

# Selective flotation of scheelite from calcite: A novel reagent scheme



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## ABSTRACT

Sodium oleate (NaOl) has been widely used as a collector for the scheelite flotation. However, low selectivity of NaOl and large amount of sodium silicate (SS) needed remain tough problems. In this study, octyl hydroxamic acid (HXMA-8) was used as an associate collector with NaOl in scheelite flotation. The flotation tests showed that a novel reagent scheme, i.e., a lower dosage of SS (300 mg/L) and mixed collectors of HXMA-8 + NaOl (total concentration  $4.5 \times 10^{-4}$  mol/L, preferred mass ratio of 1:2) achieved the selective separation of scheelite from calcite. Zeta potential measurements indicated that the depressant, SS, adsorbed more strongly on calcite surface than on scheelite surface. HXMA-8 adsorbed significantly on scheelite surface either in the absence or presence of SS by chemical bonding between oxygens of HXMA-8 and surface metal ions. NaOl also adsorbed on both mineral surfaces by chemisorption, but the adsorption on calcite surface was influenced adversely by the presence of SS.

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## 1. Introduction

Scheelite, as an important tungsten-bearing mineral, is nowadays utilized mainly by flotation (Bo et al., 2015; Gao et al., 2015a, 2015b; Yin and Wang, 2014). In ore deposits, scheelite always coexists with other calcium-containing minerals such as calcite and fluorite. Owing to the same Ca active sites on their cleavage planes (Rai et al., 2002), the commonly used fatty acid anionic collector, such as sodium oleate, can strongly collect all of them and exhibit little selectivity. Cationic collectors, such as amine (Hiçiyilmaz et al., 1993) and quarternary ammonium (Hu et al., 2011; Yang et al., 2015) and collector mixture (Gao et al., 2015a, 2015b) have been used to improve the scheelite flotation.

Moreover, hydroxamate collectors, such as benzohydroxamic acid (Xian et al., 2001; Yin and Wang, 2014), naphthenic hydroxamates (Zhao et al., 2013) and amide hydroxamate (Deng et al., 2016), were also used for scheelite flotation in recent years. In fact, alkyl hydroxamates have been proved to be the selective and effective collectors for various of minerals, such as cassiterite (Sreenivas and Padmanabhan, 2002), kaolin clay (Yoon et al., 1992), bastnaesite (Fuerstenau, 1983), mixed copper oxide and sulfide minerals (Lee et al., 2009; Lee et al., 1998). Those reports indicated that the -CONHOH group in hydroxamates exhibits a strong chelating ability with metal ions exposed on the mineral surfaces. Till now, however, few work has been focused on alkyl hydroxamate as a collector for scheelite flotation.

Recent work showed that, octyl hydroxamic acid (HXMA-8), one kind of alkyl hydroxamic acids, can achieve the separation of fluorite

from calcite and apatite with a higher selectivity compared with conventionally used oleate (Pradip et al., 2002; Pradip and Rai, 2003). In this work, HXMA-8 was considered as an associate collector with oleate to improve the selectivity of scheelite flotation from calcite. The mechanism of the selective separation was studied by zeta potential measurement.

## 2. Materials and methods

### 2.1. Experimental minerals and reagents

Pure scheelite crystals were obtained from Sichuan, China, and calcite from Fujian, China. XRD spectrums (showed in Fig. 1) confirmed that the scheelite and calcite samples were over 98% and 99% pure respectively. The +37–74  $\mu\text{m}$  fraction was used for the flotation tests. Samples further ground to –5  $\mu\text{m}$  in an agate mortar were used for zeta potential measurements.

Chemically pure reagents were obtained from the following sources: octyl hydroxamic acid (HXMA-8,  $\text{C}_8\text{H}_{17}\text{NO}_2$ ) from Jusheng Science and Technology Ltd., Hubei, China; sodium oleate (NaOl,  $\text{C}_{18}\text{H}_{33}\text{O}_2\text{Na}$ ) from Baisaiqin Chemical Technology co., Ltd., Shanghai, China; sodium silicate (SS,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) from Zhuzhou Flotation Reagents Factory, Hunan, China. The molecular structures of HXMA-8 and NaOl are shown in Fig. 2. The pH was adjusted with NaOH or HCl stock solutions. Deionized water (18  $\text{m}\Omega \times \text{cm}$ ) was used for all experiments.

### 2.2. Flotation experiment

Pure mineral flotation tests were carried out in an XFG-type flotation machine (Fig. 3) with a 40 mL plexiglass cell, and the impeller speed

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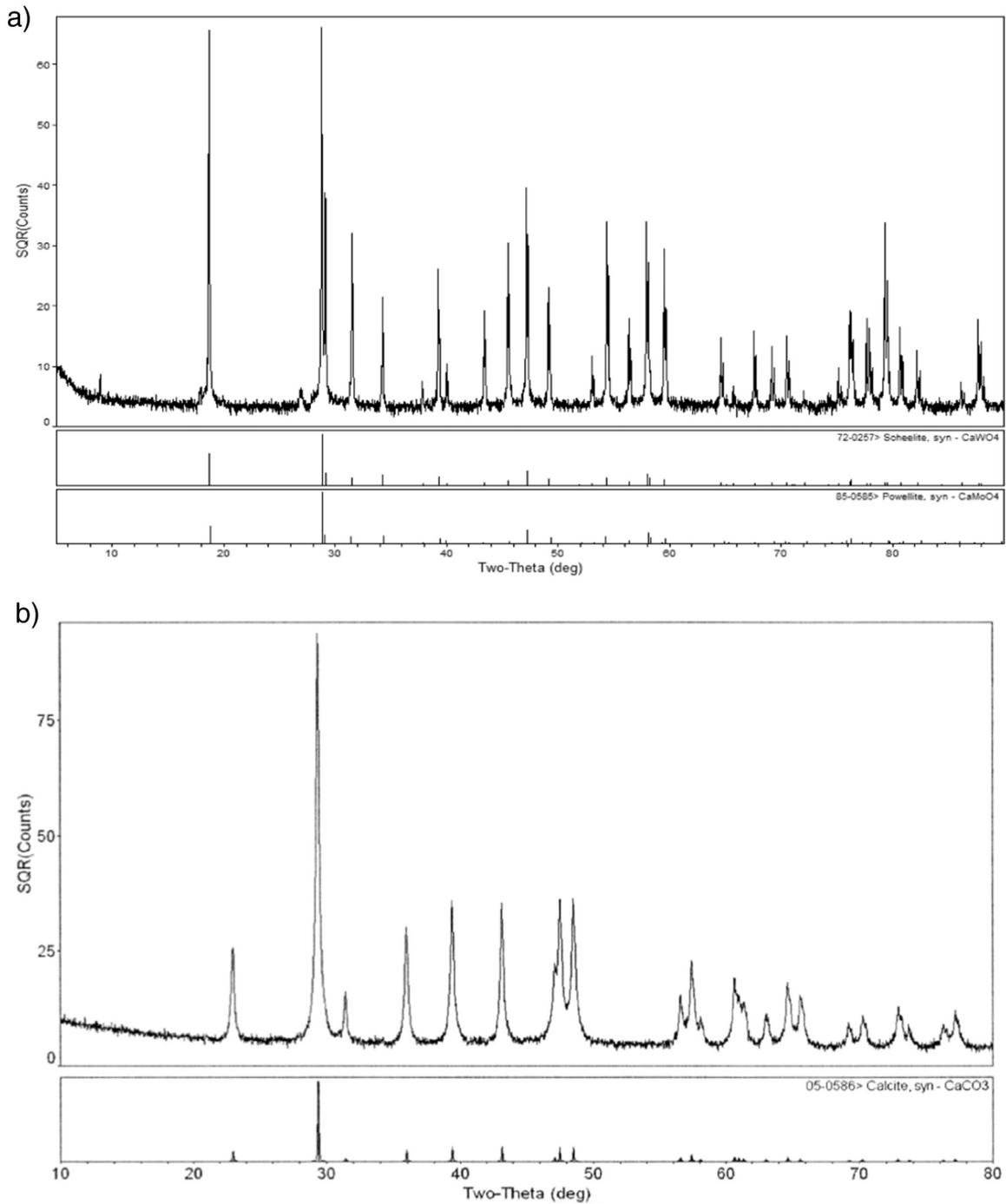


Fig. 1. XRD spectrums of the scheelite (a) and calcite samples (b) used for flotation tests.

was set to 1400 rpm. The procedure of pure mineral flotation tests is as follows: (1) adding 2.0 g minerals and 35 mL deionized water to the plexiglass cell and agitating for 1 min to obtain mineral suspension; (2) adjusting pulp pH by adding pH regulators and agitating for 2 min; (3) adding depressant and agitating for 3 min; (4) adding collector (for collector mixture, adding HXMA-8 and NaOI successively) and agitating for 3 min; (5) collecting floated products for 3 min; (6) filtering, drying, and weighing the products to calculate the recovery. The flowsheet of single mineral flotation test is presented in Fig. 4.

### 2.3. Zeta potential measurement

Zeta potential measurements were conducted at 20 °C using a zeta potential analyzer (ZetaPlus, Bruker, Germany). Mineral suspensions

containing 0.02 g of solids and 40 mL KCl (0.01 mol/L) background electrolyte were prepared in a beaker at a given pH and a collector concentration. After settling for 5 min, the supernatant liquor was used for zeta potential measurement.

## 3. Results and discussions

### 3.1. Single mineral flotation experiments

Single mineral flotation tests were conducted using HXMA-8 as the single collector at pH 8.3 (natural pH of scheelite suspension) in the absence and presence of 200 mg/L regulator SS. The results are shown in Fig. 5. In the absence of SS, scheelite recovery steadily increases with increasing HXMA-8 dosage till up to  $1.5 \times 10^{-4}$  mol/L where it reaches a

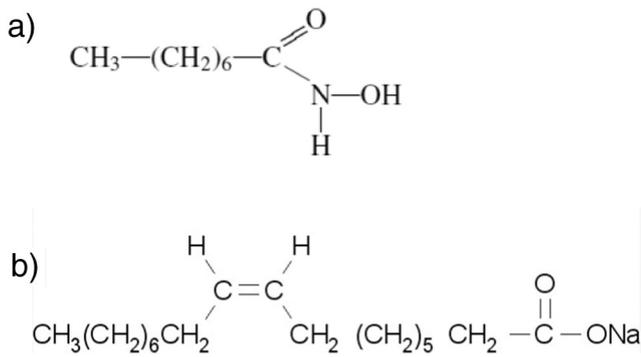


Fig. 2. Molecule structures of HXMA-8 (a) and NaOl (b).

maximum of 65.48%, which may be caused by the monolayer adsorption of collectors on scheelite surface. And then the scheelite recovery decreases when the HXMA-8 dosage is  $>1.5 \times 10^{-4}$  mol/L, which may be due to that the adsorption of HXMA-8 molecules on top of the monolayer involves reverse orientation with the function group positioned towards the pulp, or surface precipitation of calcium hydroxamate uneven distributed in outer layer of pre-adsorbed surfactants results in the less hydrophobicity for scheelite surface (Mielczarski et al., 1993; Lu et al., 1997). Calcite flotation behaves similarly, but the calcite recovery is 10–15% lower than the scheelite. The pre-addition of SS has little effect on the HXMA-8 flotation of scheelite, but partly depresses that of calcite. These results indicate that HXMA-8 is a moderate collector and exhibits some selectivity towards the separation of scheelite from calcite.

In comparison, flotation tests using NaOl as the single collector were conducted at pH 8.3 in the absence or presence of 200 mg/L SS. The results are shown in Fig. 6. In the absence of SS, the recoveries of both minerals steadily increase with increasing NaOl dosage till up to  $3 \times 10^{-4}$  mol/L, where the calcite recovery is 10% higher than scheelite. Similarly, in the presence of SS, scheelite flotation using NaOl is faintly influenced, but calcite recovery is 10% lower than that in the absence



Fig. 3. XFG flotation machine for pure mineral flotation tests.

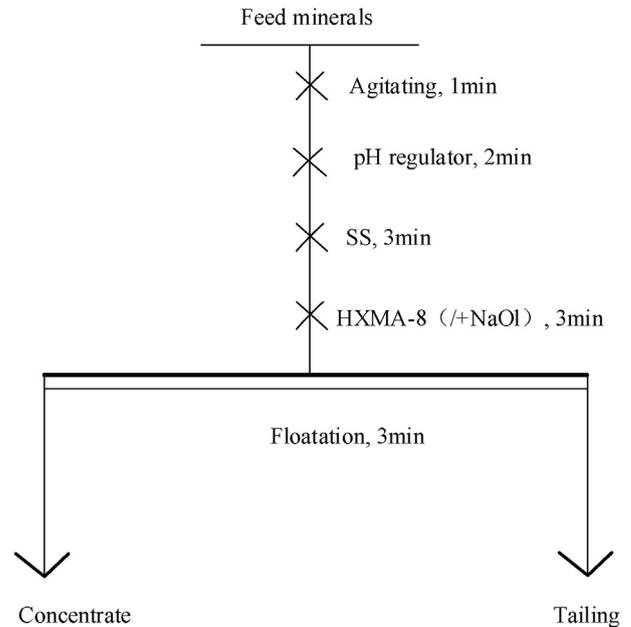


Fig. 4. Flowsheet of pure mineral flotation test.

of SS. These results indicate that NaOl is a much stronger collector than HXMA-8, but exhibits little selectivity towards the separation of scheelite and calcite.

Considering the collecting power of NaOl and the selectivity of HXMA-8, flotation tests using collector mixture of HXMA-8 and NaOl were conducted to find out the preferred mass ratio of two collectors with total dosage at  $3 \times 10^{-4}$  mol/L and pH 8.3. The results are seen in Fig. 7. It is obvious to note that a mass ratio of 0.5 of HXMA-8 to NaOl is preferred to obtain a higher selectivity between scheelite and calcite while scheelite has a higher recovery of 80%. The preferred mass ratio of 0.5 (i.e., 1:2) was chosen for the following flotation tests.

Fixed the mass ratio of HXMA-8 and NaOl to be 1:2, the flotation behavior of scheelite and calcite was investigated using different dosages of HXMA-8, and the results are shown in Fig. 8. Scheelite recovery increases clearly with the increase of HXMA-8 dosage till up to  $1.5 \times 10^{-4}$  mol/L where it gets the maximum of 84.93%, and then it sees a slight decrease with further increasing dosage. This trend is quite similar with what was shown in Fig. 5. Calcite recovery rises remarkably before it is stable at 70%. The dosages of HXMA-8 and NaOl

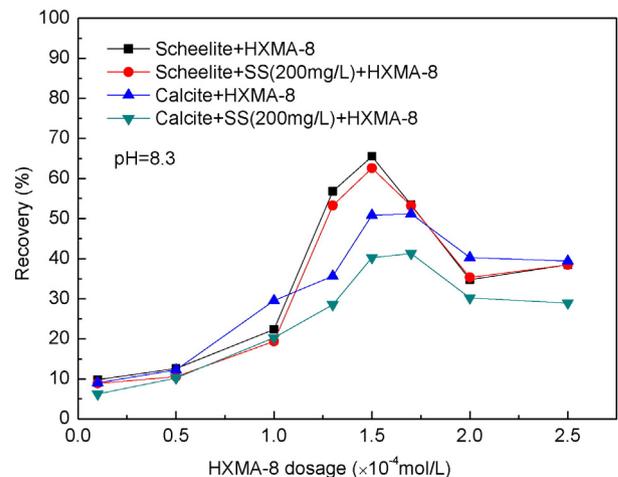


Fig. 5. Effect of HXMA-8 dosage on the recoveries of scheelite and calcite in the absence or presence of SS.

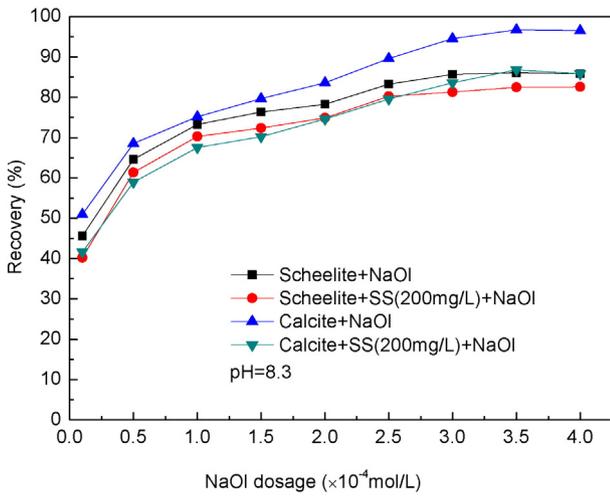


Fig. 6. Effect of NaOI dosage on the recoveries of scheelite and calcite in the absence or presence of SS.

were  $1.5 \times 10^{-4}$  mol/L and  $3 \times 10^{-4}$  mol/L, respectively, used in later tests.

The flotation behavior of scheelite and calcite using collector mixture and different dosages of SS was investigated, and the results are seen in Fig. 9. The results indicate that the presence and the dosage (below 300 mg/L) of SS have little influence on the scheelite recovery. However, calcite recovery markedly drops to <10% when the SS dosage is over 300 mg/L. Thereby 300 mg/L SS was chosen for the following tests.

The pulp pH on the preferred reagent combination of SS + (HXMA-8 + NaOI) was studied, and the results are presented in Fig. 10. Scheelite recovery is notably higher than calcite over the entire pH range studied. It is worth noting that the flotation selectivity remains perfect in the wide range pH 8–10. These results demonstrate that the scheelite separation from calcite can be effectively achieved at pH 8–10 using a novel reagent scheme of SS + HXMA-8 + NaOI.

### 3.2. Zeta potential measurement results

To uncover the separation mechanism of the novel reagent scheme, zeta potentials of scheelite and calcite in the absence and presence of the different reagents were measured, and the results are provided in Fig. 11.

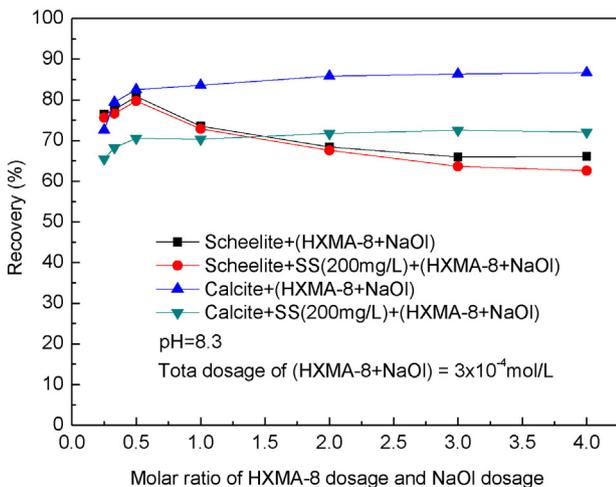


Fig. 7. Effect of the mass ratio of collector mixture of HXMA-8 and NaOI on the recoveries of scheelite and calcite.

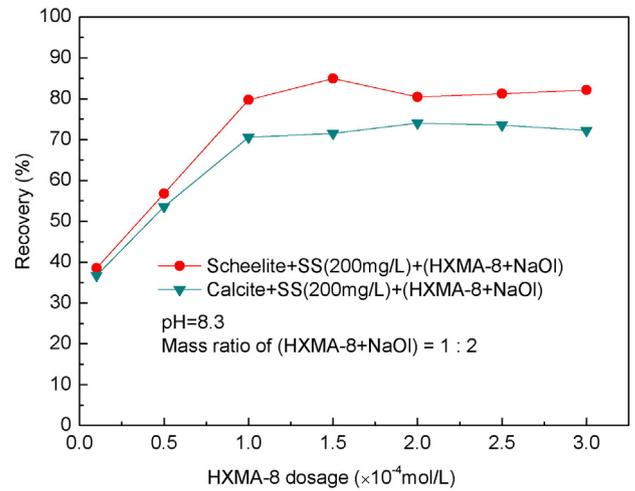


Fig. 8. Effect of HXMA-8 dosage on the recoveries of scheelite and calcite using collector mixture of HXMA-8 and NaOI at a mass ratio of 1:2.

Fig. 11 shows that in the pH range of 6–11, bare scheelite is negatively charged, which agrees well with other reports (Gao et al., 2016; Gao et al., 2015a, 2015b; Bo et al., 2015; Hu and Xu, 2003; Yang et al., 2015). In the absence of any reagent, the IEP (Isoelectric Point) of calcite is pH 8.8, which is in the range of previous reports (Somasundaran and Agar, 1967).

From Fig. 11(a) and (b), the change of zeta potential of scheelite is much larger than that of calcite when interacted with HXMA-8, indicating that HXMA-8 adsorbs more strongly on scheelite surface. This intense adsorption may be attributed to the formation of O—Ca bonds between oxygens of hydroxamic acid and surface Ca sites. Recent work showed that the mineral and reagent with similar O—O distance are more likely to form —O— metal and =O metal bonds (Yin and Wang, 2014). The O—O distance in hydroxamic group (2.842 Å) is closer to that in scheelite lattice (2.899 Å) and not comparable to 2.224 Å in calcite (Deng et al., 2016), leading to a much stronger interaction of HXMA-8 with scheelite. However, when interacting with NaOI, the zeta potential change of scheelite is much smaller than that of calcite, mainly due to a relatively weak interaction of anionic oleate species with negatively charged scheelite surface by chemisorption (Rai et al., 2002; Hu et al., 2012; Pugh and Stenius, 1985).

The addition of SS causes a less zeta potential decrease for bare scheelite than for calcite at pH > 8, indicating that SS adsorbs more strongly on bare calcite surface than on scheelite surface. The reason

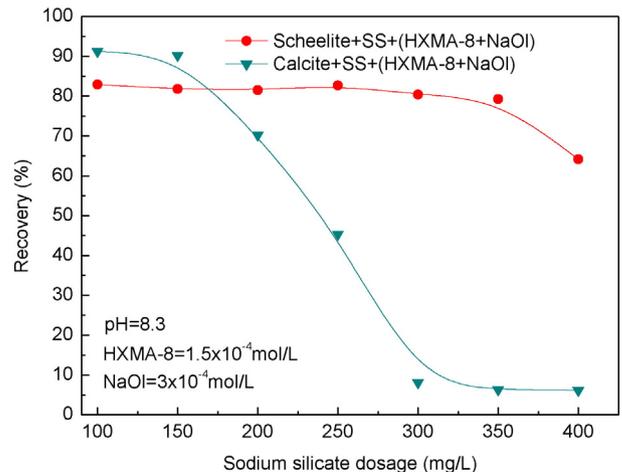


Fig. 9. Effect of SS dosage on the recoveries of scheelite and calcite using collector mixture of HXMA-8 and NaOI.

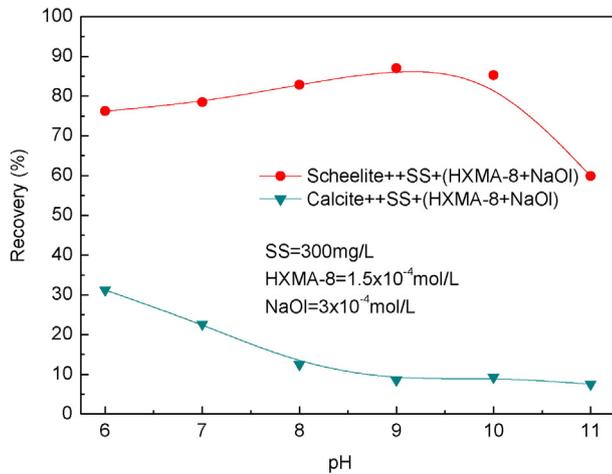


Fig. 10. Effect of pulp pH on the recoveries of scheelite and calcite using depressant SS and collector mixture of HXMA-8 and NaOI.

may be that anionic species ( $\text{SiO}(\text{OH})_3^-$ ) of SS can easily adsorb on positively charged calcite driven by electrostatic attraction in comparison with negatively charged scheelite surface (Yang et al., 2008; Bo et al., 2015; Mishra, 1982).

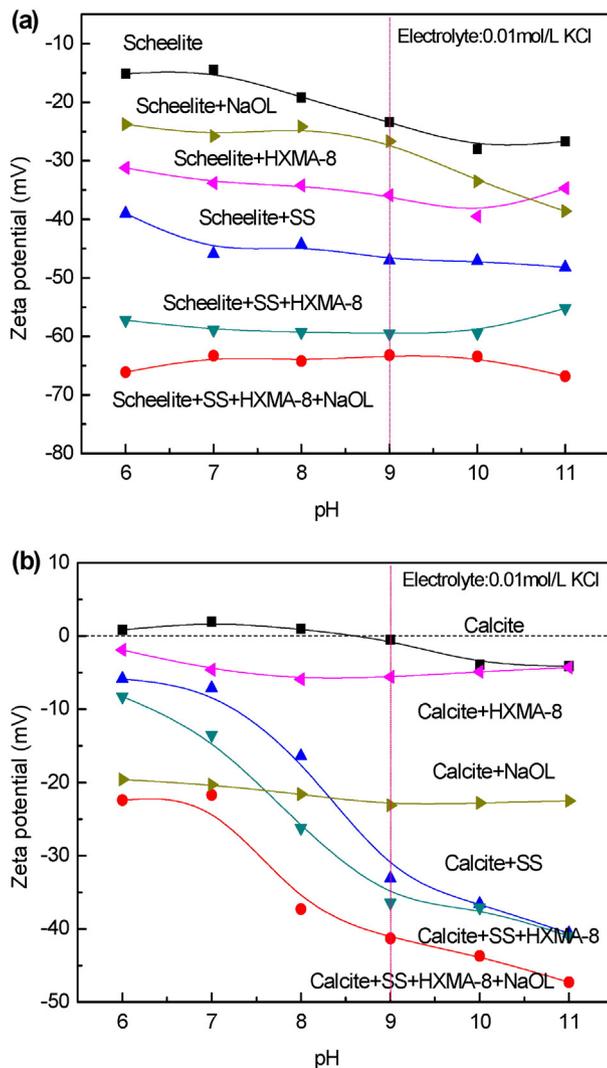


Fig. 11. Effect of the addition of different reagents on the zeta potential of scheelite (a) and calcite (b) minerals (SS = 200 mg/L; NaOI =  $3 \times 10^{-4}$  mol/L; HXMA-8 =  $1.5 \times 10^{-4}$  mol/L).

After the addition of HXMA-8, zeta potential witnesses a much larger decrease on scheelite + SS than on calcite + SS at pH 9, indicating that HXMA-8 still has a strong adsorption ability on SS pre-adsorbed scheelite surface than on calcite + SS surface, and that the SS pre-adsorption has negligible influence on the adsorption of HXMA-8 on scheelite surface. And then, the addition of NaOI causes a zeta potential decrease by 6 mV on “calcite + SS + HXMA-8”, which is much less than 23 mV decrease from calcite to calcite + NaOI, indicating that the presence of SS prevents the adsorption of oleate (Marinakis and Shergold, 1985). However, the zeta potential decrease by 3.8 mV from “scheelite + SS + HXMA-8” to “scheelite + SS + HXMA-8 + NaOI” is similar with 3.4 mV from scheelite to scheelite + NaOI, implying that SS has little effect on the adsorption of NaOI on scheelite (Rao et al., 1990).

#### 4. Conclusions

In this work, octyl hydroxamic acid (HXMA-8) was used as an associate collector with NaOI for scheelite flotation. A novel reagent scheme, i.e., 300 mg/L of SS depressant and  $4.5 \times 10^{-4}$  mol/L of HXMA-8 + NaOI collector mixture (preferred mass ratio of 1:2) at pH 8–10, was proved to achieve the selective flotation separation of scheelite from calcite.

Zeta potential measurements indicated that the depressant, SS, adsorbed more strongly on calcite surface by electrostatic attraction. Collector HXMA-8 adsorbed more strongly on scheelite surface than on calcite in the absence and presence of SS. The interactions of HXMA-8 and scheelite were inferred to be O—Ca bonds. The presence of SS affected adversely the adsorption of NaOI on calcite surface, while it had little effect on the NaOI adsorption on scheelite surface.

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