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Effect of depressants in the selective flotation of smithsonite and calcite using cationic collector

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Abstract: This work studied the effects of sodium hexametaphosphate (SHMP), tanning extract, water glass (WG) and calcium lignosulfonate (CLS) as depressants for the separation of smithsonite from calcite by using a cationic collector called octadecylamine acetate (ODA). Micro-flotation experimental tests showed that CLS can greatly and selectively depress calcite. When the dosages of CLS used were 20 and 40 mg/L, a concentrate with Zn grades of 42.54% and 49.32% and Zn recoveries of 81.66% and 68.00% was achieved in the flotation separation of mixed mineral (1:1 smithsonite:calcite). Zeta potential and adsorption measurements revealed that the adsorption of CLS on calcite's surface was greater than that on smithsonite's surface. When CLS was added, the adsorption of ODA was hindered greatly on the calcite's surface but slightly on the smithsonite's surface.

Keywords: smithsonite, calcite, selective separation, depressant

1. Introduction

Zinc ranks as the top eight non-ferrous metal and is occupying an important position in the industry (Feng et al. 2019; Ghosh et al. 2002; Liu et al. 2015). The demands for zinc oxides have increased with the gradual exhaustion of zinc sulfide (Irannajad et al., 2009; Luo et al., 2019; Navidi Kashani and Rashchi, 2008). Smithsonite, or zinc spar, is a zinc carbonate (ZnCO3) and a typical oxidized zinc ore associated with calcite (CaCO3). Smithsonite and calcite belong to the calcite-group of minerals; therefore, their floatability and surface properties are isomorphous with one another (Shi et al. 2013), this characteristic makes separating smithsonite from calcite difficult.

Flotation is an effective method for the separation of non-ferrous metals (Hosseini and Forssberg, 2007; Önal et al., 2005). Two main methods for separating smithsonite and calcite have been recently recognized by many scholars. One is direct flotation with fatty acid collectors (Bulatovic, 2010; Kiersznicki et al., 1981; Pereira and Peres, 2005) and the other is sulfidization and use of ammonium cationic collectors or xanthates for flotation (Kiersznicki et al., 1981; Önal et al., 2005; Wang et al., 2017). The latter is widely used due to its excellent indicators (Chen et al., 2018; Önal et al., 2005; Pereira and Peres, 2005).

Smithsonite and calcite have good floatability when ammonium cationic collectors are used, ever without a depressant. Therefore, adding effective depressants will improve the selective separation of smithsonite and calcite. In this study, different depressants were selected and tested to identify the most effective in terms of separating smithsonite from calcite. One of these depressants is sodium hexametaphosphate (SHMP) used as a dispersant for serpentine (Lu et al. 2019)， apatite and kaolinite (Ding et al., 2007; Ramirez et al., 2018). Another depressant is tannin, a non-toxic organic reagent, employed as an alternative depressant in selective flotation of sulfides due to its surfactant properties on pulp particles (Sarquís et al., 2014). As typical depressants, water glass (WG) and calcium lignosulphonate (CLS) play an important role in mineral flotation (Liu et al., 2019).

In this study, octadecanamide acetate (ODA) was used as a collector. In order to depress calcite, contribute to the industrial beneficiation of smithsonite; sodium hexametaphosphate (SHMP), tannin,

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water glass (WG), and calcium lignosulphonate (CLS) have been comparative studied for the first time in this system. Micro-flotation tests were conducted to show their effects on calcite. Finally, zeta-potential measurements and adsorption measurements were used to assess the validity of results.

2. Materials and methods

2.1. Pure minerals and reagents

The smithsonite used in this experiment was bought from the Yunnan Province of China. Calcite was obtained from the Hunan Province of China. The massive pure minerals were processed by hand-crushing, hand-selecting, grounding and screening. A sample of—74 to 37 μm fraction was used in the flotation tests. The fraction of—37 μm was used for adsorption measurements and a part of fine fraction (−2 μm) was obtained for the zeta potential measurements. Element (Table.1) and X-ray diffraction (XRD) analyses (Fig. 1) revealed that the purity levels of smithsonite and calcite samples were 99% and 95%, respectively. The specific surface areas of smithsonite and calcite were 0.96 and 0.48 m^2/g, respectively, as determined by a specific surface area analyzer (3H-2000BET-A, BEST, China).

Table.1 Element analyses of smithsonite and calcite

Elements	Al	Ca	O	Si	Zn	C	Fe	Others
Calcite	0.06	51.20	32.73	0.11	0.04	15.3	-	0.56
Smithsonite	0.07	1.05	20.85	0.11	63.95	11.74	1.29	0.94

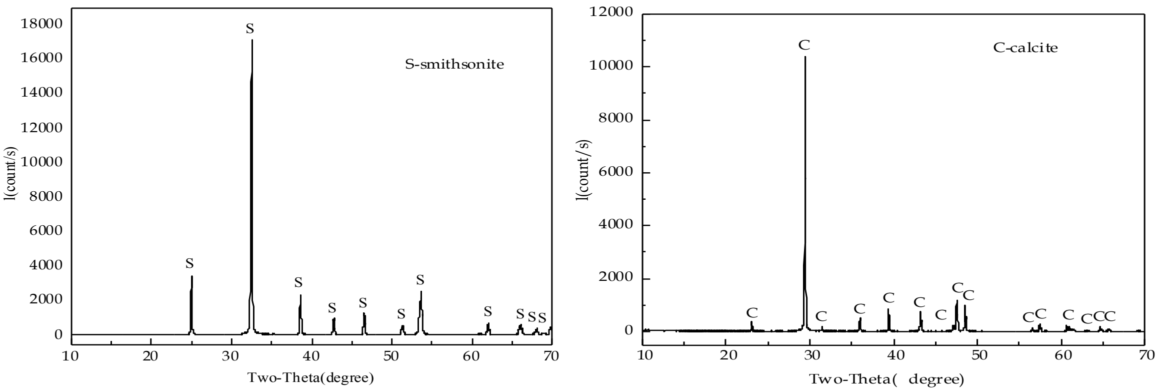

Fig. 1. X-ray diffraction (XRD) patterns of the smithsonite and calcite samples

CLS, SHMP, tannin and water glass (the modulus of water glass is 3.3) were obtained from Fine Chemical Research Institute, Kemeo Chemical Reagent Co., Ltd. (Tianjin, China), Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China), and Yousuo Chemical Technology Co., Ltd. (Shandong, China), respectively. Chemically pure ODA, which was used as a collector, was bought from Bailingwei Technology Co., Ltd. (Beijing, China). Analytical grade pure sodium sulphide, which was used as an activator, was bought from Chemical Reagent Factory (Guangzhou, China). Analytical grade pure HCl and NaOH were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China) and were used to adjust the pH value. All the depressants used were of analytical grade except the water glass. Deionized water was used for all tests.

2.2. Micro-flotation experiments

Pure mineral flotation tests were conducted in an XFG flotation machine (Jilin Exploration Machinery Factory, China) with a 40 cm^3 plexiglass cell at an impeller speed of 1900 rpm. In brief, 2.0 g of pure mineral was placed in the flotation cell with 35 cm^3 of deionized water and then conditioned for 1 min. The pulp was stirred for 1 min after a pH regulator was added. The conditioning time for sodium sulfide, depressant, and collector were set at 3, 2, and 2 min, respectively, and the froth collection time was at 3 min. Finally, the concentrate and tailing were filtered, dried and weighed. The flowsheet of pure mineral floatation is shown in Fig. 2.

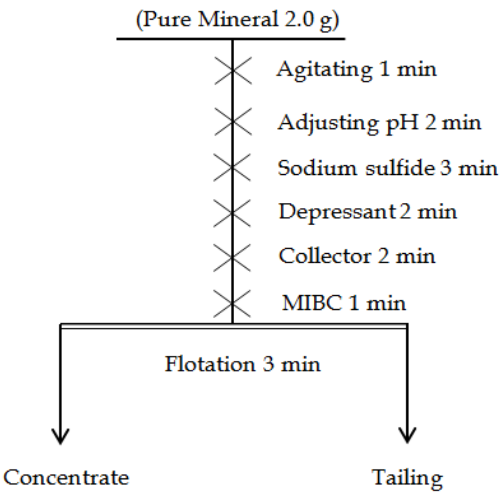

Fig. 2. Flowsheet of pure mineral flotation

2.3. Zeta potential measurements

Zeta potential measurements were performed using a Zeta Plus zeta potential meter (Bruker, Karlsruhe, Germany). A diluted mineral suspension was prepared by adding 0.03 g of mineral samples to 40 cm^3 of KCl (10^{-3} mol/dm^3) background electrolyte. The adding order of reagents is same as that in the flotation experiment. After sedimentation for 5 min, the supernatant liquid was sucked out and used for the measurement. The tests were repeated three times, and the average values were calculated.

2.4. Adsorption measurements

The sample preparation is as follows: the pure mineral (2.0 g) was placed in a plexiglass cell (40 cm^3) filled with 35 cm^3 of deionized water, and then treated with the same reagent scheme as the flotation process. The conditioned slurry suspension was added in a 50 cm^3 vial and shaken for 30 min in an air-thermostat at 25 °C. The suspension was centrifuged at 9000 rpm for 20 min, and the supernatant was obtained for adsorption amount measurements, which were conducted with TOC-LCPH Analyzer (Shimadzu, Kyoto, Japan).

The measured concentrations of organic carbon (OC) and organic nitrogen (ON) are linearly related to ODA with a linear correlation coefficient of 0.9955 as depicted in Fig. 3.

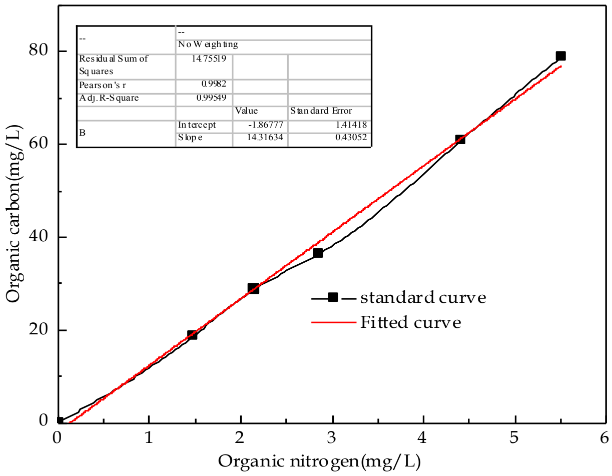

Fig. 3. Standard curves of the linear relationship between OC and ON in ODA

Total organic carbon (TOC) and total organic nitrogen (TON) were measured in the supernatant after LSC and ODA additions, respectively. The ON of ODA is also the TON in the supernatant because nitrogen is only present in ODA. First, the amount of OC from ODA can be calculated from the amount of ON by the linear curve. Second, the OC from LSC can be determined by the TOC in the supernatant minus the OC from ODA. The concentrations of ODA and LSC in the supernatant were determined. Finally, the amount of ODA and LSC adsorbed on mineral surface can be calculated by the following equation:

$$\delta = \frac{V(C_0 - C)}{mA} \tag{1}$$

where δ is the amount of ODA or LSC adsorbed on minerals surface (mg/dm^3), C_0 is the total concentration of ODA or LSC (mg/ dm^3), C is the final ODA or LSC concentration (mg/dm^3), and A is the specific surface area of smithsonite and calcite sample (m^2/g); m= 2 g; and V =0.04 dm^3.

3. Results and discussion

3.1. Single mineral flotation experiment results

Fig. 4 shows the recoveries of smithsonite and calcite when ODA was added at pH 9. When the ODA concentration was below 1×10^{-4} mol/dm^3, the recoveries of smithsonite and calcite increased with the added amount of ODA. When the ODA concentration exceeded 1×10^{-4} mol/dm^3, the recovery of smithsonite remained unchanged, whereas that of calcite continuously increased. As depicted in Fig. 4, the optimal concentration of the collector should be 1×10^{-4} mol/dm^3. The results indicate that ODA has a good collecting ability for smithsonite and calcite. Therefore, it is hard to separate them if no depressant is used.

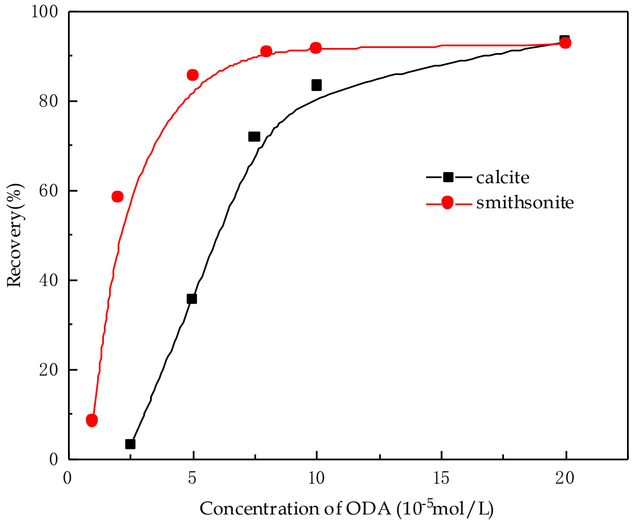

Fig. 4. Flotation results of smithsonite and calcite as a function of ODA concentration at pH 9

Fig. 5 shows the effect of pH on the flotation performance of smithsonite and calcite with 1×10^{-4} mol/dm^3 ODA. As shown in Fig. 5, calcite and smithsonite both have good flotation recovery at a pH range of 7–12. Therefore, a suitable depressant must be added when using ODA as collector for the flotation separation of smithsonite and calcite.

3.2. Test for depressant selection

The tendency of the flotation recoveries of smithsonite and calcite as a function of SHMP concentration at pH 9 with 1×10^{-4} mol/dm^3 ODA is shown in Fig. 6. The flotation recoveries of smithsonite and calcite decreased with the increase in SHMP dosage due to the interaction of SHMP interact with the metal species on the surface of the two minerals surface, thus increasing their surface hydrophilicity (Ding et al., 2007). Therefore, SHMP is not a suitable depressant for the flotation separation of smithsonite from calcite in this system.

Flotation results of smithsonite and calcite at pH 9 as a function of tannin concentration with 1×10^{-4} mol/dm^3 ODA are shown in Fig. 7. The recovery of calcite decreased rapidly with the increase in tannin concentration from 0 mg/dm^3 to 1 mg/dm^3 mainly because tannin chelate with Ca ions on the calcite's surface (Sarquís et al., 2014). However, based on the smithsonite flotation results, by increasing tannin concentration the recovery of smithsonite decreased to below 5%, which suggested that tannin could not act as a suitable depressant to retrieve smithsonite after flotation.

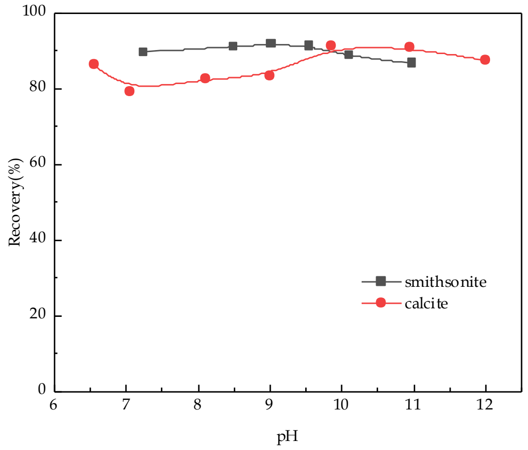

Fig. 5. Flotation results of smithsonite and calcite as a function of pH with 1×10^{-4} mol/L ODA

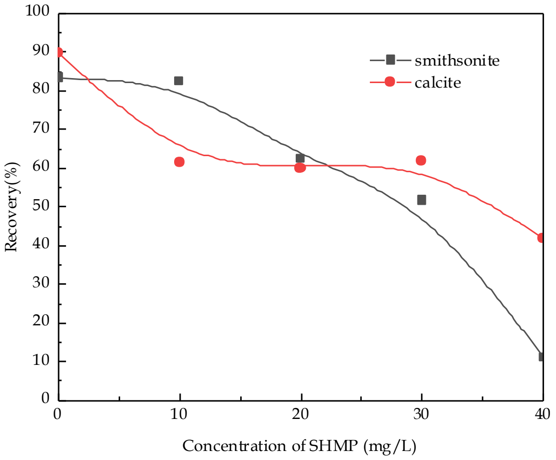

Fig. 6. Flotation results of smithsonite and calcite at pH 9 as a function of SHMP concentration with 1×10^{-4} mol/L ODA

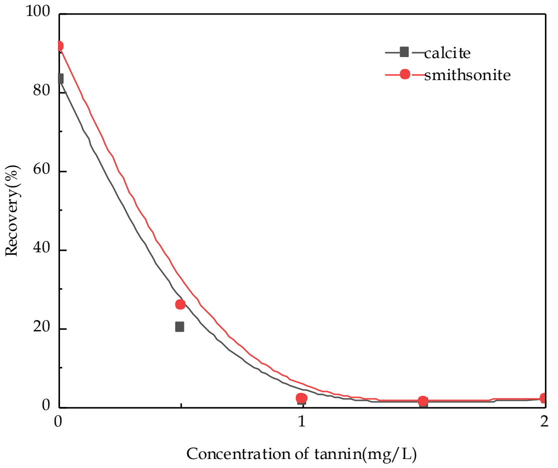

Fig. 7. Flotation results of smithsonite and calcite at pH 9 as a function of tannin concentration with 1×10^{-4} mol/L ODA

Fig. 8 presents the flotation recoveries of smithsonite and calcite as a function of WG concentration at pH 9 with 1×10^{-4} mol/dm^3 ODA. According to Fig. 8, WG is an effective depressant for smithsonite and calcite. However the recovery of smithsonite was only less than 10% and that of calcite was less than 20% when the amount of WG exceeded 200 mg/dm^3, This phenomenon occurred because $SiO(OH)^{3-}$ species were adsorbed on the surface of smithsonite and calcite, thus blocking the adsorption of the collector (Bo et al., 2015; Dong et al., 2018). Hence, WG is not a promising depressant for the separation of smithsonite from calcite.

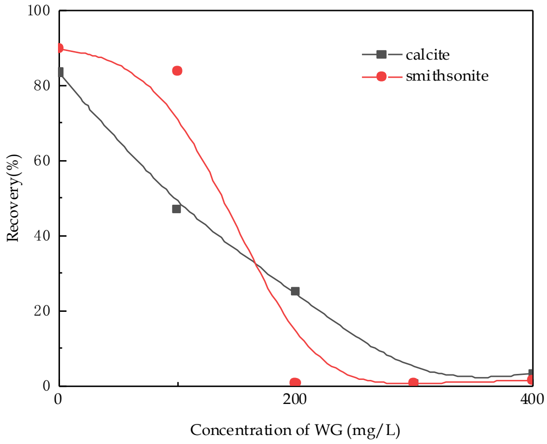

Fig. 8. Flotation results of smithsonite and calcite at pH 9 as a function of tannin concentration with 1×10^{-4} mol/L ODA

The effect of CLS concentration on the flotation recoveries of smithsonite and calcite is shown in Fig. 9. CLS had an outstanding depression effect on the floatability of calcite. In the range of 0—20 mg/dm^3, the flotation recovery of calcite decreased rapidly from 83.25% to 1.5%, whereas that of smithsonite remained above 80%. The mechanism is that LS^{2-} can be adsorbed on calcite by forming the chemical bond Ca-S-O. The adsorption of CLS may interfere with that of ODA on the calcite surface, resulting in the strong depression effect for calcite (Feng et al., 2018; Le Guern et al., 2000). Therefore, the separation of smithsonite from calcite in the presence of CLS is possible.

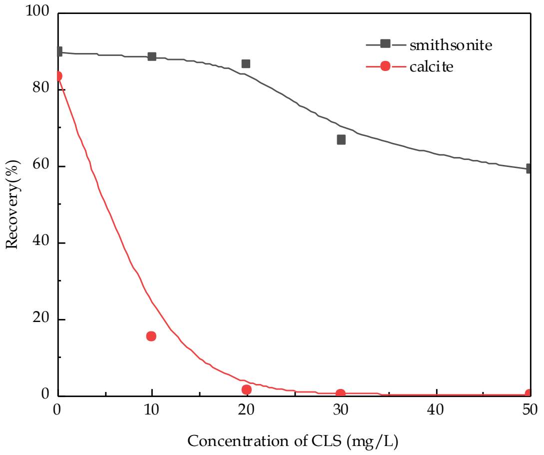

Fig. 9. Flotation results of smithsonite and calcite at pH 9 as a function of CLS concentration with 1×10-4 mol/L ODA

The flotation results of smithsonite recovery and Zn grade at pH 9 in the presence of CLS and 1×10^{-4} mg/dm^3 ODA for a 1:1 mixture of smithsonite and calcite are shown in Table 2. When the CLS dosages were 20 and 40 mg/dm^3, the grades of zinc were 42.5% and 49.3%, respectively, and its recoveries were 81.7% and 67.9%, respectively. The results of mixed minerals flotation tests agreed with those of the single mineral flotation tests, indicating that CLS can be selected as an effective depressant with this reagent scheme.

Table. 2 Flotation results of smithsonite recovery and Zn grade at pH 9 in the presence of CLS and 1×10^{-4} mol/dm^3 ODA for a 1:1 mixture of smithsonite and calcite

CLS dosage (mg/dm^3)	Zn grade in original mixture (%)	Zn grade in concentrate (%)	Zn grade in tailing (%)	Zn recovery in concentrate (%)
20	26.07	42.54	9.97	81.66
40	26.03	49.32	13.40	68.00

3.3. Zeta potential measurement

The zeta potential data for smithsonite and calcite as a function of ODA with and without reagents are shown in Fig. 10. Smithsonite and calcite showed negative potentials after sulfidization, and as the increasing amount of ODA, a cationic collector, the potential of both minerals increased gradually. The adsorption amount of ODA on the minerals' surfaces increased with its dosage, and this finding is consistent with those of single mineral flotation experiments. The zeta potential of calcite showed a downward trend when CLS was added. The tendency and negative charge of CLS (Ansari and Pawlik, 2007) prove that a large amount depressants were adsorbed on calcite's surface. The tendency calcite's zeta potential was smooth with the increase in ODA dosage after the reaction between calcite and CLS, proving that calcite no longer adsorbed the collector after the interaction with depressant. However, the potential of smithsonite was still increased with the ODA dosage in the presence of CLS, indicating that the adsorbed amount of ODA on smithsonite was also increasing. In conclusion, the small absorbed amount of CLS slightly lowered the absorbed amount of ODA on smithsonite surface, resulting in a certain decrease in potential after the depressant was added. The high adsorbed amount of CLS on calcite surface greatly hindered the adsorbed amount of ODA, resulting in the nearly unchanged potential of calcite with the increase in ODA dosage. This finding is important for flotation studies because CLS can be used to selectively separate smithsonite from calcite with ODA as the collector.

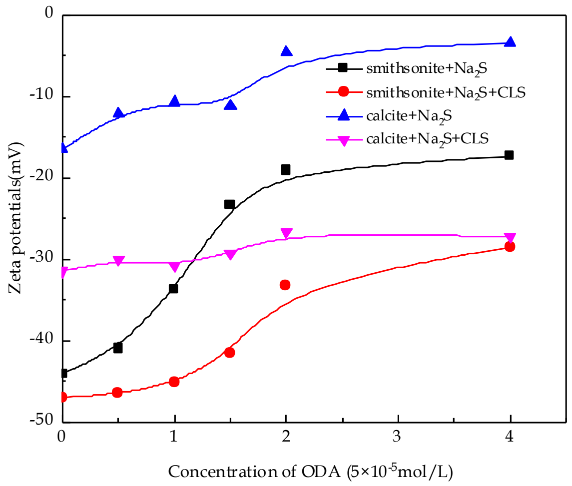

Fig. 10. Effect of reagent adding on the zeta potential of smithsonite and calcite at pH 9 as a function of ODA concentration

3.4. Adsorption measurement results

Fig. 11 shows the adsorption amount of CLS on smithsonite and calcite surface as a function of CLS concentration at pH 9. As depicted in Fig. 11, when the dosage of CLS increased, the adsorption of CLS on calcite increased rapidly, whereas that on smithsonite only increased slightly. The results suggest that CLS can be considered as an appropriate depressant in this system. Fig. 12 shows the relationship between the adsorption amount of ODA on the surface of smithsonite and calcite with 20 mg/dm^3 CLS at pH 9. The adsorption capacity of ODA on smithsonite was slightly changed with the addition of CLS while the adsorption capacity of ODA on calcite decreased rapidly. The measurement results agreed with the zeta potential measurement results.

According to the zeta potential and adsorption measurement results, the adsorption of CLS on the calcite surface was greater than that on smithsonite, and greatly lowered the adsorbed amount of the collector. The schematic diagram of selective adsorption model is depicted in Fig. 13.

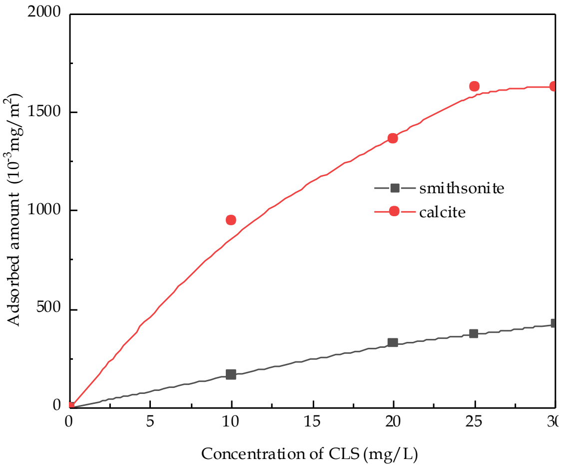

Fig. 11. Adsorption amount of CLS on smithsonite and calcite surface as a function of CLS concentration at pH 9

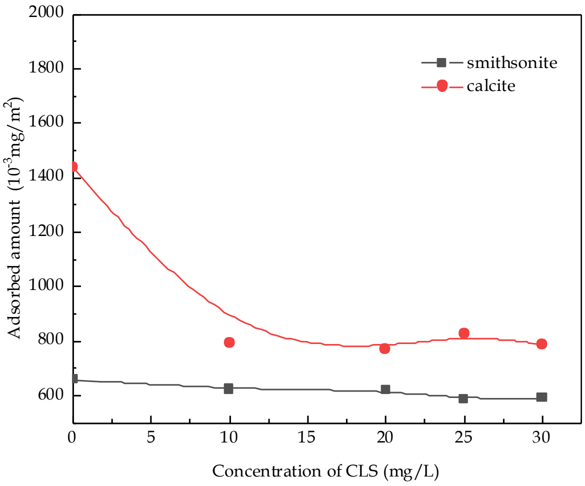

Fig. 12. Adsorption amount of ODA on smithsonite and calcite surface as a function of CLS concentration at pH 9

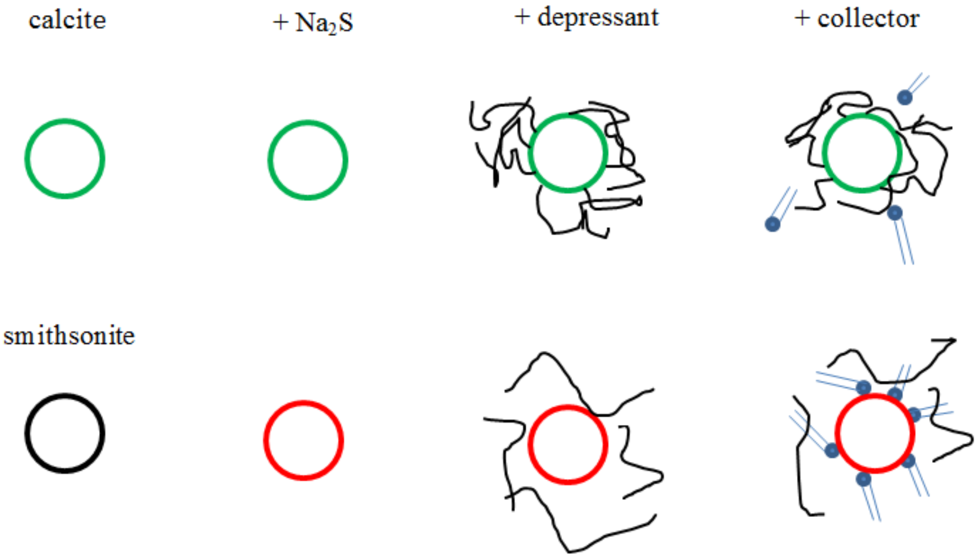

Fig. 13. Schematic diagram of adsorption model of reagents on smithsonite and calcite

4. Conclusions

This study shows that smithsonite and calcite can be floated with octadecylamine acetate (ODA) as the collector. In order to depress calcite, we compared the depressant effects of sodium hexametaphosphate (SHMP) tannin, water glass (WG), and calcium lignosulfonate (CLS) in this system for the first time. The results showed that SHMP, tannin and WG effectively depress calcite with ODA. However, these depressants are not feasible to use for the flotation separation of smithsonite and calcite in this system due to the decreased recovery of smithsonite. The experimental results also showed that CLS can effectively reduce the recovery of calcite almost without affecting the recovery of smithsonite. It is accessible to separate smithsonite from calcite due to the selective adsorption of CLS as a depressant. The results of zeta potential and adsorption measurements indicated that CLS is adsorbed on the calcite's surface and hinders the absorption of ODA, whereas it has minimal effect on smithsonite. Under these circumstances, CLS is the appropriate depressant in separating smithsonite from calcite using a cationic collector. Furthermore, since calcite is one of the most commonly occurring gangue minerals in ores and the tested depressants are commonly used in industry. This study also provides guidance for the flotation practices of some other minerals.

Acknowledgments

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