

Article

Influence of Sodium Carbonate on the Flotation Separation of Smithsonite and Calcite by Sulfuration-Amine Method

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Abstract: Sulfuration-amine flotation is the most commonly used method to separate zinc oxide ore, but its shortcomings such as unstable separation index and poor applicability to high mud-content raw ore limit its application in industry. In this study, the influence mechanism of sodium carbonate on the flotation separation of smithsonite and calcite by the sulfuration-amine method was investigated by chemical analysis of the flotation solution, contact angle measurement, Zeta potential test, and XPS analysis. The results showed that sodium carbonate significantly improved the flotation separation performance of smithsonite and calcite. The chemical analysis of the flotation solution showed that sodium carbonate hindered the dissolution of smithsonite, reducing its negative impact on the flotation of smithsonite. The results of the zeta potential and XPS tests showed that sodium carbonate enhanced the electronegativity of the smithsonite surface, and in an alkaline environment, sodium carbonate was favorable for the adsorption of dodecylamine on the surface of smithsonite, while sodium carbonate and high alkalinity enhanced the inhibitory effect of sodium hexametaphosphate on calcite. The study proved that sodium carbonate could be an effective modifier to promote the flotation separation of smithsonite and calcite using the sulfuration-amine method.

Keywords: smithsonite; calcite; sodium carbonate; sulfuration-amine; flotation separation



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1. Introduction

As a common non-ferrous metal, zinc possesses good wear resistance and ductility, and is widely used in industries such as galvanization, zinc-based alloys, and chemical products [1,2]. However, with the large consumption of zinc, zinc sulfide ore, the primary resource for extracting zinc in industry, is severely depleted [3]. Therefore, the efficient utilization of zinc oxide ores has attracted more attention from researchers [2]. Flotation is widely used in various beneficiation plants for the recovery of zinc oxide ores. However, the difficulty of the flotation of zinc oxide ores increased due to the large variety of ore types, diverse surface characteristics, and complex co-association relationships [4]. Zinc oxide is usually associated with gangue minerals such as silicates and carbonates, in which smithsonite is often associated with calcite [5,6]. Calcite, as a common gangue mineral, exhibits a strong affinity for both anionic and cationic collectors, which adversely affects the recovery of the target minerals [7].

The main separation process of zinc oxide ore is direct flotation and a series of combined pretreatment process around flotation. These include gravity separation-flotation, roasting-flotation, flocculation-flotation, and other processes. The process of curing zinc oxide minerals can be strengthened by the roasting-flotation method when treating fine carbonate zinc oxide ores. After pretreatment, sulfide film is formed on the surface of zinc oxide minerals, which makes the floating property of zinc oxide minerals similar to that of common sulfide minerals [8]. The most common flotation technique used for the flotation

of zinc oxide ores is sulfuretted by Na_2S , followed by pretreatment with conventional cationic collectors, namely, the sulfuration-amine flotation method [9,10]. However, this method has suffered unstable separation index and poor applicability to high-mud content original ores, which severely limits its industrial application [11,12]. In the research of sulfide flotation of oxidized ore, there are three representative views on the formation mechanism of sulfide or the action mode of the vulcanizing agent and oxidized mineral: first, chemical adsorption of sulfur ion or hydrogen sulfide ion on oxidized mineral surface; second, the ion exchange between sulfur ion and the complex anion of oxidized mineral; and, third, both chemisorption and ion exchange can generate metal sulfide [13,14]. Sodium silicate, sodium hexametaphosphate, and other depressants are widely used to depress the gangue minerals. Sodium hexametaphosphate, as a typical inorganic modifier, is often used to inhibit the floating of calcite in the flotation process [9,10,15]. However, depressants often have a negative effect on the flotation of smithsonite [16]. Therefore, it is particularly important to improve the floatability of smithsonite while effectively depressing the gangue minerals. Sodium carbonate is the most common modifier in mineral flotation [15–17], which cannot only adjust the pH value of the pulp but also form a carbonate precipitate with metal ions on the surface of minerals [18]. Saturated CO_3^{2-} can inhibit the flotation of calcite, which may be due to the adsorption of carbonate on the calcite surface, resulting in changes in the surface properties of calcite [19,20]. It can be deduced that sodium carbonate may be a promising modifier in the flotation of zinc oxide ores. However, the mechanisms of CO_3^{2-} interacting with the surface of smithsonite and its influence on the flotation separation of smithsonite and calcite are not clear.

Therefore, in this study, the sulfide-amine method was used to float smithsonite. Sodium hexametaphosphate was used as the depressant for gangue mineral, while sodium carbonate was used as the modifier. The effect of sodium carbonate on the flotation separation of smithsonite and calcite was investigated through micro-flotation tests. The interaction mechanism between CO_3^{2-} and the surfaces of smithsonite and calcite was revealed by chemical analysis of the flotation solution, contact angle measurement, zeta potential test, and XPS analysis. This study aims to investigate the effect of sodium carbonate on the flotation separation of smithsonite and calcite using the sulfuration-amine method. From this research, the unstable separation index of smithsonite from calcite and gangues and the problem of poor applicability of the sulfuration-amine method in the high mud content raw ore flotation can be solved by the addition of sodium carbonate. The results can also provide important guidance for the flotation separation of zinc oxide from calcium-containing salt minerals.

2. Materials and Methods

2.1. Materials and Reagents

High-grade smithsonite (>95%) and calcite (>95%) pure minerals were obtained from Lanping Bai Pumi Autonomous County, Nujiang Lisu Autonomous Prefecture, Yunnan Province, and Linwu County, Chenzhou City, Hunan Province, Hunan Province in China, respectively, and used as experimental samples in this study. Both minerals were hand-selected and ground in ceramic ball mill. The ground samples were dry screened to obtain the samples with $-74 + 38 \mu\text{m}$ size for the X-ray diffraction measurement, micro-flotation tests and contact angle measurements. Samples with particle size of $-5 \mu\text{m}$ were used for zeta potential tests and XPS analysis. The X-ray diffraction patterns of smithsonite particles were recorded by an X-ray diffractometer (D/MAX-2600, Rigaku International Corporation, Tokyo, Japan) with Cu $k\alpha$ radiation at 40 kV and 20 mA. Jade software (MDI Jade 6) (Livermore, CA, USA) was used to analyze the detection results. As shown in Figures 1 and 2, there were no noise peaks in the XRD patterns and all the peaks belong to the smithsonite and calcite, respectively, and no impurity was over 5 wt% for each sample.

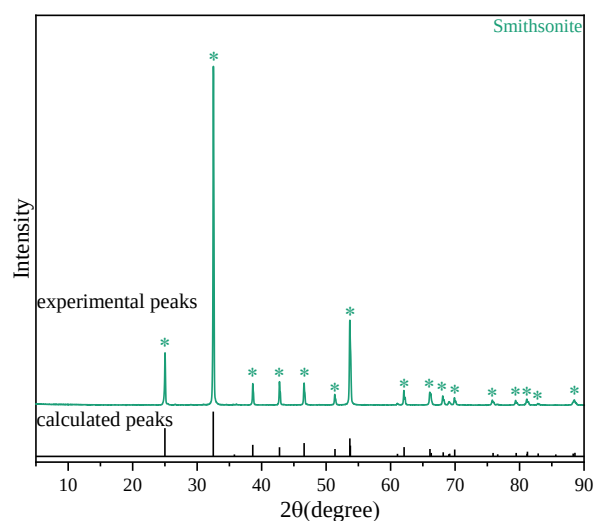


Figure 1. XRD pattern of smithsonite. “*” is peaks of wave only, and no other meaning, experimental datas compared with calculated datas.

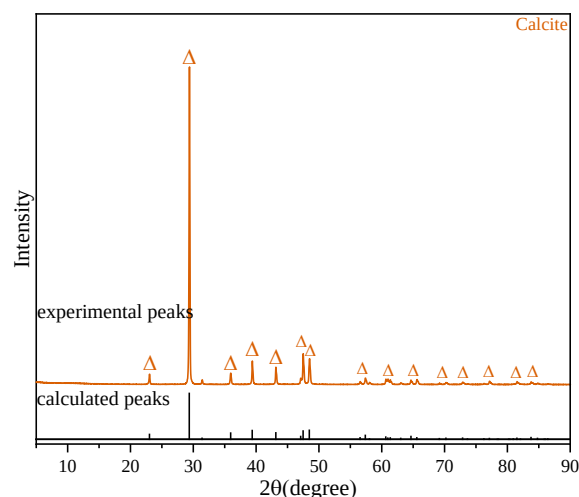


Figure 2. XRD pattern of calcite. Triangles is peaks of wave only, and no other meaning, experimental datas compared with calculated datas.

Sodium hexametaphosphate $((\text{NaPO}_3)_6)$ was used as a depressant, dodecylamine $(\text{C}_{12}\text{H}_{27}\text{N})$ as the collector, sodium sulfide as the sulfurizing reagent, sodium carbonate as the modifier, sodium hydroxide (NaOH) as pH modifiers, and all reagents are of analytical grade. Deionized (DI) water, with resistivity of $18.2 \text{ M}\Omega$, was prepared with an Elix 5 and a Millipore-UV plus water purification system (Millipore Inc., Canada), which was used throughout the micro-flotation tests and other tests.

2.2. Micro-Flotation Test

Micro-flotation tests were conducted on an XFG 5–35 flotation machine (Jilin Exploration Machinery Factory, China) using a flotation cell with a capacity of 40 mL, and the stirring speed was set at 1800 r/min. These flotation experiments were conducted by using 2.0 g smithsonite or calcite particles in the flotation cell with an air flowrate of $60 \text{ cm}^3/\text{min}$, and the pulp was pre-dispersed in an ultrasonic bath for 300 s. Modifiers and collectors were added sequentially for additional 120 s for every reagent addition. Lastly, the gas valve of the micro-flotation cell was opened for 180 s of froth collection, and all products were finally dried and weighed to analyze recovery. All the micro-flotation experiments were performed three times. As the neutralization reaction of smithsonite and calcite under acidic conditions, the flotation tests were only carried out in an alkaline environment. In

the preliminary exploration experiments, 15 mg/L of dodecylamine and 1250 mg/L of sodium sulfide were appropriate conditions for smithsonite flotation.

2.3. Contact Angle Measurements

The contact angle was measured by the sessile drop using a JY-82B Kruss DSA goniometer (Dataphysics, Germany), and pure smithsonite or calcite powders pretreated with DI water, pure smithsonite or calcite powders pretreated with sodium hexametaphosphate, sodium sulfide and dodecylamine, and pure smithsonite or calcite powders pretreated with sodium hexametaphosphate, sodium sulfide, sodium carbonate, and dodecylamine were used as samples to compress into tablets. The pretreatment conditions were the same as those in flotation tests. 4 g smithsonite or calcite powders were pressed into a circular plate for 60 s under 15 MPa pressure using a compressor (ZHY-401B, Beijing zhonghe venture technology development Co. LTD., China). For a typical contact angle measurement, DI water was sucked into a micro syringe and generated a droplet with 6 μ L at the end of the syringe needle, and then the sample was raised to contact with the water droplet, after which a contact angle was formed and measured. Each contact angle test was performed at least 3 times.

2.4. Zeta Potential Measurement

Zeta potential measurements were carried out using a zetasizer (Nano ZS90, Malvern Instruments, Worcester, UK). 100 mg of mineral samples ($-5 \mu\text{m}$) were added to 80 mL of 1×10^{-3} mol/L KCl solution, the desired reagents were added using a magnetic stirrer to disperse at 300 rpm, and the solution was adjusted to the desired pH. After settling for 600 s, the supernatant was collected for zeta potential measurement. Multiple measurements were taken and average values were obtained.

2.5. XPS Measurements

The XPS measurements were conducted with a 250 XI X-ray photoelectron spectrometer from ThermoFisher Scientific, USA. The Al K α radiation source ($h\nu = 1486.6 \text{ eV}$) was used, the vacuum degree was around 5.0×10^{-9} mbar, and the scanning range was 1400 eV~0 eV. Smithsonite pretreated with DI water; smithsonite pre-treated with sodium hexametaphosphate, sodium sulfide, and dodecylamine; smithsonite pretreated with sodium hexametaphosphate, sodium sulfide, sodium carbonate, and dodecylamine; calcite pre-treated with DI water; calcite pre-treated with sodium hexametaphosphate, sodium sulfide and dodecylamine; and calcite pretreated with sodium hexametaphosphate, sodium sulfide, sodium carbonate, and dodecylamine were all used as samples for XPS analysis. The C1s peak at 284.6 eV was employed to correct binding energies. The obtained spectra were fitted and plotted using XPS Peak 4.1 software.

3. Results and Discussion

3.1. Micro-Flotation Results of Smithsonite and Calcite

The effects of sodium carbonate on the flotation separation of smithsonite and calcite were investigated in the sulfuration-amine system using sodium hexametaphosphate as the depressant. Single mineral flotation tests consisted of three parts (Figures 3–5), aimed at exploring the effects of pH, sodium hexametaphosphate, and sodium carbonate on the flotation of zinc and calcite. As shown in Figure 3, when the pH of the pulp was around 12.0, the maximum recovery of 85.60% for smithsonite was achieved, while the recovery of calcite decreased to the value of 69.25%. As displayed in Figure 4, with the increase of sodium hexametaphosphate dosage, the recovery of calcite rapidly decreased at the pH 12.0, indicating that sodium hexametaphosphate effectively depressed calcite, while the floatability of smithsonite deteriorated, and the recovery of calcite decreased to 42.58% at a sodium hexametaphosphate dosage of 10 mg/L. Further research was conducted on the effect of sodium carbonate on the flotation separation of smithsonite and calcite. As the dosage of sodium carbonate increased, the recovery of smithsonite reached 94.65%, while

calcite was further depressed with a recovery of only 10.25%. In this case, a significant difference in floatability between smithsonite and calcite was achieved, and the final pH of the pulp was around 12.4. This indicated that a high concentration of sodium carbonate can effectively promote the flotation separation performance of smithsonite and calcite.

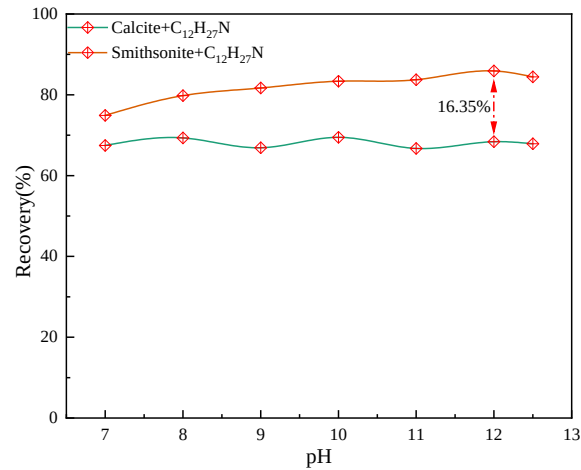


Figure 3. Flotation separation results of smithsonite and calcite as a function of pH.

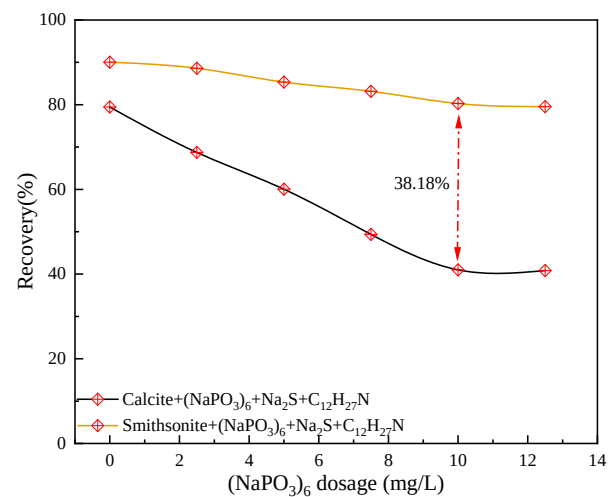


Figure 4. Effect of sodium hexametaphosphate dosage on the flotation of smithsonite and calcite.

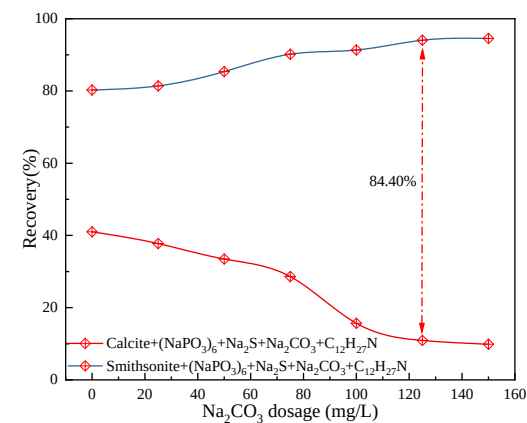


Figure 5. Effect of sodium carbonate dosage on the flotation of smithsonite and calcite.

3.2. Dissolved Components Analysis of Smithsonite

The dissolved components on the surface of smithsonite as a function of pH are shown in Figure 6. It can be seen that the Zn^{2+} , ZnOH^+ , and ZnHCO_3^+ ions existed on the smithsonite surface at a pH around 8. When $\text{pH} > 8$, with the increase of pH, the contents of Zn^{2+} and ZnOH^+ decreased continuously, while the contents of CO_3^{2-} , $\text{Zn}(\text{OH})_3^-$, and $\text{Zn}(\text{OH})_4^{2-}$ increased gradually. When $\text{pH} > 10$, the surface of smithsonite mainly existed in the form of $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$, and with the increase of pH, CO_3^{2-} , $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ increased [10,21].

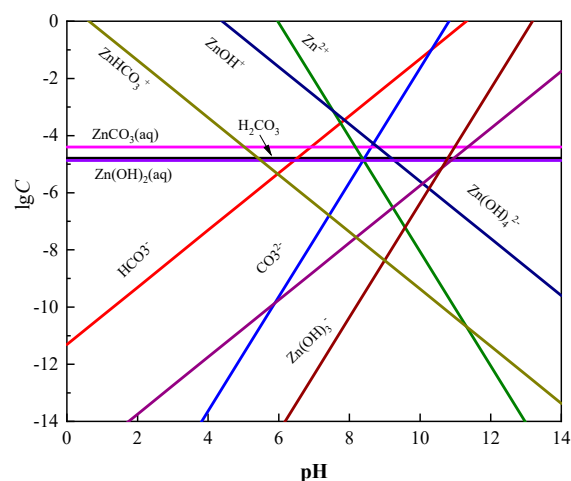


Figure 6. The effect of pH on components distribution on the surface of smithsonite.

The composition distribution of sodium carbonate as a function of pH is shown in Figure 7. It can be demonstrated that HCO_3^- was the dominant component when the pH was in the range of 6 to 10.5. When $\text{pH} > 10.5$, CO_3^{2-} was the dominant component. As shown in Figure 6, it indicated that when $\text{pH} > 8$, with the increase of pH, the content of CO_3^{2-} dissolved from smithsonite increased continuously. While in the presence of sodium carbonate, the dissociated component of CO_3^{2-} from sodium carbonate will hinder the dissolution of smithsonite, thereby reducing the adverse effect of dissolution on the flotation of smithsonite. Therefore, the dissociated component of CO_3^{2-} from sodium carbonate was a beneficial component for the flotation of smithsonite [22,23].

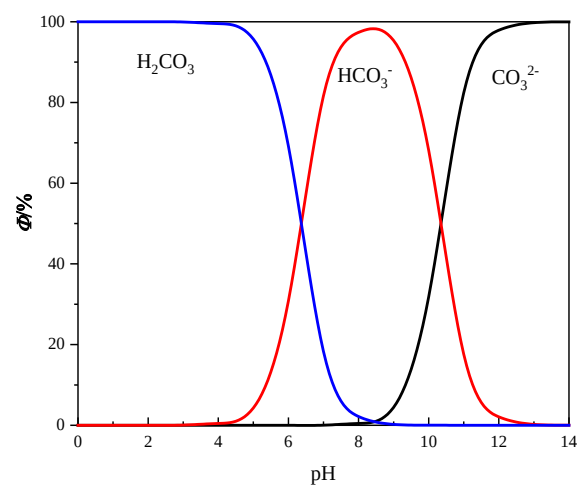


Figure 7. The component distribution of sodium carbonate as a function of pH with a concentration of $1.18 \times 10^{-3} \text{ mol/L}$.

3.3. Contact Angle Measurement

The contact angle results are shown in Figure 8. The contact angle of natural pure smithsonite powders is 44.9° , indicating that smithsonite powders suffered poor natural hydrophobicity. Under the pretreatment by sodium hexametaphosphate, sodium sulfide and dodecylamine, the contact angle of smithsonite increased to 130.8° . Moreover, after the further addition of sodium carbonate, the contact angle of smithsonite powders increased to 135.9° , indicating that sodium carbonate, as a modifier, significantly improved the hydrophobicity of smithsonite.

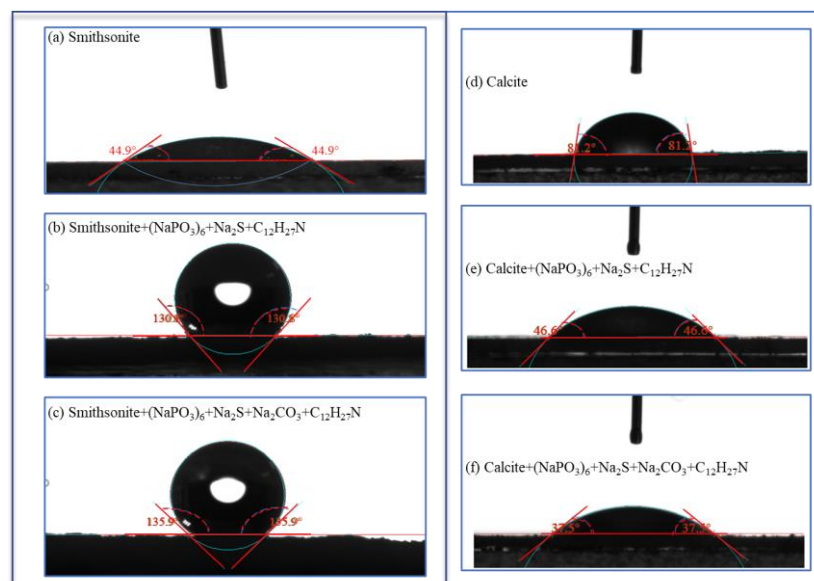


Figure 8. Contact angles of smithsonite/calcite powders under different conditions (smithsonite on the left; calcite on the right).

The contact angle of natural pure calcite powders was 81.2° , indicating that calcite presented superior natural hydrophobicity. With the pretreatment of sodium hexametaphosphate, sodium sulfide, and dodecylamine, the contact angle of calcite powders decreased to 46.6° , and with the further introduction of sodium carbonate, the contact angle of calcite powders decreased to 37.5° . It should be noted that adjusting the pH of the pulp with sodium sulfide and the addition of sodium hexametaphosphate had better depression effects on calcite powders. After the introduction of sodium carbonate, the contact angle of calcite was further reduced, which proved that sodium carbonate improved the hydrophilicity of calcite powders. Overall, all the results indicated that the addition of sodium carbonate improved the hydrophobicity of smithsonite and increased the hydrophilicity of calcite, resulting in a significant difference in the floatability of these two minerals, which was beneficial for their flotation separation. The results of the contact angle measurements were consistent with the flotation results of smithsonite and calcite.

3.4. Zeta Potential Analysis

The effects of pH on the Zeta potential of the smithsonite surface before and after the addition of reagents are shown in Figure 9. The results show that the surface charge of smithsonite decreased with the increase of pH. The isoelectric point of smithsonite was about 6.5, which was consistent with the results in previous studies [24,25]. After the addition of dodecylamine, the isoelectric point of smithsonite shifted to the right by 0.5, indicating that dodecylamine molecules had adsorbed electrostatically on the surface of smithsonite. When the pH was 12.0, the zeta potential of smithsonite dropped sharply after the addition of sodium hexametaphosphate and sodium sulfide, which indicated that the interaction between dodecylamine and smithsonite powders can be enhanced with sodium sulfide. After the further introduction of sodium carbonate, the zeta potential of smithsonite

powders decreased by 12.17 mV, compared to that only with dodecylamine. The above results demonstrated that the addition of sodium carbonate promoted the adsorption of dodecylamine on the surface of smithsonite.

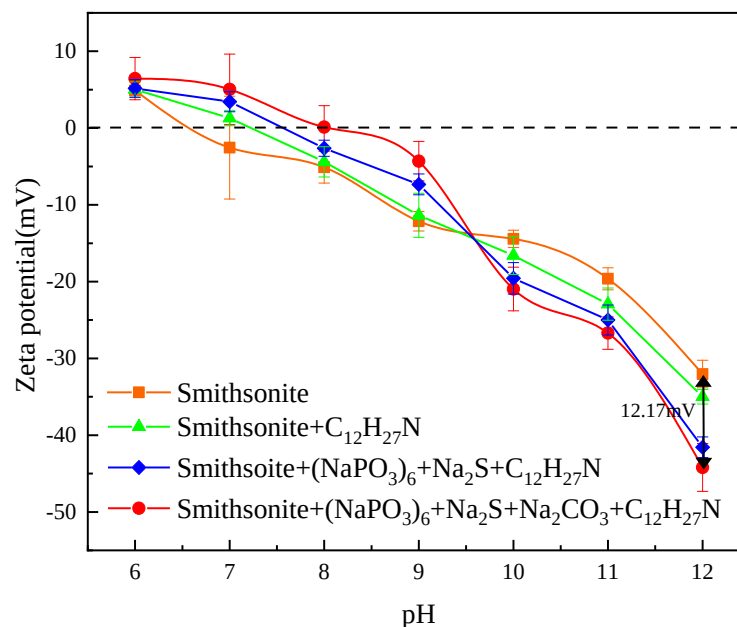


Figure 9. Effect of pH and reagents on zeta potential of smithsonite powders.

The effect of pH on the electrical properties of calcite powder is shown in Figure 10. It indicated that without any reagents, the zeta potential of calcite decreased with the increase of pH, and its isoelectric point was about 9.8, which was similar to the value in the literature [26]. After the addition of dodecylamine, the calcite potential increased and was always positively charged in the pH range of 6 to 12. After the addition of sodium hexametaphosphate, sodium sulfide, and dodecylamine, the zeta potential of calcite was reduced by about 16 mV compared with that of reagent-free condition, and its isoelectric point was shifted to the left by 1.6. This was because after adjusting the pulp with sodium sulfide, sodium hexametaphosphate was tightly adsorbed on the calcite surface in the form of electrostatic adsorption or chelation with calcium ions, which was not conducive to the interaction between dodecylamine and calcite, so the flotation of calcite particles was depressed [27,28]. After the further addition of sodium carbonate, the zeta potential of calcite continued to decrease and was negative in the pH range of 6 to 12. This indicated that the introduction of sodium carbonate resulted in the adsorption of excess free carbonate ions on the calcite surface. The complexes formed on the surface of calcite prevented the adsorption of amine molecules. In addition, after the introduction of sodium carbonate, the pH of the pulp was further increased. In this case, the amine molecules in the solution were the dominant components, and the amine molecules cannot form complexes with the Ca²⁺ on the surface of the calcite due to the chelation with calcium ions by excess free carbonate ions from sodium carbonate [29].

3.5. XPS Measurements

The chemical compositions of smithsonite and calcite surfaces before and after the pretreatment of reagents were detected by XPS measurements. Figures 11 and 12 illustrated the relative spectra of smithsonite and calcite, respectively, and the semi-quantitative results of surface chemical compositions, as shown in Tables 1 and 2, respectively. The primary elements on the surface of natural smithsonite were C, O, and Zn, and no significant impurities were found in Figure 11 and Table 1. Apparently, after the addition of sodium hexametaphosphate, sodium sulfide, and dodecylamine, as shown in Table 1, the percentage content of S increased from 1.18% to 7.96%, and the N content increased

from 0.92% to 2.38%. The adsorption of S^{2-} and HS^- ions dissociated from sodium sulfide altered the relative element content on the smithsonite surface [30,31]. The presence of unshared electrons on the nitrogen atom resulted in a combination of $-NH_2$ from dodecylamine dissolution and Zn from smithsonite. The dodecylamine molecules acted as a ligand, providing its unshared electrons to form stable complexes with Zn^{2+} . Hence, the percentage of Zn content on the smithsonite surface decreased by 0.53%. Similarly, after the further addition of sodium carbonate, the relative content of the four elements S, C, O, and Zn on the smithsonite surface changed, with a smaller variation for Zn content. According to the changes in element concentration in Table 1, compared with smithsonite pretreated with sodium hexametaphosphate, sodium sulfide, and dodecylamine, the surface content of C and N on the smithsonite increased by 0.16% and 0.14%, respectively, indicating that the smithsonite surface had more affinity for dodecylamine after the further addition of sodium carbonate.

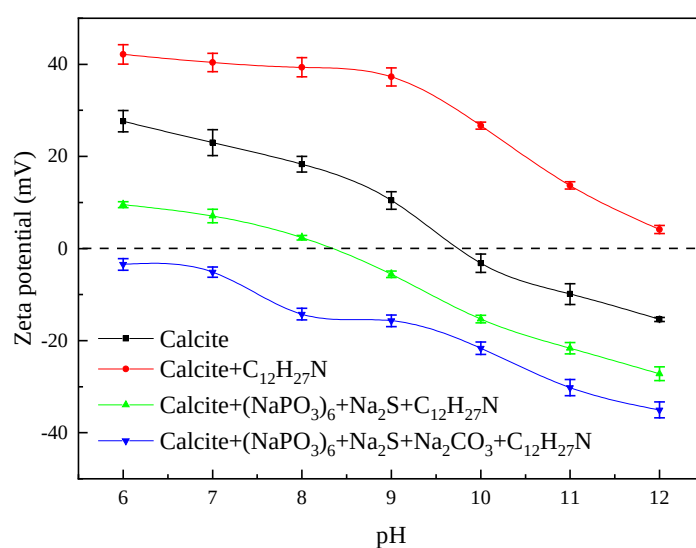


Figure 10. Effect of pH and reagents on the zeta potential of calcite powders.

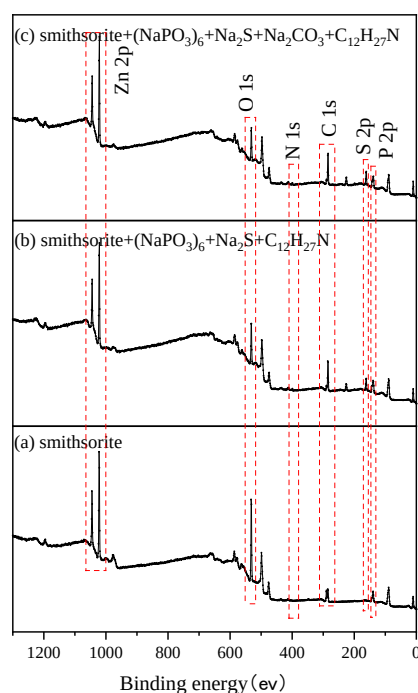


Figure 11. XPS wide-scan spectra of smithsonite before and after pretreatment of reagents.

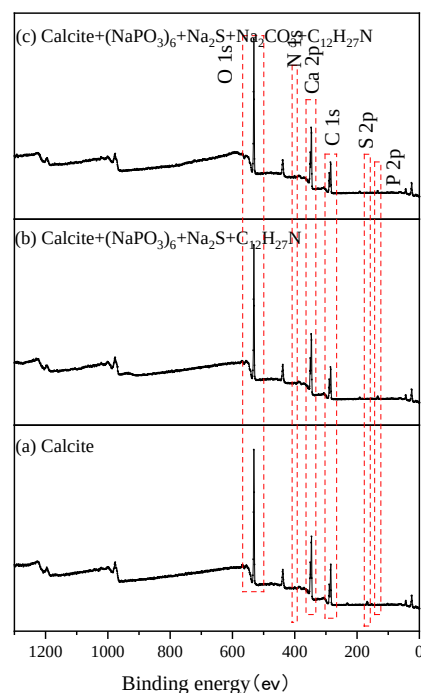


Figure 12. XPS wide-scan spectra of calcite before and after pretreatment of reagents.

Table 1. Relative atomic content of smithsonite surface.

Samples	Relative Amounts %					
	C	N	Zn	O	S	P
(a)	28.84	0.92	15.87	42.65	1.18	10.54
(b)	38.63	2.38	15.34	20.47	7.96	15.22
(c)	38.79	2.52	15.16	18.28	9.11	16.14

Table 2. Relative atomic content of calcite surface.

Samples	Relative Amounts %					
	C	N	Ca	O	S	P
(a)	42.93	1.47	11.63	41.39	1.94	0.64
(b)	39.03	2.02	12.44	43.86	0.63	2.02
(c)	38.45	2.00	12.52	44.1	0.68	2.25

Meanwhile, C, O, Ca, and P elements on the natural calcite surface were examined. Some impurities appeared on the surface of the calcite, possibly due to sample preparation and contamination by carbon dioxide in the air, but there was no effect on the analysis of the elements in general. After pretreatment of sodium sulfide and sodium hexametaphosphate, the contents of C, Ca, and P changed by 3.90%, 0.81%, and 1.38%, respectively, while the content of O increased by 2.47%, as shown in Table 2, indicating that after adjusting the pH of the pulp with sodium sulfide, sodium hexametaphosphate was more easily adsorbed on the surface of calcite [28]. After the introduction of sodium carbonate further, it can be seen that the contents of C, Ca, and P on the surface of calcite changed by 0.44%, 0.40%, and 0.23%, respectively, indicating that the addition of sodium carbonate enhanced the adsorption of sodium hexametaphosphate on the surface of calcite, resulting in a decrease in the adsorption of dodecylamine on the surface of calcite, which was consistent with the flotation results of calcite.

To further identify the surface differences of samples, the fitting of Zn 2p and Ca 2p peaks was conducted. The fitting Zn 2p peaks of smithsonite samples are shown in Figure 13. Zn 2p

3/2 and Zn 2p 1/2 are two spin-orbit splitting peaks with binding energies of 1023.36 eV and 1046.49 eV, respectively [32,33]. On the surface of smithsonite pretreated with sodium sulfide, sodium hexametaphosphate, and dodecylamine, as shown in Figure 13b, the binding energies of Zn 2p 3/2 and Zn 2p 1/2 were about 1023.08 eV and 1046.16 eV, respectively, corresponding to zinc-sulfur compounds and zinc hydroxide [34,35]. After the further addition of sodium carbonate, compared with Figure 13b, the binding energies of Zn 2p 3/2 and Zn 2p 1/2 were shifted by 0.04 eV and 0.05 eV, respectively. It indicated that the introduction of carbonate increased the active sites on the surface of smithsonite, which was beneficial to the adsorption of dodecylamine on the smithsonite surface [36,37].

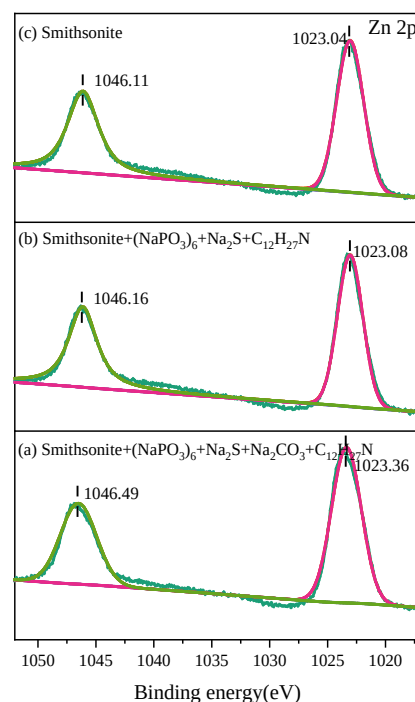


Figure 13. XPS Zn 2p spectra of smithsonite before and after pretreatment of reagents.

The fitting Ca 2p peaks of calcite samples are shown in Figure 14. The XPS spectrum of Ca 2p on the calcite surface includes two spin-orbit splitting peaks, Ca 2p 3/2 and Ca 2p 1/2, with the binding energies of 346.93 eV and 350.43 eV, respectively [38,39]. After pretreatment with sodium sulfide, sodium hexametaphosphate, and dodecylamine, as shown in Figure 14b, the binding energies of Ca 2p 3/2 and Ca 2p 1/2 on the calcite surface decreased by 0.09 eV and 0.12 eV, respectively. After further introduction of sodium carbonate, as shown in Figure 14c, the binding energies of Ca 2p 3/2 and Ca 2p 1/2 on the calcite surface decreased by 0.20 eV and 0.19 eV, respectively. The significant changes in the Ca 2p binding energy suggested that the addition of sodium hexametaphosphate largely altered the chemical environment of the surface elements of calcite. This may be due to the fact that the surface of calcite adsorbed more sodium hexametaphosphate, hindering the adsorption of dodecylamine and resulting in a significant decrease in the recovery rate of calcite. Additionally, it can be demonstrated that sodium hexametaphosphate may adsorb onto the surface of calcite through chelation with calcium ions. After introducing saturated sodium carbonate, the pH of the pulp further increased, making dodecylamine molecules the dominant component. However, unlike with the zinc ions on the surface of the smithsonite, dodecylamine molecules could not form metal chelate complexes with the calcium ions on the surface of calcite, further promoting the inhibitory effect of sodium hexametaphosphate on calcite.

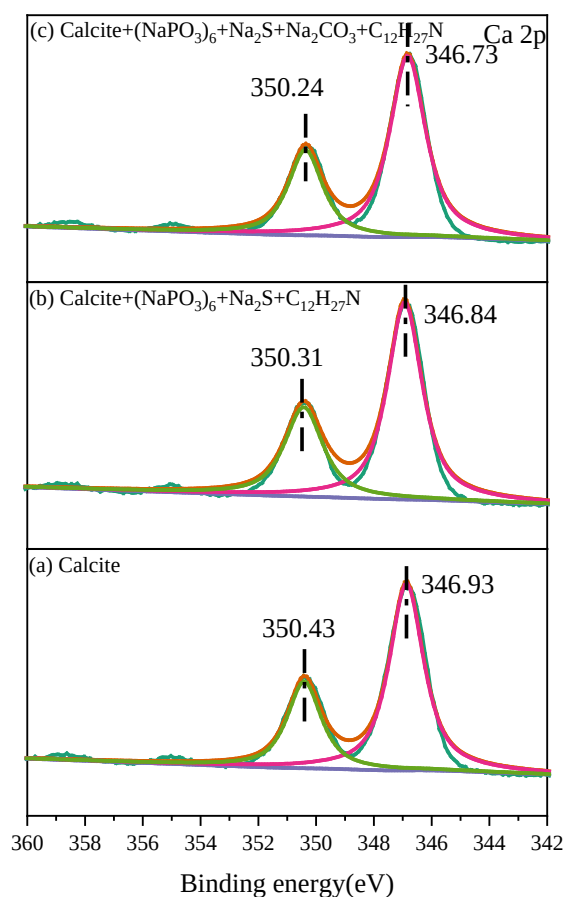


Figure 14. XPS Ca 2p spectra of calcite surface before and after pretreatment of reagents.

4. Conclusions

This study aims to investigate the effect of sodium carbonate on the flotation separation of smithsonite and calcite using the sulfuration-amine method. The flotation behavior of smithsonite and calcite was studied by micro-flotation tests. The influence mechanism of sodium carbonate on the flotation of smithsonite and calcite was investigated by chemical analysis of flotation solution, contact angle test, zeta potential test, and XPS measurement. The following conclusions are drawn:

1. The addition of sodium carbonate significantly promoted the flotation separation of smithsonite and calcite. Sodium carbonate inhibited the floatability of calcite while improving that of smithsonite.
2. The presence of CO_3^{2-} hindered the dissolution of smithsonite, thereby reducing the adverse effect of dissolution on the flotation of smithsonite.
3. Sodium carbonate increased the contact angle of smithsonite significantly and the hydrophobicity was enhanced, while the contact angle of calcite decreased and the hydrophilicity was achieved.
4. CO_3^{2-} was favorable for adsorption of dodecylamine on the surface of smithsonite, while the saturated CO_3^{2-} and high alkalinity enhanced the inhibitory effect of sodium hexametaphosphate on calcite.
5. The introduction of sodium carbonate increased the active sites on the surface of smithsonite, while CO_3^{2-} enhanced the chelation of calcium and sodium hexametaphosphate on the calcite surface.
6. Mix ores and actual ore flotation will be studied further to verify the findings in this study, and the interaction mechanism of sodium carbonate in the flotation separation of smithsonite and calcite will also be calculated in depth by density functional theory.

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