

## Mechanism of ultrasonic cavitation to improve the effect of siderite on quartz flotation

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**Abstract:** In order to effectively eliminate the effect of fine carbonate minerals on quartz flotation, the influence of fine siderite on quartz flotation was studied as well as the mechanism or role of ultrasonic treatment in the process. The results of adsorption capacity measurement and flotation solution chemical calculation show that fine siderite and its dissolved components have a great influence on the collector consumption and the surface properties of quartz. In addition, SEM, EDS and XPS analysis were used to study the surface morphology and chemical environment changes of quartz with and without ultrasonic treatment. The results of flotation test show that the recovery of quartz increase from 38.79% to 58.38% under the condition that ultrasonic time was 0.5 min and ultrasonic power was 200 W. The mechanical effect caused by ultrasonic cavitation can clean the quartz surface to a certain extent and increase its active sites, thus improving the floatability of quartz.

**Keywords:** ultrasound treatment, cover, fine siderite, CaCO<sub>3</sub> precipitate

### 1. Introduction

Although the total amount of iron ore resources in China is abundant, the high-quality iron ore resources are relatively scarce and it is difficult to develop complex refractory iron ore, which restricts the development of iron ore and steel industry in China (Zhang et al., 2021; Wang et al., 2022). Anion reverse flotation has always been one of the most common separation methods for hematite (Fe<sub>2</sub>O<sub>3</sub>) flotation (Rath and Sahoo, 2022; Wang et al., 2022). Under the condition of high alkalinity, hematite and other iron minerals are inhibited to float by the depressant, but gangue minerals are floated and finally the separation of hematite ore is achieved (Li et al., 2017; Li et al., 2021). As a typical refractory iron mineral, carbonate iron ore is usually hard to separate due to the existence of siderite (FeCO<sub>3</sub>) and iron dolomite (Ca(Mg,Fe)(CO<sub>3</sub>)<sub>2</sub>) which have a serious impact on flotation (Hao et al. 2018). Carbonate minerals such as siderite are easy to slime in grinding because of their low hardness, and interactive effect of minerals will occur on the process of hematite flotation (Luo et al. 2016), which is shown by the non-selective covering of fine siderite on the surface of hematite and quartz to make the floatability of hematite and quartz converge, making the separation difficult (Han et al., 2022). In addition, the fine-grained siderite is more soluble, and a large amount of CO<sub>3</sub><sup>2-</sup> will be produced in an alkaline environment, which will precipitate with some metal ions in the pulp or create competitive adsorption (Yin and Tang, 2020; Hao et al., 2021). It will affect the floatability of the minerals to be separated and deteriorates the flotation index. In view of the interaction effect of carbonate minerals, researchers have done a lot of work, mainly focusing on optimizing the flotation process (Yin et al. 2010) and the chemical system (Hao et al., 2019; Wang et al., 2022).

Ultrasonic cavitation means that a large number of tiny bubbles (cavitation nuclei) are produced, which can oscillate and grow over a period of time when the ultrasonic energy reaches a certain value (Chen et al., 2020; Chen et al., 2021). When the ultrasonic energy threshold is reached, the cavitation bubbles collapse and release a large amount of energy instantly, producing thermal effect, mechanical effect and chemical effect (Luo et al., 2018; Kruszelnicki et al., 2022; Zhang et al., 2022). The application of ultrasonic technology in coal and metal flotation (Ozkan, 2018; Malayoglu and Ozkan, 2019;

Hassanzadeh et al., 2020), leaching (Bu et al., 2022) and wastewater treatment is also mostly based on the transient cavitation effect of ultrasonic wave. And the relationship between the ultrasonic stable cavitation effect and selective agglomeration or nanobubble flotation has also been a research hotspot in recent years, especially in the field of coal flotation (Chen et al., 2021; Jin et al., 2021). Ahmad Hassanzadeh (Hassanzadeh et al., 2021) studied the effect of ultrasonic treatment on the floatability of pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ) and quartz. Through monitoring the solution properties such as pH, conductivity and liquid temperature, the conclusion that different ultrasonic treatment conditions indirectly affected the surface wettability of three minerals by affecting the solution properties was obtained. Lu et al. (2022) studied the effect of ultrasonic dispersion on the flotation process of copper-nickel sulfide ore, and confirmed by AFM analysis that under certain ultrasonic treatment conditions, with which the roughness and floatability of pentlandite ( $(\text{Fe,Ni})_9\text{S}_8$ ) could be improved, and therefore the separation effect of nickel pyrite ( $(\text{Fe,Ni})_9\text{S}_8$ ) and serpentine ( $\text{A}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$ ) was improved. C. Gungoren (Gungoren et al., 2019) studied the effect of ultrasound on quartz-amine flotation by considering characterization and surface chemistry aspects of minerals and bubbles in presence of ultrasound. The result shows that ultrasonic treatment can increase quartz recovery from 45.45% to 63.64% with 30 W ultrasonic application at conditioning step.

Based on the above analyses, aiming at the effect of siderite on quartz flotation system, ultrasonic cavitation equipment was used to ultrasonically treat the slurry, and the change of quartz flotation without and with ultrasonic treatment was compared in this paper. The mechanism of the interaction between minerals was studied with the help of solution chemistry calculation, SEM, EDS and XPS to find out the methods, which weaken the interaction between minerals and suit for flotation separation of complex iron ore, providing a theoretical basis for the efficient utilization of complex and difficult to separate carbonate iron ore in China.

## 2. Materials and experimental methods

### 2.1. Materials and reagents

Referring to the characteristics of the size composition of the actual carbonate iron ore, the quartz used in flotation test was hammered to below 2 mm, ground by a three-head grinder, and selected as  $-148 \mu\text{m} + 45 \mu\text{m}$  by screening. Siderite was manually selected and ground below 2 mm with a three-head grinder, and then the sample of  $-23 \mu\text{m}$  was selected by wet screening. According to X-ray diffraction and chemical composition analyses (As shown in Figure 1 and Table1), The purity of quartz in the prepared sample was more than 99% and the purity of siderite in the prepared sample was more than 95%, which meet the test requirement.

Soluble starch was employed as the depressant of siderite, sodium oleate with 98% purity used as the collector and calcium chloride with 99% purity used as the activator of quartz. NaOH solution and HCl solution were prepared to adjust the pulp pH at about 11.3. Distilled water was used in all experiments.

Table 1. Chemical component of samples

Sample	Mass fraction (%)						
	TFe	FeO	MgO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	CaO	S
Siderite	45.48	51.32	3.22	<0.01	0.66	0.26	0.04
Quartz	0.067	-	<0.01	0.13	99.54	0.065	0.015

TFe: Total Fe

### 2.2. Methods

#### 2.2.1. Flotation tests

Flotation experiments were carried out in 25 mL flotation cell with impeller speed of 1992 r/min. According to test design, a 2.0 g sample, composed of quartz and siderite in different proportion by mass was mixed with 20 mL distilled water in a mixing tank for 2 min. Then, HCl and NaOH solution

was added to keep the pulp pH at about 11.3 for 2 min. After the pulp was conditioned for 2 min with each reagent separately, the UP 400 s ultrasonic cell disruptor (Produced by Shanghai Chengzao instrument and Equipment Co.,Ltd, Shanghai, China. Ultrasonic Power: 4-400W, continuous adjustable.) was used to treat the pulp with fixed time and power. Besides, the ultrasonic working time was 5 s with the interval time of 5 s in each treatment, and then the treated pulp was transferred to the flotation cell. Afterwards the collector was added, aeration and forth removal was also finished sequentially. The flotation time was fixed for 3 min at room temperature (25 °C). After flotation, the products were collected, filtered, dried, weighed and analyzed, respectively

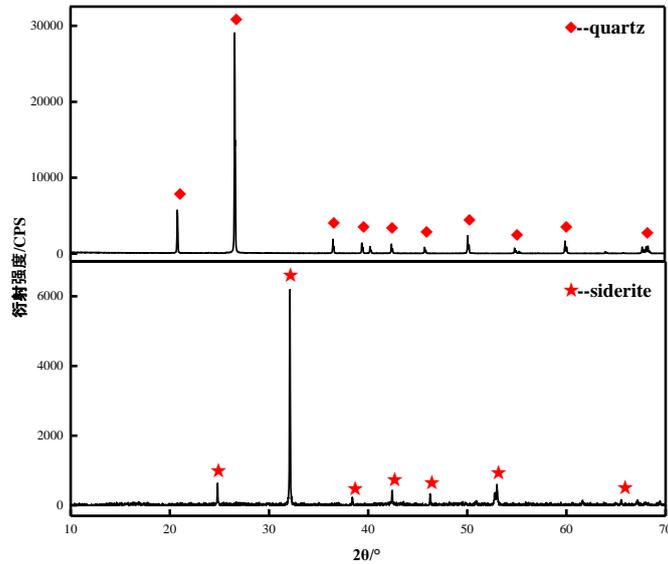


Fig. 1. X-ray diffraction pattern of quartz and siderite..



Fig. 2. Ultrasonic cell disruptor for ultrasonic treatment. (Fixed frequency: 20.056kHz,)

### 2.2.2. Determination of adsorption capacity

A 2.0 g of the mineral sample and 20 mL distilled water was placed in a stirring tank, stirred and adjusted the pH to 11.3. Each reagent was added in turn according to the requirements of flotation, and then ultrasonic treatment was carried out. The pulp was set aside after full stirring, then a portion of the supernatant was used to measure the concentration of residual sodium oleate in the supernatant by UV photometer, and the amount of sodium oleate adsorbed on the mineral surface was calculated by subtraction method.

### 2.2.3. Solution chemical calculations

Minerals commonly have a certain solubility, especially carbonate minerals (Li et al. 2021). In their saturated aqueous solutions, more mineral ions (lattice ions) are dissolved, and these ions have a great influence on the flotation process (Feng and Luo. 2013), such as changing the pH of the pulp, making it difficult to adjust the pH during the flotation of these minerals (Yin et al. 2016). Sometimes dissolved ions likely compete with collectors for adsorption and a large amount of collectors may be consumed because of the occurrence of serious precipitation reactions possibly with the activator or collector, leading to changes in mineral surface properties. Dissolved ions in the pulp and other ions usually have a dissolution balance:

$$M_m A_n = m M^{n+} + n A^{m-}, K_{sp} = [M^{n+}]^m [A^{m-}]^n \quad (1)$$

(n is the number of charges carried by the cation  $A_n^+$ ; m is the number of charges carried by the anion  $B_m^-$ ;  $K_{sp}$  is the precipitation equilibrium constant)

Through the dissolution equilibrium, not only the solubility of minerals, but also can the concentration of each dissolved component be calculated, and the LgC-pH diagram drawn from it can be used to analyze the structure of the mineral surface.

### 2.2.4. SEM and EDS spectra analysis

Quanta 250 scanning electron microscope (SEM) was used to observe the morphological characteristics of concentrates or tailings and the capping of siderite on the quartz surface (before and after ultrasonic treatment). In addition, EDS spectra attached to the SEM images was used to analyze the elemental compositions of mineral particles.

### 2.2.5. XPS analysis

The XPS measurements were obtained with a Thermo Scientific ESCALAB 250Xi spectrometer with an Al K $\alpha$  X-ray source (1486.6 eV). It was used to analyze the changes of element and content on the quartz surface before and after ultrasonic treatment so as to explore the reasons why ultrasonic treatment improved quartz flotation.

## 3. Results and discussion

### 3.1. Flotation tests

Fig. 3 shows the effect of siderite content on the floatability of quartz before and after ultrasonic treatment. With the increase of siderite content, the  $SiO_2$  recovery dropped sharply, and the grade of  $SiO_2$  in the concentrate also decreased. When the siderite content is 10%, the recovery of  $SiO_2$  drops to 27.42% and the grade of  $SiO_2$  in the concentrate also drops to 80%. It can be seen that siderite has a great influence on the recovery rate of  $SiO_2$ . The decrease of concentrate grade means that part of the siderite is mixed into the concentrate. It is speculated that the fine-grained siderite consumes a large amount of sodium oleate molecules. As a comparison, the pulp was ultrasonically treated. Under the conditions of ultrasonic time of 0.1 min and ultrasonic power of 200 W, the recovery of  $SiO_2$  improves to a certain extent. In particular, when the siderite content is 5%, ultrasonic treatment increases the recovery of  $SiO_2$  by 26%, but at the same time it can be seen that under this ultrasonic treatment condition, the grade of the concentrate is not significantly improved.

Fig. 4 shows the effect of ultrasonic time on the recovery of  $SiO_2$  when the siderite content is 5% and the ultrasonic power is fixed at 200 W. With the increase of ultrasonic time, the recovery rate of  $SiO_2$  shows a trend of first increase but then decrease, and the  $SiO_2$  grade of concentrate also decreases to a certain extent. It can be seen that too long ultrasonic time did not improve the recovery of  $SiO_2$ , but also could not improve the  $SiO_2$  grade of concentrate. When the ultrasonic time is 0.5 min, the recovery of  $SiO_2$  can be close to 60%, which is about 50% higher than that without ultrasonic treatment. At this time, the  $SiO_2$  grade of concentrate can also be maintained above 90%.

According to the flotation results in Fig. 4, it can be seen that ultrasonic treatment can improve the recovery of  $SiO_2$  to a certain extent. But with the increase of the siderite content, the  $SiO_2$  grade of the concentrate will decrease seriously, which indicates that some fine-grained siderite enters the

concentrate. Moreover, it can be seen from Fig. 4 that the excessively long ultrasonic treatment time will also lead to the reduction of the  $\text{SiO}_2$  grade of the concentrate. It is speculated that siderite consumes a part of sodium oleate and blends into the quartz concentrate.

Fig. 5 shows the effect of ultrasonic power on the  $\text{SiO}_2$  recovery under the condition that the siderite content is 5% and the ultrasonic time is 0.5 min. With the increase of ultrasonic processing power, quartz recovery first increases and then remains unchanged. When the ultrasonic processing power is higher than 200W, the quartz recovery rate can be maintained at around 60%, and the grade of concentrate quartz can also be maintained at over 90%. It can be seen that the effect of ultrasonic power on the recovery of  $\text{SiO}_2$  is not significant when the pulp is ultrasonically treated.

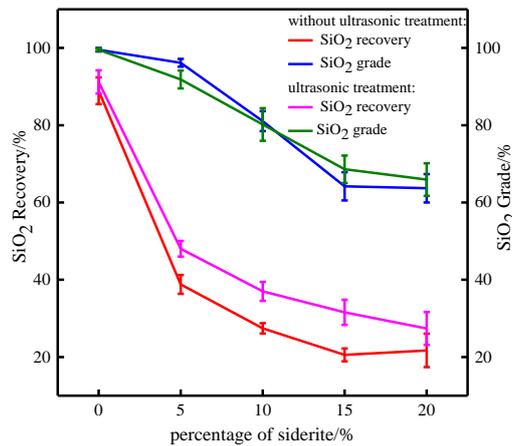


Fig. 3. Recovery and grade of  $\text{SiO}_2$  as a function of percentage of siderite. (sodium oleate dosage:225 mg/L; starch dosage: 20 mg/L; calcium chloride dosage: 100 mg/L; pH:11.3; ultrasonic time 0.1 min and power 200 W)

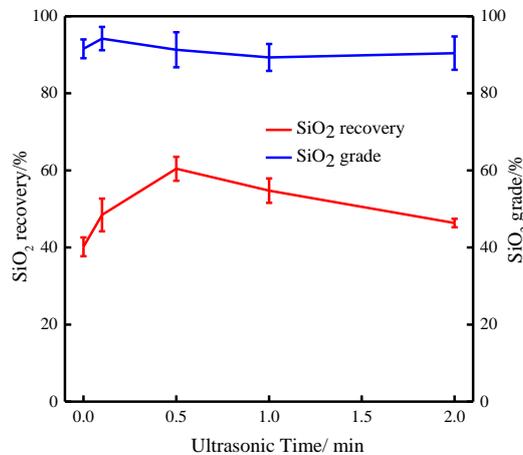


Fig. 4. Recovery and grade of  $\text{SiO}_2$  as a function of ultrasonic time. (sodium oleate dosage:225 mg/L; starch dosage: 20 mg/L; calcium chloride dosage: 100 mg/L; pH:11.3; ultrasonic power 200 W)

### 3.2. Adsorption capacity analysis

In view of this, the adsorption amount of quartz and siderite before and after ultrasonic treatment was calculated after the concentration of residual sodium oleate in the supernatant with the help of UV spectrometer measure. As shown in Table 2, ultrasonic time do not significantly change the adsorption amount of sodium oleate on the quartz surface, but have a certain effect on the adsorption amount of sodium oleate on the siderite surface. When the pulp is magnetically stirred, mechanical agglomeration of fine-grained siderite will occur. However, the collapse of cavitation bubbles can crush the agglomerated siderite which then is refined and homogenized when the pulp is ultrasonically treated. The fine-grained siderite will adsorb a large number of sodium oleate molecules due to its large surface energy, resulting in an increase in the adsorption amount of sodium oleate on the siderite surface.

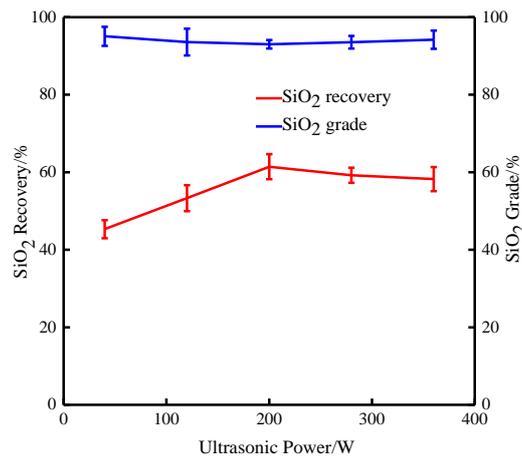


Fig. 5. Recovery and grade of SiO<sub>2</sub> as a function of ultrasonic power. (sodium oleate dosage:225 mg/L; starch dosage: 20 mg/L; calcium chloride dosage: 100 mg/L; pH:11.3; ultrasonic time 0.5 min)

Table 2 Sodium oleate adsorption on different minerals

sample	Ultrasonic time/s	adsorption of sodium oleate/(mg/g)
quartz	10	1.43
	120	1.51
siderite	10	0.46
	120	0.80

### 3.3. Effect of siderite dissolution on quartz flotation

As a carbonate mineral with strong solubility. A large number of studies have shown that the dissolution of siderite has a great influence on quartz flotation (Li et al. 2017). The effect of siderite (dissolved component) on quartz floatability was investigated by solution chemical calculations. In the siderite-quartz binary mixed ore, calcium ion not only acts as an activator of quartz, but also has a certain influence on the dissolution balance of siderite. In order to facilitate the calculation, the concentration of calcium ions is set to be 10<sup>-3</sup> mol/L. As shown in Table 3, Under this dissolution system, there are the following equilibrium reactions:

Table 3 Chemical reaction equations and equilibrium constant for the solution chemical calculations

equilibrium reaction	equilibrium constant
$\text{FeCO}_3 \rightleftharpoons \text{Fe}^{2+} + \text{CO}_3^{2-}$	$K_{sp1} = 10^{-10.68}$
$\text{Fe}^{2+} + \text{OH}^- \rightleftharpoons \text{FeOH}^+$	$\beta_1 = 10^{4.5}$
$\text{Fe}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2$	$\beta_2 = 10^{7.4}$
$\text{Fe}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3^-$	$\beta_3 = 10^{10.0}$
$\text{Fe}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_4^{2-}$	$\beta_4 = 10^{9.6}$
$\text{Ca}^{2+} + \text{OH}^- \rightleftharpoons \text{CaOH}^+$	$\beta_5 = 10^{1.4}$
$\text{Ca}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Ca}(\text{OH})_2$	$\beta_6 = 10^{2.77}$
$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	$K_{sp2} = 10^{-8.35}$
$\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$	$K_1 = 10^{10.33}$
$\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3$	$K_2 = 10^{6.35}$
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$K_w = 10^{-14}$

According to the calculation, the LgC-pH composition, shown 6 in Fig. 6, was obtained. It can be seen from the Fig. 6 that as the pH increases, the CO<sub>3</sub><sup>2-</sup> generated by the dissolution of siderite will increase rapidly. It can be calculated from Table 4 that when the pH exceeds to 9.87, CaCO<sub>3</sub> will begin to precipitate and adsorb on the quartz surface, occupying quartz active sites. On the one hand, it will seriously affect the activation of quartz by CaCl<sub>2</sub> as the activator; and on the other hand, it will make quartz exhibit the properties of calcite, thereby reducing the hydrophobicity of quartz. During the

ultrasonic treatment, due to the long time, the temperature of the pulp will also increase slightly. It is known that the equilibrium constant in the chemical equation is a function of temperature. From the above equilibrium reaction, it can be seen that the temperature will increase the solubility of siderite, thereby accelerating the formation of  $\text{CaCO}_3$  precipitate on the quartz surface that can explain why excessive ultrasonic time leads to decrease quartz recovery.

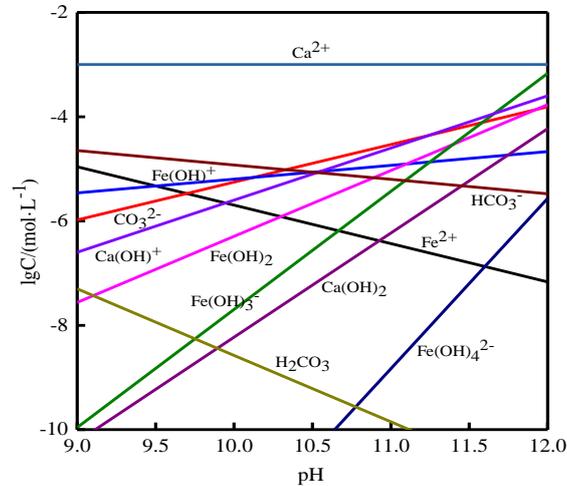


Fig. 6. LgC graph of dissolved siderite species in the presence of  $\text{Ca}^{2+}$  ( $10^{-3}$  mol/L) in solution

### 3.4. SEM and EDS analysis

In the case of siderite content of 5%, the flotation tailings without and with ultrasonic treatment were dried and sampled, and analyzed under scanning electron microscope. From Fig. 7, it can be found that the surface of large-grained minerals is covered by fine-grained minerals, and then EDS analysis is performed on the surface. As shown in the results of Fig. 8, it can be judged that point 1-1 is matrix quartz, while point 1-2 is fine-grained siderite capped and adsorbed on the surface of quartz due to the presence of iron content. Studies (Guo et al. 2018) have shown that,  $\text{Ca}^{2+}$  and  $\text{Ca}(\text{OH})^+$  are the main active components of activated quartz, which will bond with the exposed active sites on the quartz surface, thereby enhancing the hydrophobicity of quartz. However, due to the large amount of fine-grained siderite covering the quartz surface, the activation of quartz by  $\text{Ca}^{2+}$  and  $\text{Ca}(\text{OH})^+$  is blocked, which leads to the fact that during the flotation process, the capture effect of sodium oleate on quartz is also greatly weakened, and the flotation of the quartz also becomes more difficult (Li et al. 2012).

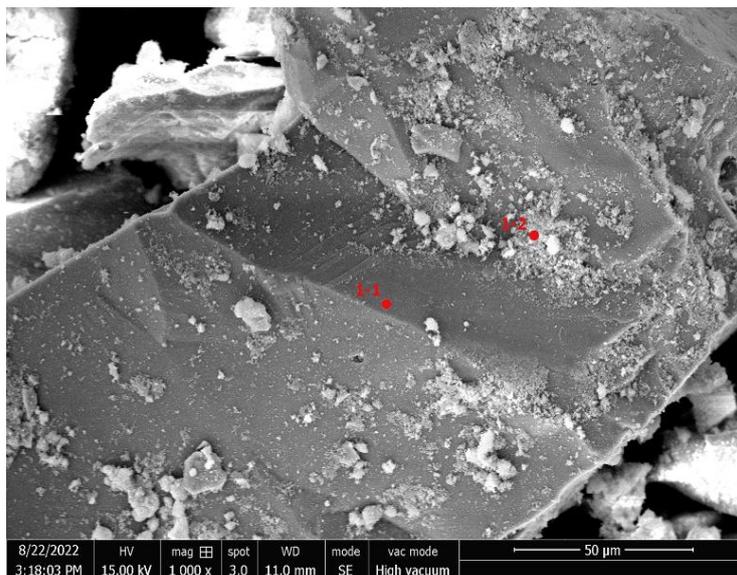


Fig. 7. The SEM image of the tailings. (without ultrasonic treatment)

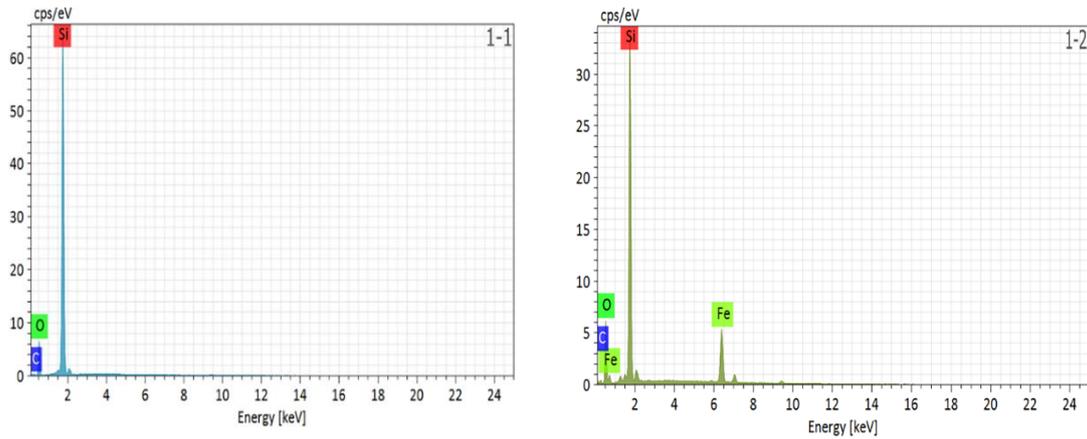


Fig. 8. EDS spectra of the tailings. (Point 1-1 and 1-2)

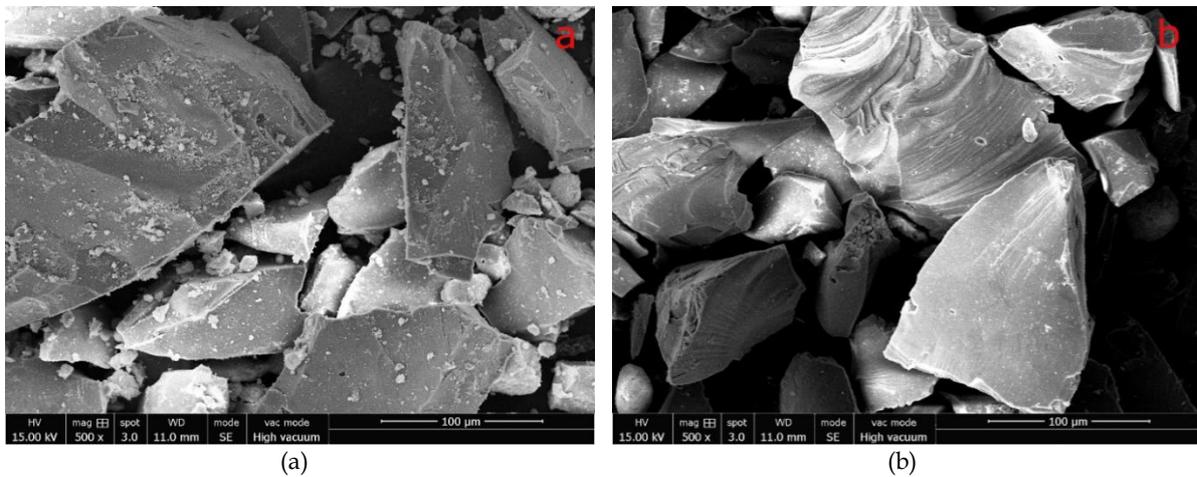


Fig. 9. SEM of flotation tailings without ultrasonic treatment(a) and concentrate with ultrasonic treatment(b)

At the same time, the flotation concentrate and tailings with and without ultrasonic treatment were analyzed by scanning electron microscope. As shown in Fig. 9, the surface of tailing without ultrasonic treatment looks “rough”, but the surface of concentrates with ultrasonic treatment (ultrasonic power 200 W and ultrasonic time 0.5 min) looks “smooth”, indicating that cleaning effect produced by ultrasonic cavitation can remove fine particles that cover the quartz surface to expose enough active site, and therefore enhance  $\text{Ca}^{2+}$  or  $\text{Ca}(\text{OH})^+$  activation ability to improve the recovery of quartz.

### 3.5. XPS analysis

The solution chemical calculation in 3.3 confirms that the dissolution of siderite make the surface of quartz present the similar properties to that of calcite. In order to explore the removal change of  $\text{CaCO}_3$  precipitates on quartz surface by ultrasonic treatment, XPS was used to analyze the binding energy of elements and to further understand the changes of chemical environment on quartz surface by ultrasonic treatment. Particularly, in order to avoid the influence of other ions dissolved by siderite, a certain amount of  $\text{Na}_2\text{CO}_3$  was added to provide  $\text{CO}_3^{2-}$  for the pulp to replace siderite with the same reagent scheme and other conditions as before.

#### 3.5.1. Analysis of XPS survey results

Fig. 10 shows the XPS spectrum of quartz before and after ultrasonic treatment. Because the ultrasonic treatment is a kind of physical method, there is no change in the types of elements on the surface of quartz by ultrasonic treatment, but there are some changes in the relative atomic concentration of the element. As shown in Table 4, the cleaning effect of ultrasonic treatment on the quartz surface decreases the concentration of C on the quartz surface from 24.17% to 19.43%.

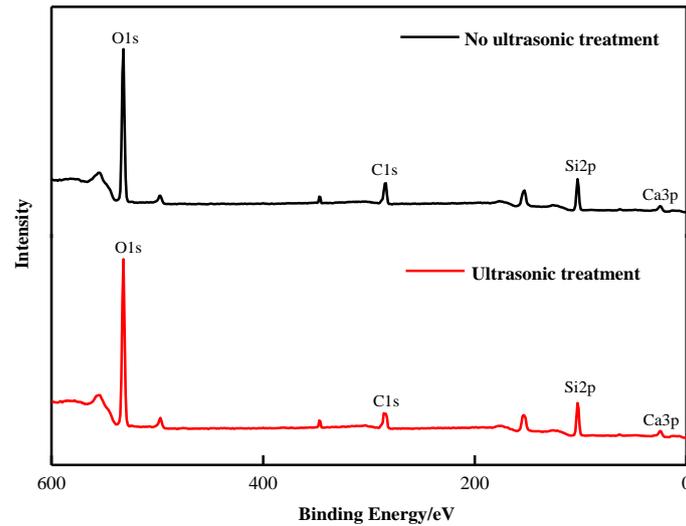


Fig. 10. XPS spectra of the quartz

Table 4 Atomic concentration of the elements for mineral samples

Sample	Atomic concentration (%)			
	C1s	O1s	Ca3p	Si2p
Quartz(NUT)	24.17	44.79	5.37	21.83
Quartz(UT)	19.43	46.61	4.95	24.39

※NUT: no ultrasonic treatment, UT: ultrasonic treatment (0.5 min, 200 W);

### 3.6. High-resolution XPS analysis of carbon (C1s) and oxygen (O1s)

Fig. 11 shows the high-resolution XPS of C1s on the quartz surface, and Table 5 shows the detailed parameters of the fitted peaks. For quartz without ultrasonic treatment, the C1s spectra fits well the three peaks at 284.50 eV, 285.06 eV and 288.14 eV on the quartz from Fig11(a). By comparing the peak binding energy with the reference, it can be concluded that the three peaks at 284.50 eV, 285.06 eV and 288.14 eV can be attributed to the pollution of carbon, which exists in the form of C-H, C=O(Hao et al. 2019, Wang et al. 2022) and  $\text{CO}_3^{2-}$ (Qian et al. 2021), and it is speculated that soluble starch and  $\text{CaCO}_3$  have different degrees of adsorption on the quartz surface. Besides, in Fig. 11(b), the high-resolution XPS of C1s on the quartz surface after ultrasonic treatment shows that the intensity of the above three peaks has changed after ultrasonic treatment, which indicates that ultrasonic treatment has changed the chemical environment on the quartz surface. It can be seen from Table 5 that the amount of different forms of carbon corresponded by different peaks all decreased in varying degrees. This indicates that ultrasonic cavitation has a certain cleaning effect on the quartz surface, and can remove the  $\text{CaCO}_3$  precipitates and starch from the quartz surface to a certain extent.

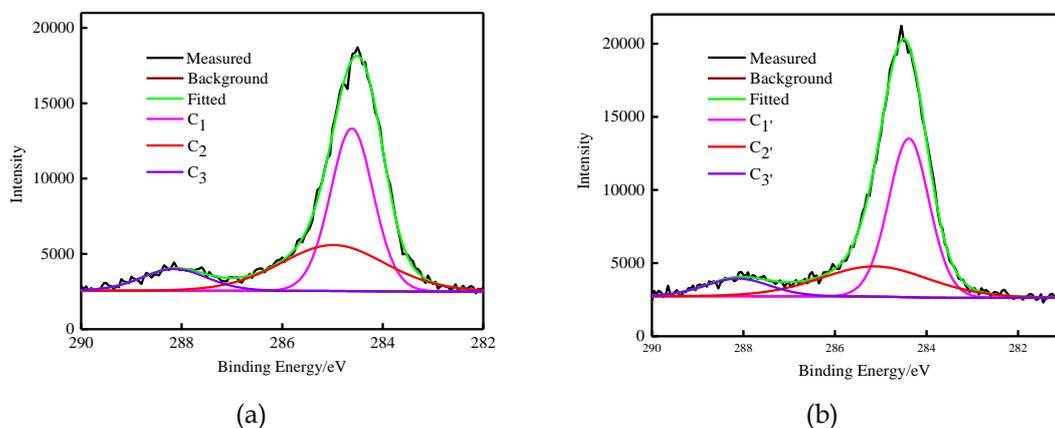


Fig. 11. High-resolution XPS of C1s on quartz. (a) no ultrasonic treat., (b) ultrasonic treat. (0.5 min, 200 W)

Table 5 Parameters of fitted peaks for C on minerals

samples	Name	Peak BE/eV	FWHM/eV	Area(P)/CPS.eV	Atomic concentration/%
Quartz(NUT)	C <sub>1</sub>	284.50	1.13	15822	14.17
	C <sub>2</sub>	285.06	1.70	5208	5.22
	C <sub>3</sub>	288.14	1.88	2834	4.53
Quartz(UT)	C <sub>1'</sub>	284.51	1.28	17418	17.23
	C <sub>2'</sub>	285.03	1.49	1438	1.82
	C <sub>3'</sub>	288.23	1.65	1332	1.51

※ NUT: no ultrasonic treatment, UT: ultrasonic treatment (0.5 min, 200 W);

Similarly, Fig. 12 and Table 6 respectively show the high-resolution XPS of O1s on the quartz surface before and after ultrasonic treatment and the detailed parameters of the fitting peak. As can be seen from Fig. 12(a), in the fitting of O1s peak of quartz, the binding energies of 532.11 eV and 532.60 eV correspond to the peak positions of Si-O and -OH respectively(Mao et al. 2022), where -OH may come from the partial electrostatic reaction of quartz with water and some structures of starch. And the peak position at 531.93 eV that corresponds to the oxygen in CO<sub>3</sub><sup>2-</sup>(Qian et al. 2021) indicates that CaCO<sub>3</sub> precipitate can generate on the quartz surface indeed.

Fig. 12 (b) shows that after the ultrasonic treatment, several absorption peaks shift to a certain extent. The position of CO<sub>3</sub><sup>2-</sup> peak shifts from 532.96 eV to 532.90 eV with a decrease of 0.06 eV, indicating that ultrasonic treatment has a certain effect on the quartz surface. The corresponding peak content at 532.10 eV increases from 17.48% to 22.44% from Table 6, proving that the quartz surface is cleaned to a certain extent after ultrasonic treatment, which increases the exposed Si and O content. In addition, the corresponding CO<sub>3</sub><sup>2-</sup> content at 531.96 eV also decrease from 12.54% to 8.86%. The results further prove that ultrasonic cavitation has a certain cleaning effect on the surface of quartz, and can desorb CaCO<sub>3</sub> precipitate on the surface of quartz to a certain extent.

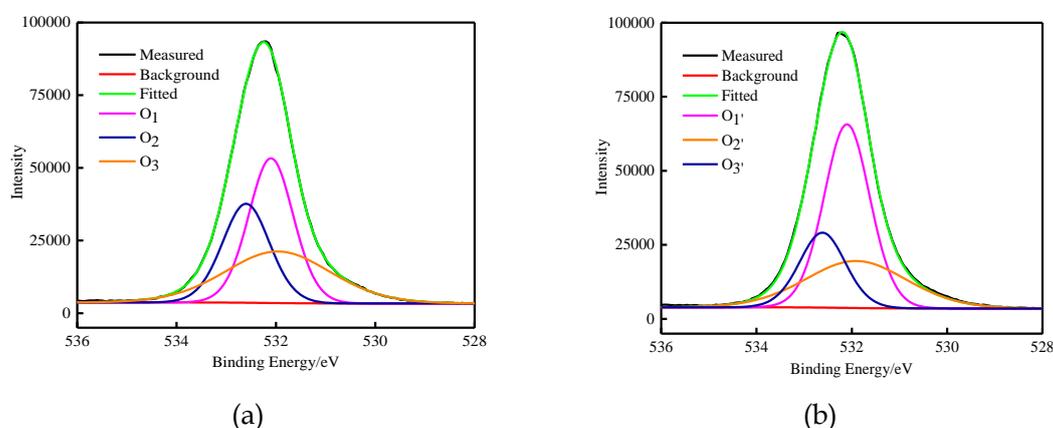


Fig. 12. High-resolution XPS of O1s on quartz. (a) no ultrasonic treat., (b) ultrasonic treat. (0.5 min, 200 W)

Table 6 Parameters of fitted peaks for O on minerals

samples	Name	Peak BE/eV	FWHM/eV	Area(P)/CPS.eV	Atomic concentration/%
Quartz(NUT)	O <sub>1</sub>	532.11	1.06	57250	17.48
	O <sub>2</sub>	532.60	1.12	48047	14.67
	O <sub>3</sub>	531.96	2.50	43385	12.54
Quartz(UT)	O <sub>1'</sub>	532.10	1.14	76294	22.44
	O <sub>2'</sub>	531.62	1.13	31023	13.22
	O <sub>3'</sub>	531.91	2.60	45172	8.86

※NUT: no ultrasonic treatment, UT: ultrasonic treatment (0.5min, 200 W)

The results of XPS investigation and high resolution XPS analysis of carbon (C1s) and oxygen (O1s) confirmed that  $\text{CaCO}_3$  precipitate can be removed from quartz surface to a certain extent by ultrasonic treatment. It also suggested that ultrasonic treatment can improve the adverse effect of siderite dissolution on the floatability of quartz.

All in all, it can be found from the previous mechanism analysis that the fine-grained siderite can not only cover the quartz surface, but also dissolve under high alkali condition to form  $\text{CaCO}_3$  precipitation with the activator  $\text{Ca}^{2+}$  and adsorb on the quartz surface, which increases the hydrophilicity of quartz and reduces the recovery rate of quartz. Besides, Fig. 13 shows the mechanism of ultrasonic cavitation effect on quartz surface. Fine siderite covered on the surface of quartz and the  $\text{CaCO}_3$  precipitate adsorbed on the quartz can be desorbed to a certain extent by energy shock wave which generates through the growth and collapse of cavitation bubble.

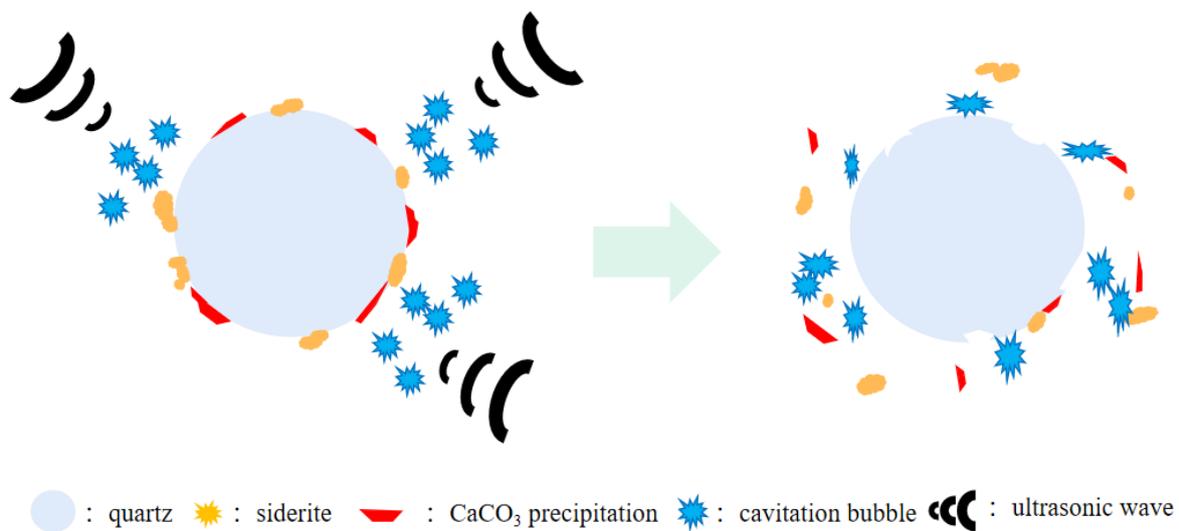


Fig. 13. The mechanism of the effect of ultrasonic cavitation on the quartz surface

#### 4. Conclusions

In this paper, the effect of ultrasonic cavitation on the improvement of quartz flotation in the presence of siderite was investigated, under the condition of siderite content of 5%, ultrasonic power of 200 W and ultrasonic time of 0.5 min, quartz flotation recovery can be increased by about 50% after ultrasonic treatment. Moreover, if the ultrasonic treatment time exceeds 1 min, the quartz recovery rate will decrease to less than 50%. Through solution chemistry calculation, SEM, EDS and XPS analysis, it can be confirmed that fine-grained siderite and  $\text{CaCO}_3$  precipitation can be removed from the surface of quartz to a certain extent by cleaning effect caused by ultrasonic cavitation.

To sum up, this paper still focuses on the impact of ultrasonic treatment on mineral surface like most researches, using ultrasonic cleaning effect to wash out impurities on mineral surfaces to restore or change the surface properties of minerals and affect flotation indicators finally. Based on the research content of this article and the literature referenced by the author, some prospects for the future application of ultrasonic cavitation in the field of mineral flotation are provided:

- Future basic research work will still focus on the impact of ultrasonic cavitation on the surface of mineral particles, flotation bubbles or pulp properties;
- Research about the types, operating methods, and processing stages of ultrasound equipment also requires continuous exploration by researchers to achieve better ultrasonic treatment effect;
- Currently, there is relatively little research on the cavitation effect of ultrasound stabilization. And the combination of ultrasonic cavitation flotation and other flotation methods, such as the interaction between ultrasonic cavitation and selective flocculation flotation, has great research and application prospects.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 52174239).

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