

# Selective flotation of scheelite from calcite and fluorite using a collector mixture



Zhiyong Gao\*, Ding Bai, Wei Sun, Xuefeng Cao, Yuehua Hu\*

School of Minerals Processing and Bioengineering, Central South University, Changsha, China

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## ABSTRACT

Collector 733, a sodium soap ( $C_{12-16}COONa$ ) is widely used industrially for scheelite flotation. Low selectivity of 733 collector is always observed. In this study, a collector mixture of 733 and MES (sodium fatty acid methyl ester sulfonate) demonstrated a high selectivity for the flotation of scheelite from calcite and fluorite. An optimal mass ratio 4:1 of 733:MES was found, producing a 65.76%  $WO_3$  concentrate grade with a recovery of 66.04% from a feed material containing only 0.57%  $WO_3$ . In addition, the effect of water hardness and water glass addition were studied. The results indicated that the presence of  $Ca^{2+}$  or  $Mg^{2+}$  had little effect on the adsorption of the collector mixture at the scheelite surface. Addition of water glass for depressing calcite and fluorite had no significant effect on the adsorption of the collector mixture on the scheelite surface. The advantages of this new collector mixture (733+MES) include lower cost, low dosage, high tolerance against water hardness and high selectivity, and this collector mixture has great potential for industrial application.

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## 1. Introduction

The flotation separation of scheelite from other calcium-containing minerals such as fluorite and calcite, is problematic, due to their similar solubility and the same active  $Ca^{2+}$  site for interaction with anionic collectors (Rai et al., 2011). Thus, using a single type of collector is unlikely to achieve selective flotation of scheelite from fluorite and calcite.

Collector 733, a sodium soap of fatty acids ( $C_{12-16}COONa$ ) made from oxidized paraffin, is widely used industrially for scheelite flotation (Li et al., 2010; Huang et al., 2010; Meng et al., 2007). However, using 733 as collector, a large amount of water glass (WG), i.e. sodium silicate, must be added to depress the calcite and fluorite and to achieve selective separation. However, excessive WG in the pulp also reduces the floatability of scheelite, requiring an increase in the dosage of collector 733 to achieve a satisfactory concentrate grade and recovery.

A more selective collector, with low cost and dosage, is required for scheelite flotation. A collector mixture is a good choice for this purpose. Recent research showed that, the flotation separation efficiency of Ca minerals could be enhanced using a mixture of anionic collectors with nonionic reagents, and collector mixture demonstrated three synergetic effects, namely enhanced mineral recovery, improved adsorption behavior of the main collector on

the target mineral surface, and enhanced adsorption selectivity (Filippov et al., 2012).

In this study, sodium fatty acid methyl ester sulfonate (MES), was considered as an assistant collector, as MES is a low cost, low irritation and low toxicity reagent with biodegradability and high tolerance against water hardness. An attempt to improve the selectivity for the flotation of scheelite from calcite and fluorite was made using a collector mixture of MES and collector 733. The mechanism of the selective separation was investigated through zeta potential measurement.

## 2. Materials and methods

### 2.1. Pure minerals and reagents

Pure fluorite and calcite were sourced from Fujian, China; and scheelite from Qinghai, China. X-ray powder diffraction data confirmed that the scheelite, fluorite and calcite samples were 95%, 99% and 99% pure, respectively. The  $-74\ \mu m$  fraction was used in the flotation tests. Samples further ground to  $-5\ \mu m$  in an agate mortar were used for zeta potential measurements.

The sources of flotation reagents were as follows: analytical grade MES ( $RCH(SO_3Na)COOCH_3$ ,  $R = C_{16-18}$ ) from Kemiou Chemical Research Institute, Tianjin, China; Technical grade 733 ( $C_{12-16}COONa$ ) and WG ( $Na_2O \cdot 2.4SiO_2$ ) from the Zhuzhou Flotation Reagents Factory, Hunan, China. The pH was adjusted with NaOH or HCl stock

\* Corresponding authors. Tel.: +86 731 88879299; fax: +86 731 88830623.

E-mail addresses: [zhiyong.gao@csu.edu.cn](mailto:zhiyong.gao@csu.edu.cn) (Z. Gao), [hyh@csu.edu.cn](mailto:hyh@csu.edu.cn) (Y. Hu).

solutions. Deionized water with a resistivity of more than  $18 \text{ M}\Omega \times \text{cm}$  was used for all experiments.

## 2.2. Flotation experiment

Single mineral flotation tests were carried out in an XFG flotation machine with a 40 mL plexiglass cell, at an impeller speed of 1800 rpm. The mineral suspension was prepared by adding 3.0 g of minerals to 40 mL of distilled water. The pH of the mineral suspensions was first adjusted by adding NaOH or HCl. Once the desired reagent was added, the suspension was agitated for 3 min and the pH measured before flotation. The flotation lasted for 4 min before the products were collected, dried, and weighed. The recovery was calculated based on the weights of the dry products obtained.

## 2.3. Zeta potential measurement

Zeta potential measurements were conducted at 20 °C using a Coulter Delsa-440SX zeta potential analyzer (Brookhaven Corporation, USA). Mineral suspensions containing 0.01% solids were conditioned in a beaker for 15 min at a given pH and a collector concentration in a  $1 \times 10^{-3} \text{ mol/L}$   $\text{KNO}_3$  background electrolyte solution.

## 3. Results and discussions

### 3.1. Single mineral flotation experiment results

Firstly, the flotation separation using 733 or MES at a dosage of 50 mg/L were evaluated by single mineral test. Flotation results show that, the preferred pulp pH ranges using 733 and MES as individual collector for scheelite flotation are 9–11 and 8–11, respectively, as shown in Fig. 1. pH 10 was further used for all flotation tests.

As shown in Fig. 2(a), using 733 alone as collector and WG as depressant, selective scheelite flotation could be achieved when the WG concentration is higher than  $3 \times 10^{-3} \text{ mol/L}$ . However, the scheelite recovery is only about 40%. Fig. 2(b) shows that MES+WG cannot achieve selective separation of the three minerals from each other, but a scheelite recovery of above 60% is possible when WG concentration is below about  $3 \times 10^{-3} \text{ mol/L}$ . A WG concentration of  $3 \times 10^{-3} \text{ mol/L}$  was subsequently used for all flotation tests.

From Fig. 2(a) and (b), it can be noted that scheelite has better floatability with MES+WG than 733+WG, indicating that MES is a

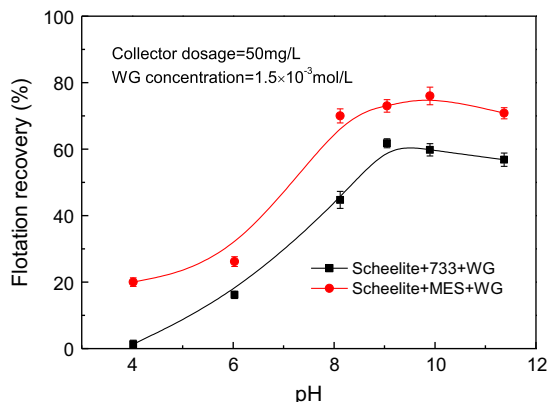


Fig. 1. Effect of pulp pH on scheelite flotation using 733 or MES as collector and WG as depressant.

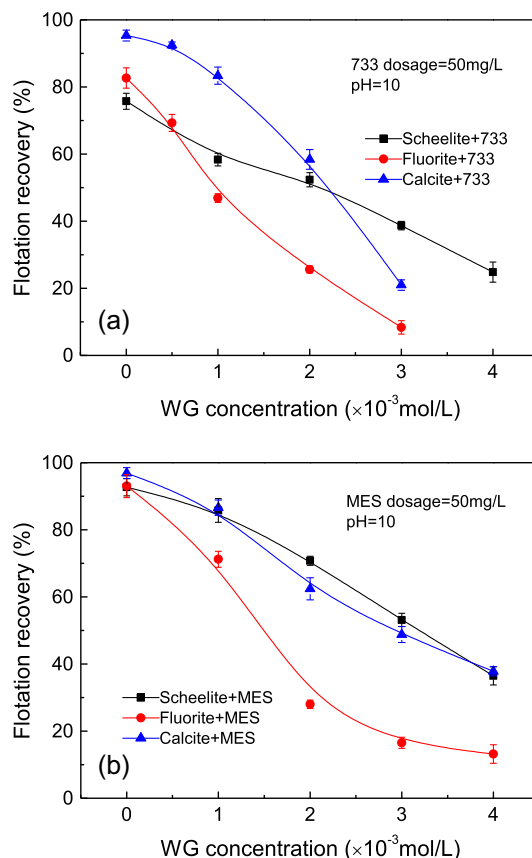


Fig. 2. Effect of WG dosage on flotation behavior of three minerals using 733 (a) or MES (b) as collector.

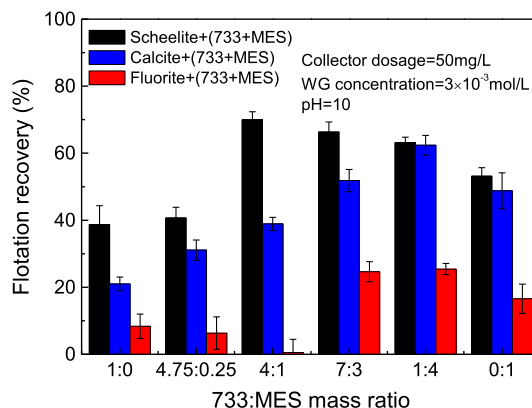


Fig. 3. Effect of mass ratio of 733+MES on flotation behavior of scheelite, fluorite and calcite.

better collector for scheelite than 733. Also, 733+WG shows better selectivity for scheelite than MES+WG.

The flotation behavior of scheelite, fluorite and calcite individually using a collector mixture of 733 and MES at different mass ratio was investigated. A series of flotation results demonstrate that the collector mixture of 733 and MES at a mass ratio of 4:1 achieves the best flotation separation performance, as shown in Fig. 3. Scheelite has a favorable recovery of 70%. However, the recovery of calcite and fluorite are 39% and 1%, respectively. Compared with the results using 733 collector as shown in Fig. 2(a), marked differences in the recovery of three minerals implies that the flotation separation performance is improved using 4:1 collector mixture 733+MES.

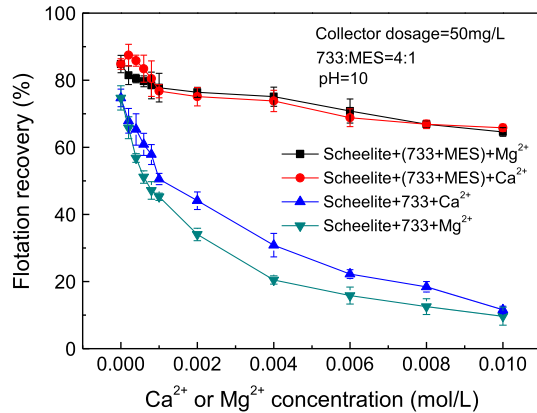


Fig. 4. Effect of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  concentration on flotation behavior of scheelite using 733 or 733+MES as collector.

It should be noted that, when the mass ratio of 733 and MES is more than 4:1, the selectivity is slightly improved while the ability of 733+MES to collect scheelite is relatively diminished. With a mass ratio of less than 4:1, decreased selectivity is obtained.

The effect of water hardness (i.e.  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  concentration) on the ability of 733 and 733+MES to collect scheelite was investigated, as shown in Fig. 4. Using 733 as collector, the scheelite recovery decreases rapidly to 50% and then to 12% at  $\text{Ca}^{2+}$  concentration of  $10^{-3}$  mol/L and  $10^{-2}$  mol/L, respectively. Whereas, using 733+MES (4:1) as collector, the scheelite recovery decreases slightly to 80% at a  $\text{Ca}^{2+}$  concentration of  $10^{-3}$  mol/L, and then to 70% at  $10^{-2}$  mol/L. The case of  $\text{Mg}^{2+}$  is similar to that of  $\text{Ca}^{2+}$ . The collecting ability of the 733+MES mixture for scheelite is less affected by the presence or concentration of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , indicating that this collector mixture has high tolerance for hard water. The high hardness tolerance of collector mixture 733+MES may be attributed to the slow crystallization rate of calcium salts of MES at room temperature (Fujiwara et al., 1993).

### 3.2. Open circuit flotation experiment results

A feed material containing 0.57%  $\text{WO}_3$  from Xihuashan Tungsten Mine (Jiangxi, China), was used for the open circuit flotation of scheelite in this study. The detailed flowsheet and reagent

scheme of the open circuit flotation are shown in Fig. 5. Note that  $\text{Na}_2\text{CO}_3$  was used to adjust the pulp pH to 10, and the WG dosage was 4500 g/t. Using the 4:1 collector mixture 733+MES, a  $\text{WO}_3$  concentrate assaying 65.76%  $\text{WO}_3$  was produced at a  $\text{WO}_3$  recovery of 66.04%. The  $\text{WO}_3$  loss to the scavenger tailings was 12.4%. For comparison, to obtain the same flotation performance using 733 alone as collector, the required dosages of 733 and WG are both 1.5 times higher than for the mixture. In addition, MES is approximately 35% cheaper than 733. The 4:1 collector mixture 733+MES shows great potential for industrial application.

### 3.3. Zeta potential measurement results

In this study, zeta potentials of scheelite, fluorite and calcite minerals in the absence and presence of various flotation reagents were measured. From Fig. 6(a), in the pH range of 2–12, pure scheelite minerals are negatively charged, which agrees well with previous reports (Hu and Xu, 2003; Rao and Forssberg, 1991). As seen in Fig. 6(b) and (c), in the absence of any reagent, an IEP (Isoelectric Point) of pH 9.7 and pH 8.5 is obtained for fluorite and calcite, respectively, in agreement with the literature (Miller et al., 2004; Somasundaran and Agar, 1967).

Fig. 6(a) shows that, in the range of pH 8–11, the addition of 733 causes a decrease by 10 mV in zeta potential of scheelite minerals, suggesting a strong interaction of negatively charged 733 species on negatively charged scheelite, possibly by chemisorption. It is striking that, in the absence or presence of WG, the addition of 733+MES (4:1) produces a greater decrease, by 30–40 mV, in scheelite zeta potential, indicating a much stronger adsorption of 733+MES on scheelite surfaces than 733 alone. This also implies that the addition of WG prior to collector addition has little influence on the adsorption of 733+MES on scheelite, which matched well with the flotation results shown in Fig. 3.

Fig. 6(b) shows that the addition of 733 or 733+MES (4:1) reverses the zeta potential of fluorite minerals from positive to negative by 50–55 mV at pH 8–10, indicating a similar adsorption behavior of 733 or 733+MES species on fluorite surfaces. Here, the addition of WG prior to collector addition caused an apparent shift of zeta potential of “fluorite+733+MES” to positive values by 10 mV at pH 10, indicating that the presence of WG hinders the 733+MES adsorption on fluorite surfaces.

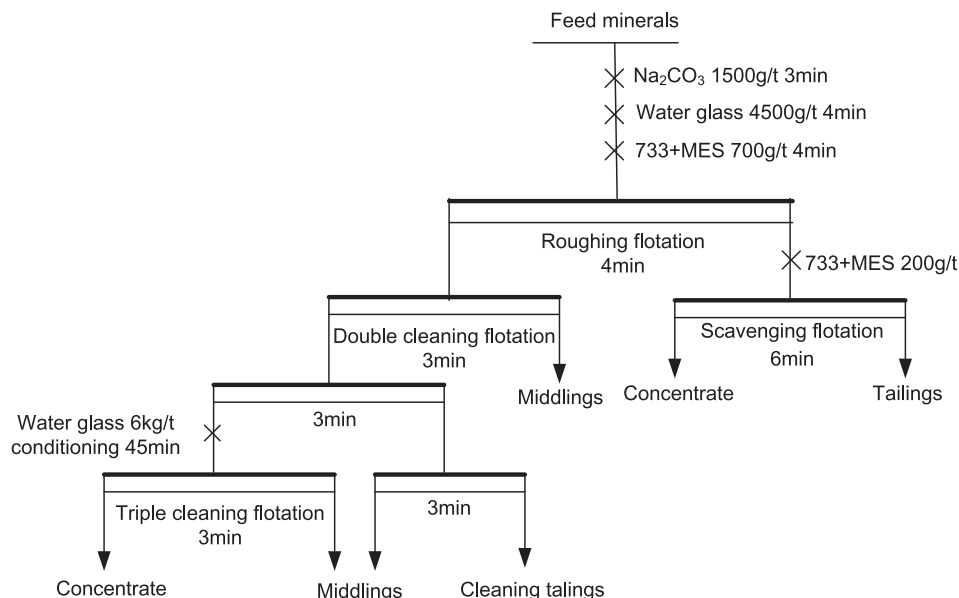


Fig. 5. The open circuit flowsheet of scheelite flotation (including the scheme of flotation reagents).

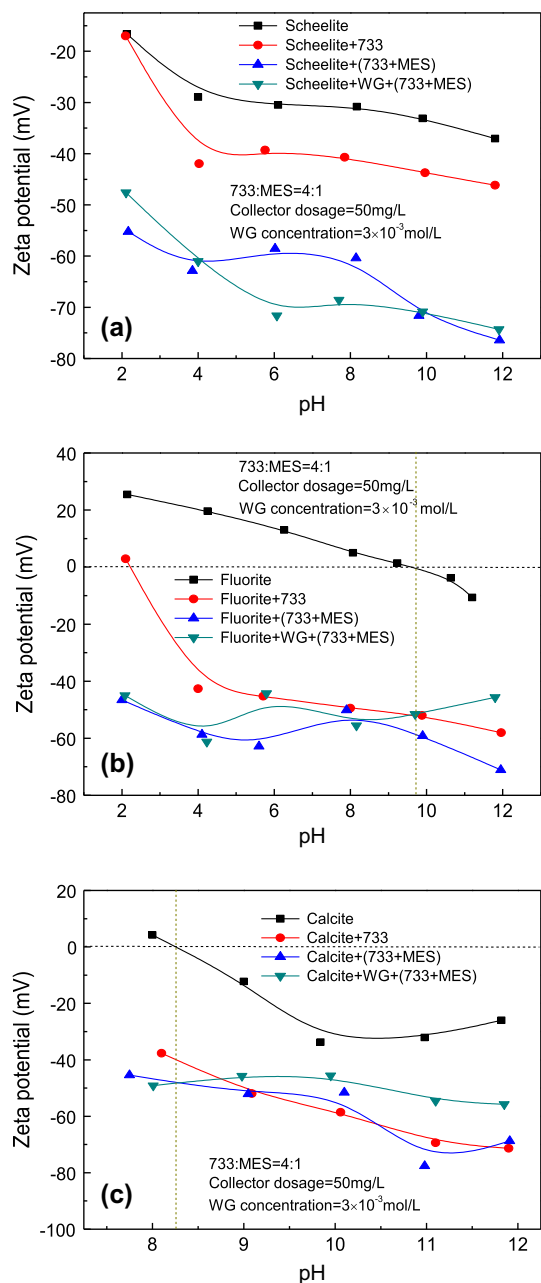


Fig. 6. Effect of different reagent adding on the zeta potential of scheelite (a), fluorite (b) and calcite (c).

Fig. 6(c) shows that the addition of 733 or 733+MES (4:1) causes similar zeta potential changes for calcite minerals. As for calcite, the addition of WG prior to collector addition leads to an obvious shift of zeta potential values of “calcite+733+MES” to positive values.

From the above, 733+MES (4:1) has a much stronger adsorption on scheelite surfaces than 733 alone, while 733 and 733+MES (4:1) exhibit a similar interaction towards fluorite and calcite. More importantly, the addition of WG prior to collector addition has an adverse impact on the adsorption of 733+MES on calcite and fluorite, but has little influence on the 733+MES adsorption on scheelite.

#### 4. Conclusions

The collector mixture of 733+MES at mass ratio of 4:1, is selective to scheelite than 733 alone. The addition of WG prior to collector addition has little impact on the adsorption of 733+MES towards scheelite, but has an adverse impact on the 733+MES adsorption on fluorite and calcite. The 4:1 collector mixture 733+MES with WG ( $3.0 \times 10^{-3}$  mol/L) at pH 10 could achieve selective flotation of scheelite from fluorite and calcite. With a lower cost, lower dosage, higher selectivity and higher tolerance against water hardness, the collector mixture 733+MES exhibits great potential for industrial application in scheelite flotation.

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