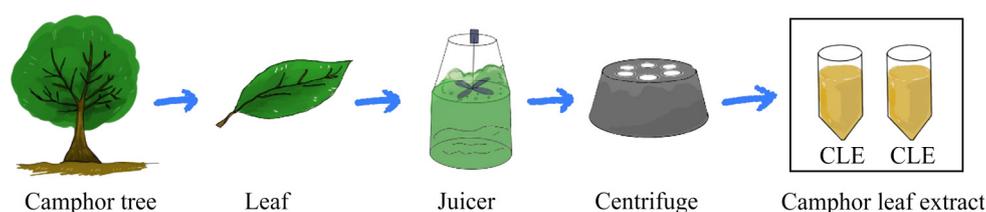


**Fig. 1** X-ray diffraction patterns of calcite (a) and scheelite (b)

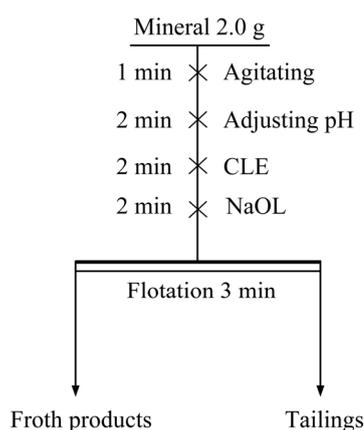
Group Co., Ltd., China). The pulp of the camphor leaves was sucked out with a syringe and centrifuged to separate the liquid and solid. The schematic of the preparation of camphor leaf extract is shown in Fig. 2. This supernatant solution was used as the depressant and named CLE. The concentration of this solution is replaced by the concentration of total organic carbon ( $\text{mg/L}$ ) as determined by TOC-LCPH analyzer (Shimadzu, Kyoto, Japan).

### 2.3 Flotation experiment

Flotation was conducted in an XFG flotation machine (Exploring Machinery Plant, Changchun, China) with a 40 mL cell and impeller speed of 1992 r/min. The order of flotation was shown in Fig. 3. In brief, 2.0 g of mineral and 40.0 mL of water were added to the flotation cell, and then each reagent was added and stirred for 2 min. The froth was scraped out using a plastic blade for 3 min. The froth products were dried and then weighed to calculate the flotation recovery.



**Fig. 2** Schematic diagram for preparation of camphor leaf extract



**Fig. 3** Flow chart of pure mineral flotation

## 2.4 Contact angle measurements

The contact angle was measured by a sessile liquid drop method [30]. A piece of pure calcite and scheelite was cut into flat surfaces parallel to the top and bottom. The samples were polished with three fineness abrasive papers in the coarse-to-fine order. The finest abrasive paper has a particle size of less than 0.1  $\mu\text{m}$ . The samples were washed thoroughly with water in ultrasonic wave for 2 min, conditioned in each reagent solution for 2 min, and subjected to the contact angle measurement. The pH of the solution was adjusted individually using HCl and NaOH. After each test, the sample was re-polished to obtain a fresh surface and then subjected to the next measurement. Every condition was repeated three times, and each result was read twice.

## 2.5 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR was used to detect the CLE components. A Spectrum One FTIR (Shimadzu Corporation, Kyoto, Japan) was used, and potassium bromide tablet and transmission methods were adopted. The analysis was conducted from 4000 to 400  $\text{cm}^{-1}$  using 32 scans with a resolution of 2  $\text{cm}^{-1}$ .

The sample was prepared as follows: 2 g of minerals were added to the solution with 35.4 mg/L

CLE. After being stirred for 10 min, the pulp was filtered and rinsed five times with water to remove the non-adsorbed reagent. The minerals on filter paper were dried in a vacuum oven at 40  $^{\circ}\text{C}$ . After drying, the minerals were placed in a 10 mL test tube with a stopper and added with 3 mL of methyl alcohol (HPLC grade, evaporation residue less than 5 mg/L). The minerals in methyl alcohol were shaken at 40  $^{\circ}\text{C}$  for 24 h in a temperature-controlled shaker to extract the reagent adsorbed on their surface. After centrifugation to remove the minerals, the methyl alcohol was completely evaporated at 40  $^{\circ}\text{C}$ . Another 3 mL of methyl alcohol was vaporized as a blank control. FTIR was also used to detect the residue after evaporation.

## 2.6 Atomic force microscopy imaging

The adsorption of the substance on the calcite surface was detected by Multimode 8 (Bruker, USA) in the air under the ambient temperature of 20  $^{\circ}\text{C}$  [31]. The test probe (Scanasyt-air, Bruker, USA) was a single silicon nitride probe with a resonance frequency of 70 kHz, and a spring constant of 0.4 N/m. The AFM images were analysed using the software NanoScope Analysis 1.9.

Fresh calcite cleavage plane was smashed and picked to obtain a flat and clean surface. The samples were stirred in the solution with CLE concentration of 35.4 mg/L, rinsed gently with DI water, and dried naturally. Contamination was prevented throughout this process. Another fresh calcite cleavage plane was used as a blank control.

## 2.7 Zeta potential measurement

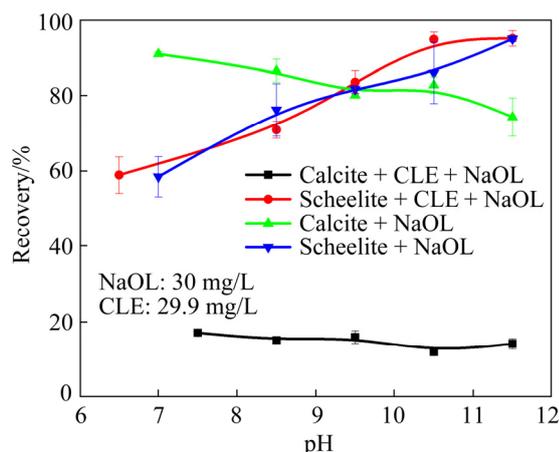
Zeta potential measurements were conducted in a zeta potential analyzer (Malvern Instruments Ltd., United Kingdom) to analyse the surface electrical properties. 40 mg calcite or scheelite sample (<5  $\mu\text{m}$ ) was added to 40 mL 0.001 mol/L KCl supporting electrolyte. The pH was adjusted with HCl or NaOH to desired value. CEL was added to form 15.0 mg/L CLE solution and stirred

for 2 min. The pulp was precipitated for 2 min to remove large particles. Three measurements were repeated, and the average was applied.

### 3 Results

#### 3.1 Flotation experimental results

Figure 4 shows the effect of pH on the recovery of calcite and scheelite with and without depressant. NaOL was used as the collector at a concentration of 30.0 mg/L. In the absence of CLE depressant, the calcite and scheelite exhibited good floatability and were difficult to separate. In the presence of 29.9 mg/L CLE depressant, the recovery of calcite was less than 20%. However, the depressant had minimal influence on the flotation of scheelite. The different floatabilities of calcite and scheelite with CLE treatment indicated that this agent had a selective depressing effect on calcite, and the depression was not affected by pH.



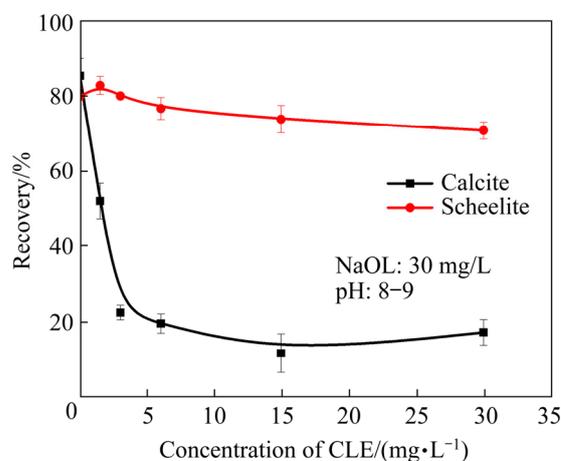
**Fig. 4** Recovery of calcite and scheelite using different reagents

Figure 5 shows the relationship between flotation recovery and CLE concentration. When CLE was added, the recovery of calcite decreased sharply with the increase in the depressant CLE concentration. This result shows that CLE has a strong depression effect on calcite. On the contrary, even when CLE concentration increased, scheelite still had a good recovery (>70%). At CLE concentration of 29.9 mg/L, the recoveries of calcite and scheelite were 17.3% and 70.8%, respectively.

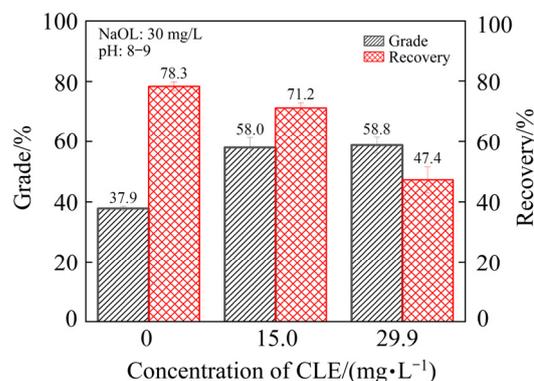
The depress effect of CLE on a mixture of scheelite and calcite (mass ratio of 1:1,  $WO_3$  grade of 39.7%) was studied on the basis of single

mineral flotation, and the result is shown in Fig. 6. When the depressant CLE was not added, the grade and recovery of  $WO_3$  in froth products with 30 mg/L NaOL were 37.9% and 78.3%, respectively. This result means that calcite and scheelite were not separated. When the depressant CLE (15.0 mg/L) was added,  $WO_3$  grade was increased to 58.0%, and the recovery decreased to 71.2%, indicating that calcite is more depressed than scheelite in the mixed ore. When the concentration of CLE increased to 29.9 mg/L, CLE also exhibited a degree of depression effect on scheelite, and the recovery of  $WO_3$  was reduced to 47.4%. In mixed mineral systems, the behavior of the minerals often deviates from what is expected by single mineral flotation [32]. In the pulp,  $CaCO_3$  precipitates on the scheelite surface, resulting in the latter having the nature of the former [33]. This phenomenon explains why scheelite was also slightly depressed.

Selectivity index (SI,  $S$ ) is an indicator for evaluating flotation separation efficiency and is calculated by Eq. (1), which denotes the recovery



**Fig. 5** Relationship between minerals recovery and concentration of CLE



**Fig. 6** Flotation recoveries and grades of  $WO_3$  in mixed ore of calcite and scheelite

and rejection of two components [34]. Large SI value corresponds to good separation performance.  $R_a$  represents the recovery of scheelite in flotation concentrate, and  $J_b$  represents the recovery of calcite in the flotation tailing. The results are given in Table 1. When CLE (15.0 mg/L) was used as the depressant, the SI value was 2.62, which was more remarkable than the value of 0.77 without CLE. CLE has a certain selective depression effect on calcite, from a comprehensive grade and recovery perspective.

$$S = \sqrt{\frac{R_a \times J_b}{(100 - R_a) \times (100 - J_b)}} \quad (1)$$

**Table 1** Selectivity index (SI) values in different flotation reagent schedules

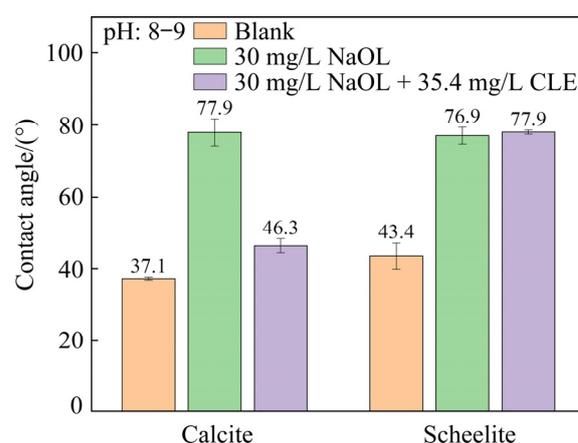
$c(\text{CLE})/(\text{mg} \cdot \text{L}^{-1})$	$R_a/\%$	$J_b/\%$	SI
0	77.99±2	14.16±2.5	0.77±0.1
15.0	71.18±1.7	72.94±5.2	2.62±0.4
29.9	47.33±4.2	83±1.6	2.11±0.3

### 3.2 Contact angle results

Contact angles were measured to investigate the wetting behaviours of CLE on calcite and scheelite, and the results are presented in Fig. 7. Generally, the contact angle is positively correlated with hydrophobicity and floatability. The contact angles of fresh calcite and scheelite were 37.1° and 43.4°, respectively, which increased to 77.9° and 76.9°, respectively, after 30 mg/L NaOL was added. This finding indicates that oleate is adsorbed on the mineral surfaces and has increased the floatability of calcite and scheelite. When 35.4 mg/L CLE was added before NaOL, the contact angle of the calcite increased slightly from 37.1° to 46.1°, and that of the scheelite increased from 43.6° to 77.9°. This result indicates that CLE has no effect on scheelite hydrophobicity adjusted by NaOL, but could maintain calcite hydrophilicity.

### 3.3 AFM imaging results

Usually, organic macromolecular depressants work through pre-adsorption on the mineral surface, preventing that of collectors [15]. Therefore, AFM was applied to observing the calcite surface and determining whether the substances were absorbed on the surface. The height and 3D images of calcite in the absence of CLE are given in Figs. 8(a, b).



**Fig. 7** Contact angles of calcite and scheelite with different agents

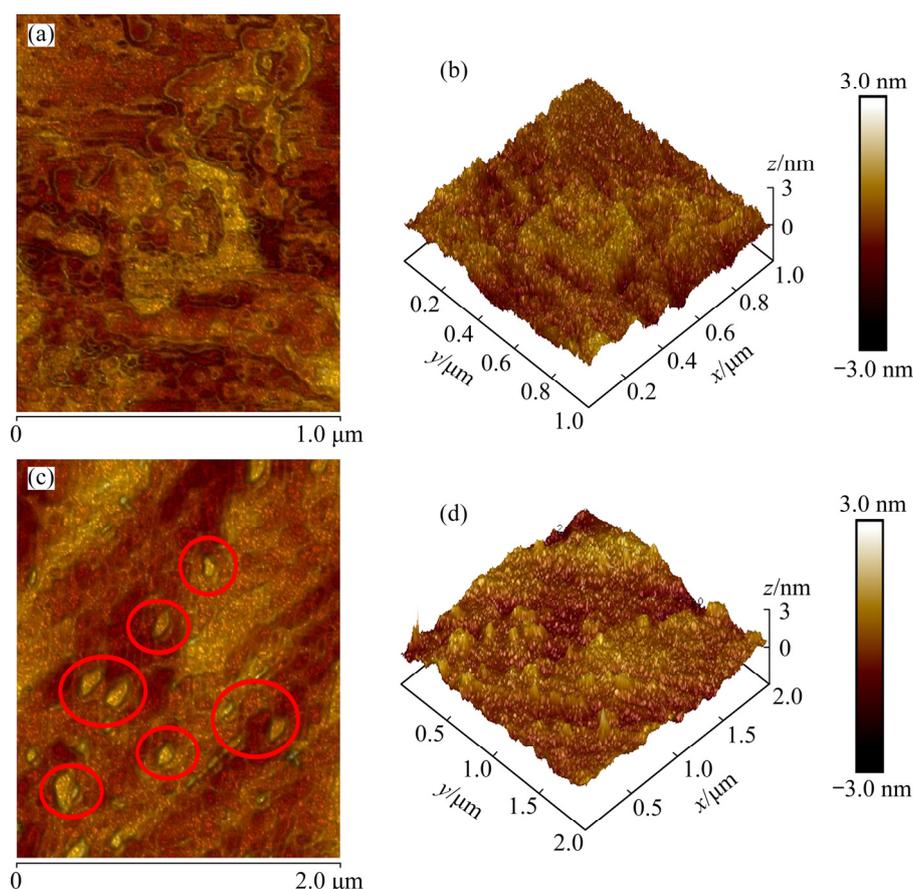
The freshly cleaved calcite was clean and flat with few impurities, and root-mean-squared roughness was 0.363 nm. The adsorption morphology on the mineral surface could be intuitively reflected. Figures 8(c, d) shows that the surface morphology of calcite changed after treatment with 35.4 mg/L CLE at pH 8–9. Many protrusions evenly appeared on the surface as indicated by the red circle. This result indicates that the components have spot-shaped adsorption on calcite.

### 3.4 FTIR results

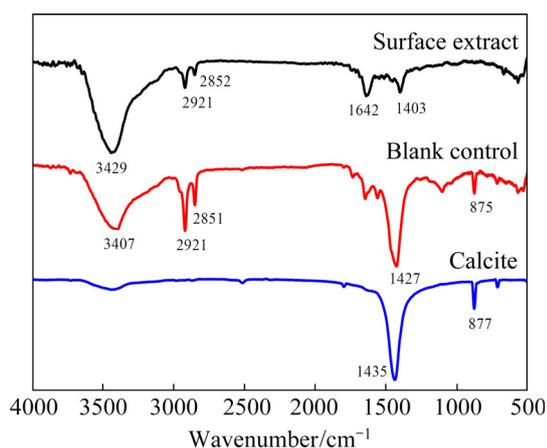
The components of camphor leaf extract are highly complex for direct analysis to distinguish the various substances in CLE. From the perspective of adsorption, the adsorbed substances were extracted from the mineral surface, and the substances that do not work were ignored.

Figure 9 shows the FTIR spectra of calcite, blank control (calcite treated with methyl alcohol), and surface extract (calcite conditioned with CLE and treated methyl alcohol). In the spectra of the calcite and blank control, the strong peaks at 1435 and 1427  $\text{cm}^{-1}$  represented the stretching vibration of  $\text{CO}_3^{2-}$  of calcite [3]. From the spectrum of blank control, it can be speculated that the main components of blank control were methanol residue and calcite. From the spectrum of surface extract, it can be speculated that the main component was the active ingredient of CLE.

In the spectrum of blank control (Fig. 9), the peak at 3407  $\text{cm}^{-1}$  corresponded to the stretching of —OH groups and intermolecular and intramolecular hydrogen bonds [3,35]. The —OH groups



**Fig. 8** AFM morphologies of bare calcite (a, b) and calcite treated with 35.4 mg/L CLE at pH 8–9 (c, d): (a, c) Height image; (b, d) 3D image



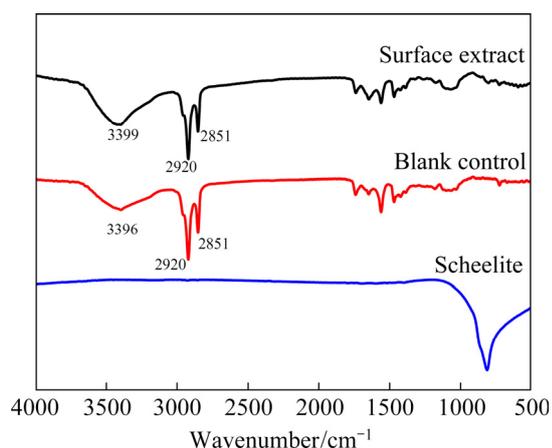
**Fig. 9** FTIR spectra of calcite, blank control, and surface extract

were from impurities of methyl alcohol and hydroxylation of calcium on residual calcite surface [36]. The absorption peaks at 2921 and 2851  $\text{cm}^{-1}$  were attributed to the stretching of  $-\text{CH}_2-$  and  $-\text{CH}_3$ , respectively [37]. For peak intensities, those of hydroxyl peak and methylene peak were almost the same. Numerous unidentifiable

peaks were also found in the fingerprint area ( $1300-400 \text{ cm}^{-1}$ ).

In the spectrum of surface extract (Fig. 9), the peaks of  $-\text{OH}$ ,  $-\text{CH}_2-$  and  $-\text{CH}_3$  were observed at 3429, 2921, and 2852  $\text{cm}^{-1}$ , respectively. The absorption peaks were observed at 1642 and 1403  $\text{cm}^{-1}$  due to the asymmetric and symmetric stretching vibrations of the carboxylate group, respectively. Compared with that in the blank control sample, the intensity of  $-\text{OH}$  peak was much stronger than that of  $-\text{CH}_2-$  and  $-\text{CH}_3$ . With methanol residue as a reference, the proportion of hydroxyl in the surface extract was significantly higher than that in the methanol residue. Hence, hydroxyl-containing organics might be present in the surface extract. Hydroxyl is a hydrophilic group found in many organic depressants [15]. The hydroxy group on the mineral surface enhances the mineral hydrophobicity. In conclusion, the substances exhibiting the depression effect in CLE were the organic compounds that contain several hydroxyl groups.

Figure 10 shows the FTIR spectra of scheelite, blank control (scheelite treated with methyl alcohol), and surface extract (scheelite conditioned with CLE and treated methyl alcohol). In the same way as analysis above, it can be seen that the —OH peak at  $3399\text{ cm}^{-1}$  of surface extract is stronger than that of blank control, and much smaller than —CH<sub>3</sub> and —CH<sub>2</sub> peaks. It can be concluded that a little amount of CLE was also adsorbed on the scheelite surface.

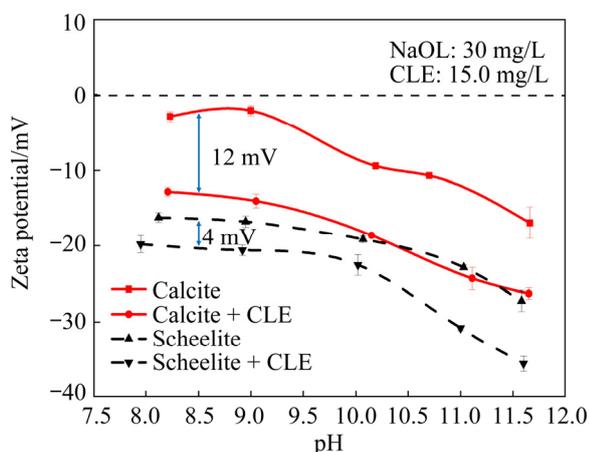


**Fig. 10** FTIR spectra of scheelite, blank control, and surface extract

### 3.5 Zeta potential results

Zeta potential plays an important role in depicting interfacial interaction phenomena in the flotation field. The adsorption of reagents on the surface of calcium-containing minerals could change zeta potential of mineral surface [14].

Figure 11 displays the zeta potential of calcite and scheelite as a function of pH. Due to the preferred dissolution of calcium ions, the calcite



**Fig. 11** Zeta potential of calcite and scheelite as function of pH

and scheelite surfaces are negatively charged in pH rang of 8.0–12.0. After CLE treatment, the zeta potential of calcite was negatively shifted about 12 mV, and the zeta potential of scheelite was negatively shifted about 4 mV. The sharp negative shift of calcite in the entire pH range indicates the large amount of CLE adsorption on the surface of calcite. Moreover, it is also indicated that the CLE was adsorbed on the scheelite surface with a small amount.

## 4 Discussion

When NaOL was used as the collector, calcite and scheelite exhibited good floatability and were difficult to separate without applying a depressant. The flotation experiment showed that CLE had a strong depression effect on calcite, but minimal effect on scheelite. In mixed mineral systems, the behavior of the minerals often deviates from what is expected by single mineral flotation [32]. In the pulp, CaCO<sub>3</sub> precipitates on the scheelite surface, resulting in the latter having the nature of the former [33]. This phenomenon explains why scheelite was also slightly depressed. The depression effect of CLE did not change over the whole range of pH, suggesting that this depressant has stability in practical application. The contact angle results were consistent with those from the flotation test, indicating that CLE could keep the surface wettability of calcite at a low level. The components in CLE acting as calcite depressant were adsorbed on the calcite surface and hindered the NaOL adsorption, thus rendering the surface hydrophobicity.

With the use of the proposed method, the preparation of the depressant is simple and only requires camphor leaves. The concentrator to be used could be equipped with a juicer for the direct production of depressant. This process requires no complex chemical reactions, no harsh reaction conditions, no pollution in the synthetic agent process, and no long-distance transportation of agents. By directly using plants, this method has achieved energy efficiency and environment-friendliness. Given that CLE comes directly from plants, this material is easily biodegradable. Leaf residues can be used as fertilizer to return to the soil.

Infrared spectrum analysis indicated that the

adsorbed components on the surface of calcite contained a large number of hydroxyl groups, explaining why calcite became hydrophobic and depressed. Accurately interpreting the infrared spectrum is difficult due to the interference of impurities in methanol. For example, the apparent interference of carbonyl groups makes it difficult to identify the presence of carbonyl groups in CLE. Hence, the functional component has not been isolated. Regardless, this method of extracting adsorbents from mineral surfaces may be feasible to other analysis techniques. Researchers with relevant expertise could analyse these substances in future studies. This work is beneficial to the further study of the direct application of plant-based depressants and provides new ideas for the research and development of new flotation agents.

## 5 Conclusions

(1) When CLE was used in single mineral flotation, the flotation of calcite was depressed from 85.4% to 17.3%, and the scheelite recovery remained at a high level. In mixed mineral systems, the grade of  $WO_3$  was increased from 37.9% to 58.0%, and the recovery of  $WO_3$  decreased from 78.3% to 71.2% with 15.0 mg/L CLE; however, scheelite flotation deteriorated at high concentration of CLE (29.9 mg/L).

(2) The adsorption morphology detected using AFM had confirmed the existence of active ingredients on calcite. The active ingredients in CLE were adsorbed on the calcite and thus impeded the NaOL adsorption. Zeta potential measurements and Infrared spectrum revealed a much higher adsorption amount of CLE on the calcite surface than that on the scheelite surface; this result can explain the significant decrease in calcite recovery.

(3) Infrared spectrum results indicated that the adsorbed components on the surface of calcite contained a large number of hydroxyl groups that make calcite hydrophobic. CLE is an easily biodegradable, economic and environment-friendly depressant for separating calcite and scheelite.

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## References

- [1] KUPKA N, RUDOLPH M. Froth flotation of scheelite—A review [J]. *International Journal of Mining Science and Technology*, 2018, 28(3): 373–384.
- [2] WANG Xu, SONG Hao, JIAO Fen, QIN Wen-qing, YANG Cong-ren, CUI Yan-fang, ZHANG Zheng-quan, ZHANG Jian, LI Hao-bing. Flotation behavior and adsorption mechanism of salicylhydroxamic acid in artificial mineral anosovite [J]. *Journal of Central South University*, 2019, 26(4): 806–812.
- [3] DONG Liu-yang, JIAO Fen, QIN Wen-qing, ZHU Hai-ling, JIA Wen-hao. Effect of acidified water glass on the flotation separation of scheelite from calcite using mixed cationic/anionic collectors [J]. *Applied Surface Science*, 2018, 444: 747–756.
- [4] ZHONG Chun-hui, FENG Bo, CHEN Yuan-gan, GUO Meng-chi, WANG Hui-hui. Flotation separation of molybdenite and talc using tragacanth gum as depressant and potassium butyl xanthate as collector [J]. *Transactions of Nonferrous Metals Society of China*, 2021, 31(12): 3879–3890.
- [5] WANG Yun-fan, PAN Zu-chao, QIN Wen-qing, JIAO Fen. A simple and rapid HPLC method for the quantitative determination of sodium oleate in flotation study [J]. *Minerals Engineering*, 2019, 141: 105842.
- [6] CHEN Chen, SUN Wei, ZHU Hai-ling, LIU Run-qin. A novel green depressant for flotation separation of scheelite from calcite [J]. *Transactions of Nonferrous Metals Society of China*, 2021, 31(8): 2493–2500.
- [7] JIA Wen-han, QIN Wen-qing, CHEN Cen, ZHU Hai-ling, JIAO Fen. Collecting performance of vegetable oils in scheelite flotation and differential analysis [J]. *Journal of Central South University*, 2019, 26(4): 787–795.
- [8] WEI Zhao, SUN Wei, HAN Hai-sheng, HU Yue-hua, WANG Ruo-lin. Selective flotation of scheelite from calcite using Pb-BHA complexes as collector and Al-Na<sub>2</sub>SiO<sub>3</sub> polymer as depressant [J]. *Minerals Engineering*, 2018, 120: 29–34.
- [9] FENG Bo, LUO Xian-ping, WANG Jin-qing, WANG Peng-cheng. The flotation separation of scheelite from calcite using acidified sodium silicate as depressant [J]. *Minerals Engineering*, 2015, 80: 45–49.
- [10] HAN Hai-sheng, XIAO Yao, HU Yue-hua, SUN Wei, NGUYEN ANH V, TANG Hong-hu, GUI Xia-hui, XING Yao-wen, WEI Zhao, Wang Jian-jun. Replacing Petrov's process with atmospheric flotation using Pb-BHA complexes for separating scheelite from fluorite [J]. *Minerals Engineering*, 2020, 145: 106053.
- [11] KANG Jian-hua, SUN Wei, HU Yue-hua, GAO Zhi-yong, LIU Run-qing, ZHANG Qing-peng, LIU Hang, MENG Xiang-song. The utilization of waste by-products for

- removing silicate from mineral processing wastewater via chemical precipitation [J]. *Water Research*, 2017, 125: 318–324.
- [12] DONG Liu-yang, WEI Qian, JIAO Fen, QIN Wen-qing. Utilization of polyepoxysuccinic acid as the green selective depressant for the clean flotation of phosphate ores [J]. *Journal of Cleaner Production*, 2021, 282: 124532.
- [13] SOMASUNDARAN P. Adsorption of starch and oleate and interaction between them on calcite in aqueous solutions [J]. *Journal of Colloid and Interface Science*, 1969, 31(4): 557–565.
- [14] LUO Yuan-jia, ZHANG Guo-fan, LI Chang-bin, MAI Qiong-yin, LIU Hong-jiang, ZHOU Hao, SHI Qing. Flotation separation of smithsonite from calcite using a new depressant fenugreek gum [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2019, 582: 123794.
- [15] ZHOU He-peng, ZHANG Yong-bing, TANG Xue-kun, CAO Yi-jun, LUO Xian-ping. Flotation separation of fluorite from calcite by using psyllium seed gum as depressant [J]. *Minerals Engineering*, 2019, 159: 106514.
- [16] TIAN Meng-jie, GAO Zhi-yong, HAN Hai-sheng, SUN Wei, HU Yue-hua. Improved flotation separation of cassiterite from calcite using a mixture of lead(II) ion/ benzo-hydroxamic acid as collector and carboxymethyl cellulose as depressant [J]. *Minerals Engineering*, 2017, 113: 68–70.
- [17] DONG Liu-yang, JIAO Fen, QIN Wen-qing, LIU Wei. Selective flotation of scheelite from calcite using xanthan gum as depressant [J]. *Minerals Engineering*, 2019, 138: 14–23.
- [18] HALEEM N, ARSHAD M, SHAHID M. Synthesis of carboxymethyl cellulose from waste of cotton ginning industry [J]. *Carbohydrate Polymers*, 2014, 113: 249–255.
- [19] WONGVITVICHOT W, PITHAKRATANAYOTHIN S, WONGKASEMJIT S, CHAISUWAN T. Fast and practical synthesis of carboxymethyl cellulose from office paper waste by ultrasonic-assisted technique at ambient temperature [J]. *Polymer Degradation and Stability*, 2021, 184: 109473.
- [20] SHARMA G, SHARMA S, KUMAR A, AL-MUHTASEB A, NAUSHAD M, GHAFAR A, MOLA G, STADLER F. Guar gum and its composites as potential materials for diverse applications: A review [J]. *Carbohydrate Polymers*, 2018, 199: 534–545.
- [21] WANG Xu, SONG-hao, JIAO Fen, QIN Wen-qing, YANG Cong-ren, CUI Yan-fang, ZHANG Zheng-quan, ZHANG Jian, LI Hao-bing. Utilization of wastewater from zeolite production in synthesis of flotation reagents [J]. *Transactions of Nonferrous Metals Society of China*, 2020, 30(11): 3093–3102.
- [22] WANG Jun, SU Ben-zheng, JIANG Hai-qiang, CUI Ning, YU Zong-yuan, YANG Yu-han, SUN Yu. Traditional uses, phytochemistry and pharmacological activities of the genus *Cinnamomum (Lauraceae)*: A review [J]. *Fitoterapia*, 2020, 146: 104675.
- [23] FENG Z. Study on active components and biological activities from residues of leaves and twigs of camphor tree after distillation [D]. Beijing: Chinese Academy of Forestry, 2018. (in Chinese)
- [24] DOS SANTOS E, LEITÃO M, AGUERO ITO C, SILVA-FILHO S, ARENA A, SILVA-COMAR F, NAKAMURA CUMAN R, OLIVEIRA R, NAZARI FORMAGIO A, LEITE K. Analgesic and anti-inflammatory articular effects of essential oil and camphor isolated from *Ocimum kilimandscharicum Gürke* leaves [J]. *Journal of Ethnopharmacology*, 2021, 269: 113697.
- [25] ZARUBAEV V V, GARSHININA A V, TRETIK T S, FEDOROVA,VA., SHTRO A A, SOKOLOVA A S, YAROVAYA O I, SALAKHUTDINOV N F. Broad range of inhibiting action of novel camphor-based compound with anti-hemagglutinin activity against influenza viruses in vitro and in vivo [J]. *Antiviral Research*, 2015, 120: 126–133.
- [26] WANG Chong-qing, WANG Hui, LIU You-nian. Purification of Pb(II) ions from aqueous solution by camphor leaf modified with succinic anhydride [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2016, 509: 80–85.
- [27] XIAO Hua-yun, WANG Yan-li, TANG Cong-guo, LIU Cong-qiang. Indicating atmospheric sulfur by means of S-isotope in leaves of the plane, osmanthus and camphor trees [J]. *Environmental Pollution*, 2012, 162: 80–85.
- [28] HU Fei, TU Xiao-Fang, THAKUR K, HU Fan, LI Xiao-li, ZHANG Ying-Shuo, ZHANG Jian-Guo, WEI Zhao-jun. Comparison of antifungal activity of essential oils from different plants against three fungi [J]. *Food and Chemical Toxicology*, 2019, 134: 110821.
- [29] CHEN Shu-jun, ZHAO Hua-jun, CHEN Si-yi, WEN Pu-shan, WANG Hao, LI Wen-po. Camphor leaves extract as a neoteric and environment friendly inhibitor for Q235 steel in HCl medium: Combining experimental and theoretical researches [J]. *Journal of Molecular Liquids*, 2020, 312: 113433.
- [30] CUI Yan-fang, JIAO Fen, QIN Wen-qing. Flotation separation of fluorite from calcite using sulfonated lignite as depressant [J]. *Separation and Purification Technology*, 2020, 242: 116698.
- [31] PAN Zu-chao, WANG Yan, WANG Yun-fan, Jiao Fen, QIN Wen-qing. Understanding the depression mechanism of sodium citrate on apatite flotation [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2020, 588: 124312.
- [32] AMANKONAH J O, SOMASUNDARAN P, ANANTHAPADMABHAN K P. Effects of dissolved mineral species on the dissolution/precipitation characteristics of calcite and apatite [J]. *Colloids and Surfaces*, 1985, 15: 295–307.
- [33] SOMASUNDARAN P, AMANKONAH J O, ANANTHAPADMABHAN K P. Mineral–solution equilibria in sparingly soluble mineral systems [J]. *Colloids and Surfaces*, 1985, 15: 309–333.
- [34] TIAN Meng-jie, GAO Zhi-yong, JI Bin, FAN Rui-ying, LIU Run-qing, CHEN Pan, SUN Wei, HU Yue-hua. Selective flotation of cassiterite from calcite with salicylhydroxamic acid collector and carboxymethyl cellulose depressant [J]. *Minerals*, 2018, 8(8): 316.
- [35] WANG Li, SUN Wei, HU Yue-hua, XU Long-hua. Adsorption mechanism of mixed anionic/cationic collectors in muscovite–quartz flotation system [J]. *Minerals Engineering*, 2014, 64: 44–50.

- [36] STIPP S L S, HOCELLA M F. Structure and bonding at the calcite surface as observed with X-ray photoelectron spectroscopy (XPS) and (LEED) [J]. *Geochimica et Cosmochimica Acta*, 1991, 55: 1723–1736.
- [37] SCHEUING D R, WEERS J G. A fourier transform infrared spectroscopic study of dodecyltrimethylammonium chloride/sodium dodecyl sulfate surfactant mixtures [J]. *Langmuir*, 1990, 6(3): 665–671.

## 樟叶提取物作为新型环境友好抑制剂在白钨矿与方解石浮选分离中的应用

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**摘要:** 采用简单的物理方法, 直接榨取樟叶汁液作为白钨矿和方解石分离的抑制剂。通过接触角测量、傅里叶转换红外光谱测试和原子力显微镜研究樟叶提取物中活性成分及其抑制机理。浮选试验表明, 樟叶提取物对方解石有较强的抑制作用, 对白钨矿的抑制作用较小。原子力显微镜检测证实方解石表面吸附有樟叶提取物的有效成分。红外光谱结果表明, 吸附在方解石表面的组分含有大量的羟基, 这些羟基使方解石疏水。Zeta 电位和红外光谱结果表明, 樟树叶提取物在方解石表面的吸附量远大于在白钨矿表面的吸附量。樟叶提取物在白钨矿和方解石浮选分离中具有潜在的应用价值。

**关键词:** 白钨矿; 方解石; 浮选; 樟叶提取物; 抑制剂

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