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Effect of depressants in the selective flotation of smithsonite and calcite using potassium lauryl phosphate as collector

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Abstract: In order to selectively separate smithsonite and calcite using potassium lauryl phosphate as collector and reveal the depression mechanism, the approaches of micro-flotation and zeta potential measurements were adopted. The effects of sodium hexametaphosphate (SHMP), water glass (WG), carboxymethyl cellulose (CMC) and lignosulfonate calcium (LSC) as depressants on smithsonite and calcite have been studied through micro-flotation. The single mineral flotation tests show that LSC can depress calcite, but it has little effect on smithsonite flotation. Flotation separation of a mixture of smithsonite and calcite can be completed to obtain a zinc concentrate grade up to 33.85% Zn with a recovery of 70.06%. The zeta potential results illustrate that LSC has higher tendency to be adsorbed on the surface of calcite. However, there is little adsorption of LSC on smithsonite.

Keywords: smithsonite, calcite, flotation, depressant, separation

1. Introduction

At the present time, zinc is one of the main non-ferrous metals, and its application has been increased rapidly in recent decades (Asadi et al., 2017). Normally, zinc sulfide-ores are primary raw materials for zinc production. But with the depletion of the deposits, the exploitation of other ores such as carbonates can be considered as important sources of zinc metals to meet future demands. Smithsonite ($ZnCO_3$) is one of the major sources of zinc carbonate ores. Both smithsonite and calcite are calcite-group minerals which are isomorphous with one another (Kaspar, 1959). In general, flotation is the common method for the separation of smithsonite from calcite due to their relatively similar physical properties (Irannajad et al., 2009). However, it is difficult to separate smithsonite from calcite minerals due to the conversion of the soluble components in smithsonite and calcite (Shi et al., 2013; Wang, 2016).

In recent years, phosphate ester has developed rapidly due to its good performance (Gad, 2014; Glaser et al., 2016; Phillips et al., 2016; Tjioe et al., 2016). It is always used in daily chemicals, coating metallurgy, plastic, leather and other fields. Phosphate ester is a kind of anionic surfactant. This kind of surfactant has good emulsification, solubilization, foaming and its structure is close to natural phospholipids (Buchholz et al., 2012; Wang and Miller, 2018). Therefore, it is biodegradable and has great application prospect (Mott et al., 2013; Liu et al., 2016; Tan et al., 2016). Although phosphate ester can be used effectively in the flotation of smithsonite, its selectivity in separation of smithsonite from calcite is often inadequate. In order to ameliorate the situation, effective depressants need to be selected for the separation of smithsonite and calcite (Araújo and Lima, 2017). Hence, the current study focused on the separation of smithsonite and calcite.

In this work, the effects of potassium lauryl phosphate concentration and pH values in micro-flotation of smithsonite and calcite were analyzed. In order to depress calcite, sodium hexametaphosphate (SHMP), water glass (WG), carboxymethyl cellulose (CMC) and lignosulfonate calcium (LSC) were used as depressants. The flotation separation of smithsonite and calcite was conducted in the mixed mineral system with a varied weight ratio. Zeta potential measurements were also conducted to illustrate the interaction mechanisms between lignosulfonate calcium (LSC) and minerals (smithsonite and calcite).

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2. Materials and methods

2.1. Single samples and reagents

The as pure as possible samples, from smithsonite and calcite minerals, were obtained from Yunnan Province and Hunan Province, China, respectively. The samples were crushed using a crusher and ground using an agate mortar. The products were then dry sieved to obtain 100% −74 μm product. The X-ray Diffraction (XRD) analyses of sample were shown in Fig. 1 and Fig. 2. XRD analyses were performed on a Bruker D8 Advance X-ray powder diffractometer with Cu Ka radiation (Bruker Co., German). According to the results of the XRD analyses, the purity of samples was very high. Chemical analyses show that the purities of $ZnCO_3$ and $CaCO_3$ are over 90% and 95%, respectively. CP grade potassium lauryl phosphate was obtained from the Wuhan Zhuochuang Biochemical Chemical Company (Hubei, China). AR grade SHMP, WG and LSC were obtained from Kemiou Chemical Research Institute, Tianjin, China. AR grade CMC (DS=1.2) was obtained from Aladdin Biochemical Technology Company (Shanghai, China). HCl (hydrochloric acid) and Na_2CO_3 (Sodium carbonate) were used as pH regulators. Distilled water was used for all tests.

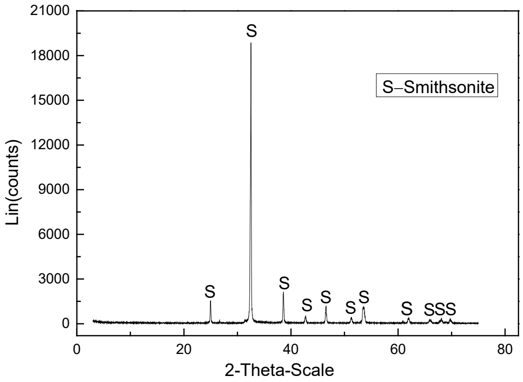

Fig. 1. The XRD spectrum of pure smithsonite sample

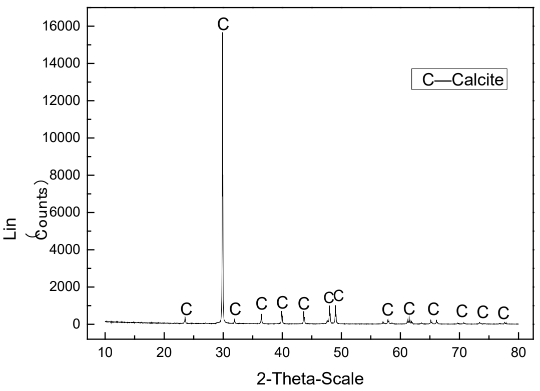

Fig. 2. The XRD spectrum of pure calcite sample

2.2. Flotation tests

The flotation tests were carried out in an XFG-1600 flotation machine (made by Jilin Exploration Machinery Factory, China). The volume of the cell is 40 cm^3. The stirring speed was fixed at 1600 r/min. The mineral suspension was prepared by adding 2.0 g of mineral to 35 mL of water. The pulp was continuously stirred for 1 min with a pH regulator, 2 min with the depressant and the collector. The pH of the solution was measured before the flotation, and the flotation was conducted for 2 min. For single mineral tests, the dry weights of the concentrates and tails were measured and used to calculate the corresponding mineral recovery. For mineral mixture, the concentrates and tails were assayed for Ca and Zn to use to calculate the recovery of metal. Each micro-flotation test was implemented three times, the average reported as the final value.

2.3. Zeta potential tests

Zeta potential measurements were performed in 1×10^{-3} mol/dm^3 KCl background electrolyte solution using Malvern Zetasizer Nano ZS90 analyzer instrument. The suspensions (0.01% mass fraction) with small amount of minerals were dispersed in a beaker magnetically stirred for 2 min. After 5 min of settling, the pH value of the suspension was measured and the supernatant was collected for zeta-potential measurements. The zeta potential of each sample was measured three times in this work, and the average was reported as the final value.

3. Results and discussion

3.1. Flotation studies

3.1.1. Single mineral flotation

Fig. 3 shows the flotation recoveries, reported in the floated fraction, of smithsonite and calcite, when they are floated as single mineral, as a function of pH with 2×10^{-4} mol/dm^3 potassium lauryl phosphate.

Both smithsonite and calcite show good flotation in the pH region from 7 to 11 and the optimum condition for smithsonite flotation around pH 8-10. The high recoveries of smithsonite and calcite in the alkaline pH maybe attributed to the interaction between $ROPO_3^{2-}$ and Ca or Zn ions on mineral surface (Wang et al., 2016). Fig. 3 also demonstrates that it is difficult to separate smithsonite from calcite without depressants.

Fig. 4 shows the effect of potassium lauryl phosphate dosage as a collector on the flotation of smithsonite and calcite at pH 8. The results in Fig. 4 indicate that flotation recoveries of smithsonite and calcite in the floated fractions increase sharply with the increasing potassium lauryl phosphate concentration when it is less than 2×10^{-4} mol/dm^3 and 1×10^{-4} mol/dm^3, respectively. Above 2×10^{-4} mol/dm^3 potassium lauryl phosphate, the flotation recoveries of smithsonite and calcite can reach the maximum around 90% and remain constant.

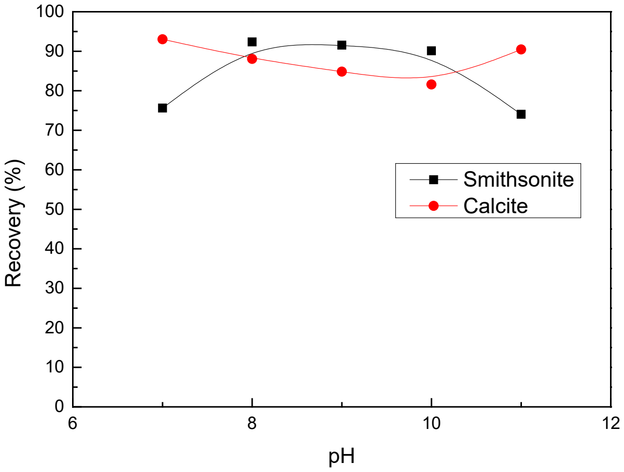

Fig. 3. Flotation results of smithsonite and calcite as a function of pH with 2×10^{-4} mol/dm^3 potassium lauryl phosphate

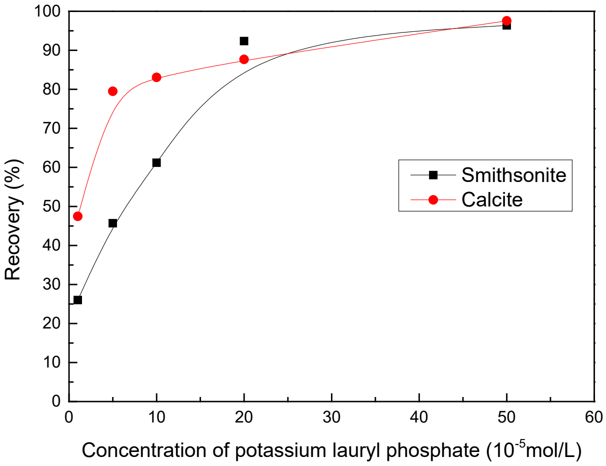

Fig. 4. Flotation results of smithsonite and calcite at pH 8 as a function of potassium lauryl phosphate concentration

3.1.2. Calcite depression results

Fig. 5 presents the single-mineral flotation recoveries of smithsonite and calcite as a function of the concentration of Sodium Hexametaphosphates (SHMP) as a depressant at pH 8. It shows that flotation recovery of calcite in the floated fraction decreases sharply with the increase in SHMP concentration. This may be attributed to the fact that SHMP has a strong complexing effect on Ca ions, and it can selectively dissolved Ca ions on the surface (Liu et al., 2016). As result, it then lessens the surface cation points and decreases the electric potential (Ding et al., 2007). According to the interaction between SHMP and Ca ions, the mechanism of depression of Ca-bearing minerals with SHMP is possibly due to the formation of Ca(II) complexes by SHMP. However, it cannot act as a suitable depressant to depress smithsonite because of its negative impact on smithsonite and calcite flotation at the same time by adding its concentration.

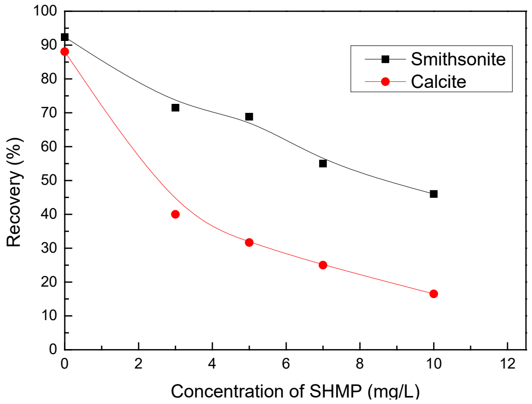

Fig. 5. Flotation results of smithsonite and calcite at pH 8 as a function of SHMP concentration with 2×10^{-4} mol/dm^3 potassium lauryl phosphate

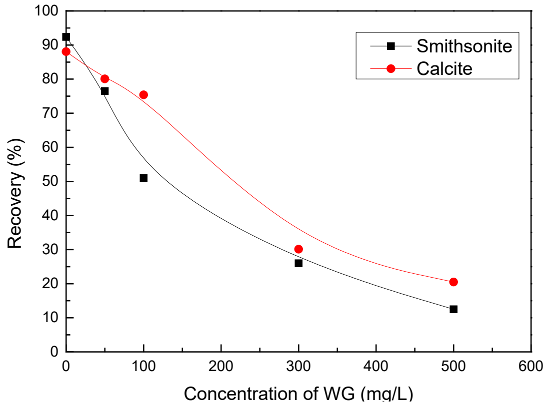

Fig. 6. Flotation results of smithsonite and calcite at pH 8 as a function of WG concentration with 2×10^{-4} mol/dm^3 potassium lauryl phosphate

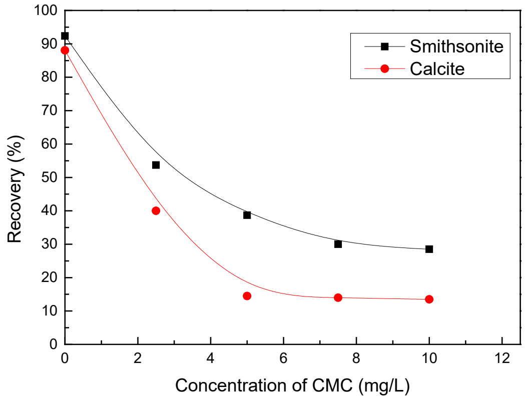

Fig. 7. Flotation results of smithsonite and calcite at pH 8 as a function of CMC concentration with 2×10^{-4} mol/dm^3 potassium lauryl phosphate (DS = 1.2)

The effect of water glass (WG) concentration as a depressant on the flotation recoveries of smithsonite and calcite is shown in Fig. 6. As we can see from Fig. 6, WG is a more effective depressant for smithsonite than calcite. The addition of WG decrease the recoveries of smithsonite and calcite sharply, and recoveries are less than 20% in the absence of 500 mg/dm^3 WG, which is mainly due to the fact that Si(OH)$_4$ species, a possible result with the increases of WG concentration, can form hydrophilic colloidal silica that adsorb on the smithsonite and calcite (Feng et al., 2015; Dong et al., 2018). As result, the separation of smithsonite from calcite is impossible in the presence of WG.

In order to depress calcite, carboxymethyl cellulose (CMC (DS=1.2)) is used as a depressant. The result can be clearly seen in Fig. 7. As shown in Fig. 7, CMC can depress the flotation of both smithsonite and calcite. The recoveries of smithsonite and calcite can be as low as 30% and 10% respectively by increasing CMC concentration to 7mg/dm^3. Carboxyl and hydroxyl groups of the carboxymethyl cellulose molecules can provide protons, while carboxyl groups on the surface of carbonate minerals can accept protons. Thus, some polar groups in carboxymethyl cellulose are adsorbed on the mineral surface by hydrogen bonding, while many other hydroxyl groups make the mineral surface hydrophilic by associating with water (Wang and Somasundaran, 2005; Cao and Ji, 2006; Tian et al., 2017). On the basis of the result, it is demonstrated that CMC cannot separate smithsonite from calcite at pH 8.

Results obtained with lignosulfonate calcium (LSC) concentration variation between 0.0 and 70 mg/ are plotted in Fig. 8. The effect of LSC on the recovery of calcite is very obvious, but it has little effect on smithsonite flotation. The recovery of calcite is less than 30% with 30 mg/dm^3 LSC, while the recovery of smithsonite can be kept at about 70%. It can thus be expected that calcium plays a key role in the adsorption mechanism of lignosulphonate on the surface of calcite. The reason is most likely that the surface of calcite is positively charged at pH 8, which can generate electrostatic adsorption with the negatively charged LSC and enhance the adsorption capacity of lignin sulfonate on the surface of calcite. Calcium may play, through electrostatic interactions, the role of a bridge between the surface of the calcite and the lignosulphonate (Guern et al., 2000). Therefore, the selective depressant effect of LSC on calcite was analyzed through interactions between the LSC micelles and mineral particles at water/particle interface (Chen et al., 2018). Calcium species on the calcite surface appear to act as adsorption sites for the anionic polyelectrolytes (Ma and Pawlik, 2007). The above results indicate that LSC could act as a suitable depressant to depress calcite on smithsonite flotation.

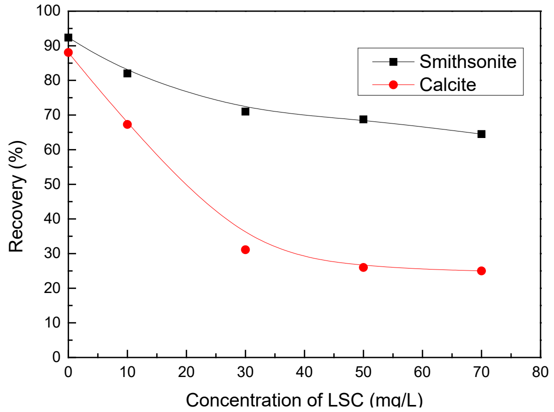

Fig. 8. Flotation results of smithsonite and calcite at pH 8 as a function of LSC concentration with 2×10^{-4} mol/dm^3 potassium lauryl phosphate

3.1.3. Separation of mixture mineral

The single mineral flotation results indicate that that it may be possible to depress calcite on smithsonite flotation with potassium lauryl phosphate when using lignosulfonate calcium (LSC) as depressant. Mixed smithsonite and calcite flotation tests have been conducted with 3×10^{-4}mol/dm^3 potassium lauryl phosphate collectors at pH 8 using 40 mg/dm^3 LSC and the result is shown in Table 1. It can be seen from Table 1 that the recovery of smithsonite is 70.06% and the grade of Zinc is 33.85%. While the recovery of calcite is 27.55% and the grade of Calcium is 11.03%. The results suggest that an effective separation of smithsonite from calcite can be achieved with the reagent scheme of potassium lauryl phosphate as collector and LSC as depressant.

Table 1 Flotation results of mixed smithsonite/calcite

Products	Yield / %	Zinc grade/ %	Zinc recovery/ %	Calcium grade/ %	Calcium recovery/ %
Concentrate	50.75	33.85	70.06	11.03	27.55
Tailings	49.25	14.90	29.94	29.89	72.45
Feed	100.00	24.52	100.00	20.32	100.00

3.2. Zeta potential results

Figs. 9 and 10 presents the zeta potential of smithsonite and calcite with and without reagents as a function of pH, respectively. The IEP (isoelectric point) of smithsonite occurs at pH 7.9, while the IEP of calcite occurs at pH 9.2, similar to the studies of Hu and Yan (Hu et al., 1995; Yan et al., 2017). It can be seen from Fig. 9 that the addition of LSC alone causes a decrease by 7mV in zeta potential of smithsonite around pH 8, indicating a weak interaction of negatively charged LSC species on negatively charged smithsonite. In the presence of LSC and potassium lauryl phosphate, the zeta potential of smithsonite is more negative (decreases from −8 mV to −53 mV) compared to LSC alone, illustrating that conditioning of smithsonite with LSC prior to potassium lauryl phosphate addition cannot prevent the adsorption of collectors on smithsonite surface.

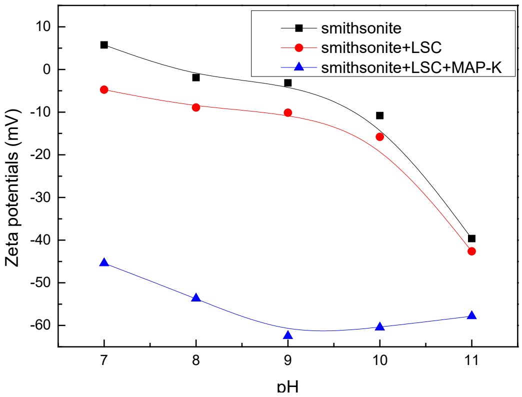

Fig. 9 Effect of reagent adding on the zeta potential of smithsonite as a function of pH (LSC (lignosulfonate calcium) = 30 mg/dm^3, MAP-K (potassium lauryl phosphate) = 2×10^{-4} mol/dm^3)

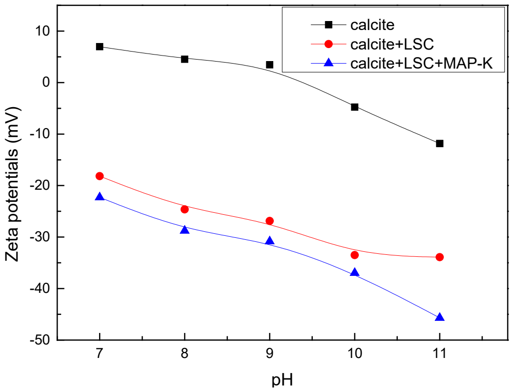

Fig. 10 Effect of reagent adding on the zeta potential of calcite as a function of pH (LSC (lignosulfonate calcium) = 30 mg/dm^3, MAP-K (potassium lauryl phosphate) = 2×10^{-4} mol/dm^3)

Fig. 10 shows that the zeta potential of calcite decreases significantly in the presence of LSC, it changes from positive to negative by 24mV around pH 8. In the presence of LSC and potassium lauryl phosphate, the surface charge of calcite changes slightly comparing to the result of addition of the LSC alone.

The zeta potential results illustrate that conditioning of smithsonite with LSC prior to potassium lauryl phosphate addition does not prevent the adsorption of potassium lauryl phosphate on smithsonite but demonstrates that the presence of LSC hinders the potassium lauryl phosphate adsorption on calcite surfaces. The result is very important for flotation studies because of the difficulty in selective separation of smithsonite from calcite when using potassium lauryl phosphate (MAP-K) as collector.

4. Conclusions

(1) Flotation tests show that smithsonite and calcite can be floated with potassium lauryl phosphate in the pH range of 7-11. The maximum recoveries of smithsonite and calcite can reach 90% and 85% respectively using 2×10^{-4} mol/dm^3 potassium lauryl phosphate at pH 8. In order to depress calcite, different depressants are investigated in this paper. Both water glass (WG) and carboxymethyl cellulose (CMC) cannot attain the desirable performance. Regarding sodium hexametaphosphate (SHMP) and lignosulfonate calcium (LSC) as depressants of calcite, both of them can efficiently decrease the recovery of calcite, but SHMP has more negative effect on smithsonite recovery than LSC.

(2) The separation test of manual mixed mineral shows that the recovery of smithsonite is 70.06% and the grade of Zinc is 33.85% with 3×10^{-4} mol/dm^3 potassium lauryl phosphate collectors at pH 8 using 40 mg/dm^3 LSC. The results suggest that an effective separation of smithsonite from calcite can be achieved with the reagent scheme of potassium lauryl phosphate as collector and lignosulfonate calcium (LSC) as depressant.

(3) Zeta potential measurements indicate that after pretreatment of the smithsonite and calcite with LSC does not prevent potassium lauryl phosphate absorb on smithsonite surface while it prevents potassium lauryl phosphate to adsorb on calcite surface. Under these circumstances, it can be indicated that potassium lauryl phosphate is an appropriate collector in selective separation of smithsonite from calcite when using lignosulfonate calcium (LSC) as depressant.

Acknowledgments

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