

Short communication

Flotation separation of scheelite from calcite using mixed cationic/anionic collectors

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ABSTRACT

In this study, flotation behavior of scheelite and calcite was investigated using mixed cationic/anionic collectors of dodecylamine (DDA) and sodium oleate (NaOL). Individual NaOL or DDA was also tested for comparison. The flotation results of single mineral and mixed binary minerals demonstrated a high selectivity and recovery for the flotation of scheelite from calcite at pH 7 using mixed DDA/NaOL collectors. The adsorption mechanism of the selective separation was analyzed through zeta potential measurement.

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1. Introduction

Scheelite CaWO_4 , which is the most important tungsten-containing mineral, usually coexists with other calcium-containing gangue minerals in ore deposit. Among the gangue minerals, calcite is the most common one. Flotation is usually used for the separation of scheelite from calcite (Deng et al., 2016; Y. Gao et al., 2016). However, the flotation separation is difficult since they have the same active Ca atoms on their cleavage surfaces, and hence similar flotation response to conventional fatty acid collectors (Rai et al., 2002). To achieve more effective separation, many efforts have been focused on the exploitation of new collector or mixed collectors, such as cationic (Yang et al., 2015), amphoteric (Deng et al., 2016), anionic (Xian et al., 2001), and mixed anionic/nonionic collectors (Gao et al., 2015a). Up to now, mixed anionic/cationic collectors have not been used for the separation.

Dodecylamine (DDA), a common cationic collector, shows some selectivity for the separation but relatively poor collecting power for scheelite (Arnold et al., 1978; Gao et al., 2015b). Sodium oleate, a common anionic collector, always has strong collecting power but poor selectivity for many minerals. In recent years, mixed anionic/cationic collectors have been reported to exhibit enhanced recovery and selectivity for different kinds of minerals, especially for oxide and silicate minerals, such as smithsonite (Ejtemaei

et al., 2011; Hosseini and Forssberg, 2007), feldspar (Vidyadhar and Hanumantha, 2000; Vidyadhar and Rao, 2007), hematite (Vidyadhar et al., 2012), and muscovite (Wang et al., 2014; Xu et al., 2013).

In this work, the flotation behavior of scheelite and calcite using mixed cationic/anionic collectors of DDA/NaOL was investigated by flotation experiments using single mineral and mixed binary minerals. The adsorption mechanism was analyzed through zeta potential measurement.

2. Materials and methods

2.1. Materials and reagents

Pure calcite was taken from Changsha, China; and scheelite from Qinghai, China. The X-ray powder diffraction spectrums showed that scheelite and calcite samples were 95% and 99% pure, respectively. Both minerals were ground in ceramic ball mill. The fraction sized +38–74 μm was used in flotation tests. Samples further ground (mortar and pestle) to $-2 \mu\text{m}$ in an agate mortar were used for zeta potential measurements.

Analytically pure DDA and sodium silicate (SS , $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) were supplied by Sinopharm Chemical Reagent, China. Analytically pure NaOL was provided by Hunan Huihong Reagent, China. The pH was adjusted with HCl and NaOH stock solutions. Deionized (DI) water with a resistivity of over $18 \text{ M}\Omega \times \text{cm}$ was used throughout the experiments.

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2.2. Flotation tests

Flotation tests using single mineral and mixed binary minerals were carried out in an XFG flotation machine at a spindle speed of 1700 rpm (Y. Gao et al., 2016). The mineral suspension was prepared by adding 2.0 g (1.0 g scheelite and 1.0 g calcite for mixed binary minerals) of single mineral samples to 40 mL of DI water. The pH of the suspension was adjusted and recorded. After each of the desired reagents was added, the suspension was agitated for 3 min. The flotation lasted for 3 min. For single mineral flotation, the flotation products were dried and weighed, and the recovery was calculated. For mixed binary minerals, the flotation concentrates and tails were assayed for W and Ca.

2.3. Zeta potential measurements

Zeta potential measurements were conducted at 20 °C using a Nano-ZS90 zeta potential analyzer (Malvern Instruments, UK). A dilute mineral suspension was prepared by adding 0.02 g of mineral samples to 40 mL KCl (0.01 mol/L) solution. Then the desired reagent(s) was/were added as the same order of flotation experiment, and the pH was adjusted and measured. The suspension was magnetically stirred for 10 min. After a standing of 5 min, the supernatant liquid was sucked out and used for measurement. At least 3 measurements were made for a certain experimental condition, and the average value of zeta potential and the standard deviation were calculated.

3. Results and discussions

3.1. Flotation test results

A series of flotation results showed that using DDA/NaOL could achieve an efficient separation of scheelite from calcite. The preferred order of collector addition was DDA and then NaOL. The results of effect of molar ratio of DDA/NaOL and pH level on the flotation separation were presented in Figs. A1 and A2 of supplementary material available for this article online. The results indicated that a molar ratio of 2:1 (1×10^{-4} mol/L/ 5×10^{-5} mol/L for DDA/NaOL) and pH 7 are preferred for a more favorable recovery and selectivity.

Fig. 1 shows the results of single mineral and mixed binary minerals flotation tests. It can be seen from Fig. 1(a) that individual collector (DDA or NaOL) flotation shows some selectivity. However,

the scheelite recovery is lower than 78%, and very sensitive to the SS dosage. Notice that mixed DDA/NaOL collectors show a much better selectivity. Moreover, the scheelite recovery maintains about 90%, and is little influenced by SS dosage. At SS dosage of over 300 mg/L, the scheelite recovery is 90%, and the calcite flotation is completely depressed. Fig. 1(b) shows that, using DDA/NaOL collectors at a SS dosage of 160 mg/L, both recovery and grade of scheelite reach 70% for the mixed binary minerals flotation tests.

3.2. Zeta potential measurement results

Zeta potential values of pure scheelite and calcite at pH 7 were measured to be -19.2 mV and 9.32 mV, respectively, which agreed well with previous reports (Gao et al., 2015a, 2015b; Y. Gao et al., 2016; Z. Gao et al., 2016; Hiçiyilmaz et al., 1993). Fig. 2 shows zeta potential values of scheelite and calcite in the presence of various reagents (DDA = 1×10^{-4} mol/L, NaOL = 5×10^{-5} mol/L, pH = 7).

It can be observed that the addition of 300 mg/L SS in scheelite suspension causes a decrease by 25 mV in zeta potential for scheelite. This might be mainly attributed to the physisorption of $\text{SiO}(\text{OH})_3^-$ of SS species on scheelite (confirmed by XPS results of Fig. A3(a) in supplementary material) since few Ca atoms reside on the negatively charged scheelite surfaces (Yang et al., 2008; Z. Gao et al., 2016). Then, the addition of DDA leads to an increase in zeta potential by 10 mV, indicating that DDA species could adsorb on SS pre-adsorbed scheelite by electrostatic attraction. Subsequently, the addition of NaOL creates a potential decline by 15 mV, indicating that oleate species could readily adsorb on SS + DDA pre-adsorbed scheelite.

For calcite, the addition of 300 mg/L SS produces a marked drop in zeta potential by 40 mV. This might be due to a strong chemisorption of $\text{SiO}(\text{OH})_3^-$ at Ca sites on positively charged calcite surfaces (confirmed by XPS results of Fig. A3(b) in supplementary material). Then the added DDA causes an increase by 19 mV in the potential of SS pre-adsorbed calcite. The subsequent addition of NaOL makes a little change in zeta potential, indicating that oleate species could not favorably adsorb on SS + DDA pre-adsorbed calcite.

It is tenable to conclude that SS and DDA could successively adsorb on each mineral surface, and there is a much stronger adsorption of SS on calcite surface (confirmed by XPS results of Table A1 in supplementary material). The main difference lies in that a promotion effect of pre-adsorbed DDA on the subsequent

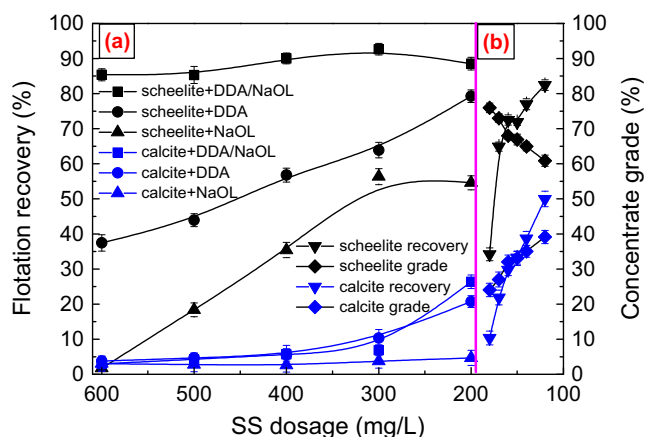


Fig. 1. Effect of SS dosage on the flotation behavior of scheelite and calcite using DDA, NaOL, or DDA/NaOL as collector in single mineral (a) and mixed binary minerals (b) flotation tests. (a) DDA = 1×10^{-4} mol/L, NaOL = 5×10^{-5} mol/L; (b) DDA = 0.5×10^{-4} mol/L, NaOL = 2.5×10^{-5} mol/L).

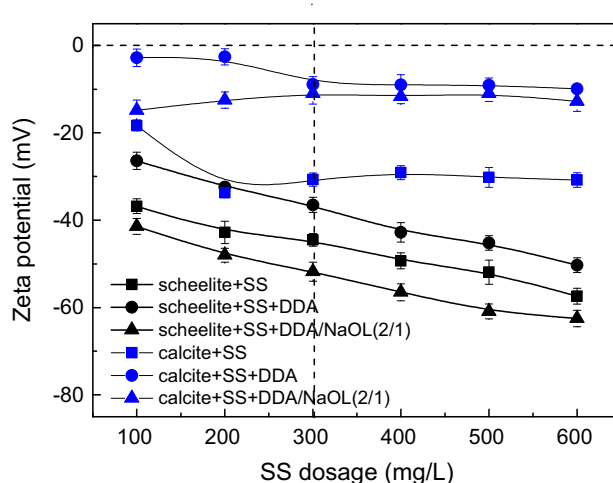


Fig. 2. Zeta potentials of scheelite and calcite in the presence of various flotation reagents.

oleate adsorption is observed on scheelite surfaces. This effect might be due to that oleate could weaken the head-head electrostatic repulsion between pre-adsorbed RNH_3^+ , and increases the hydrophobic association of lateral carbon chains (Wang et al., 2014; Hosseini and Forssberg, 2007). This effect could help build much more hydrophobic scheelite surfaces, leading to a good flotation response for scheelite. However, a much stronger SS pre-adsorption could prevent the subsequent oleate adsorption on calcite surfaces, and hence depress the calcite flotation.

4. Conclusions

Mixed cationic/anionic collectors of DDA/NaOL at 2:1 molar ratio, show stronger collecting ability and higher selectivity to scheelite flotation than individual collector. The preferred order of collector addition is DDA and then NaOL. The mixed DDA/NaOL collectors with SS at pH 7 could achieve selective flotation of scheelite from calcite. Owing to the lower dosage and higher selectivity, the mixed DDA/NaOL collectors exhibit great potential for industrial application in scheelite flotation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.mineng.2016.09.006>.

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