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The effect of sodium alginate on the flotation separation of scheelite from calcite and fluorite

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A R T I C L E I N F O

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A B S T R A C T

In this paper, the effect of sodium alginate on the flotation separation of scheelite from calcite and fluorite using sodium oleate as collector was investigated. Flotation results showed that sodium alginate could selectively depress the flotation of calcite and fluorite in pH range of 7–12 when it was added before sodium oleate. The selective depressant effect of sodium alginate was studied using zeta potential measurements, contact angle measurements and FTIR. The zeta potential measurements results showed that sodium alginate exhibited little influence on the surface charge of scheelite but had remarkable effect on that of calcite and fluorite. The results of contact angle measurements indicated that sodium alginate could produce selective, non-recoverable decrease in surface hydrophobicity of calcite and fluorite. The FTIR studies demonstrated the chemical absorption of sodium alginate on calcite and fluorite surface and no form of adsorption on scheelite surface.

1. Introduction

Scheelite ($CaWO_4$) is a typical tungstate mineral and usually co-exists with other calcium-containing minerals, such as calcite ($CaCO_3$) and fluorite (CaF_2) in scheelite deposits. By now, flotation is the most commonly used technique to separate scheelite from calcite and fluorite (Hu et al., 2012). However, due to the same Ca^{2+} species on the cleavage (Pradip et al., 2002), the calcium minerals exhibit similar surface reactivity to traditional collectors such as fatty acids and their derivatives in flotation practice. It has been widely recognized that fatty acid collectors can collect these calcium minerals by forming calcium dicarboxylates on the mineral surface through chemisorption between Ca^{2+} and carboxyl (—COO—) (Atademir et al., 1981; Rao et al., 1990; Rao and Forssberg, 1991; Ozcan and Bulutcu, 1993; Zhang and Song, 2003). Therefore, it is almost impossible to separate scheelite from calcite and fluorite using traditional fatty acid collector if no depressant is used.

Depressants in scheelite flotation, which are used for decreasing the flotability of calcite and fluorite, mainly include some inorganic salts and organic colloid. Sodium silicate and its solution with inorganic salt ions as well as organic colloid, are often applied in scheelite flotation to depress calcite and fluorite (Hanumantha Rao et al., 1989; Irannajad et al., 2009). But the sodium silicate-based depressants have also been proven to be able to adsorb on scheelite surface (Bo et al., 2015) thus showing inevitable influence on scheelite flotation (Kazmi et al., 2011; Liu et al., 2016). Phosphates, such as sodium phosphate (Na_3PO_4), sodium pyrophosphate ($Na_4P_2O_7$) and sodium hexametaphosphate ($(NaPO_3)_6$) are also common depressants in scheelite flotation (Yongxin and Changgen, 1983). However, it is hard to find a proper phosphate to depress calcite and fluorite at the same time (Changgen and Yongxin, 1983). Other depressants such as quebracho, dextrin, and starch are also demonstrated to have limited selectivity in ore flotation (Castro and Hoces, 1993; Hiçyìlmaz et al., 1993; Liu et al., 2016; Ozcan et al., 1994). The efficient separation of scheelite from calcite and fluorite remains a problem.

Sodium alginate is a kind of natural polysaccharides. It can dissolve in aqueous solution and become hydrophilic colloid. Owing to its stable properties, unique pH sensitivity and biocompatibility, sodium alginate is usually used as food thickeners, emulsifiers, stabilizers, and controlled release agents of drugs (Pawar and Edgar, 2012). As there are chelating groups such as hydroxy (HO—) and carboxyl (—COO—) in its molecule, sodium alginate has the potential for chelating calcium minerals and then making their surface hydrophilic in solutions. However, there are little published papers referring to utilizing its chelating capability in flotation field, especially in the separation of scheelite from calcite and fluorite.

In this paper, sodium alginate (NaAl) was introduced as a flotation modifier to selectively separate scheelite from calcite and fluorite using sodium oleate (NaOl) as collector. Micro-flotation tests on single mineral and mixed minerals were conducted to show the selective depressant effect of NaAl on calcite and fluorite. Zeta potential measurements, contact angle measurements and FTIR studies on minerals

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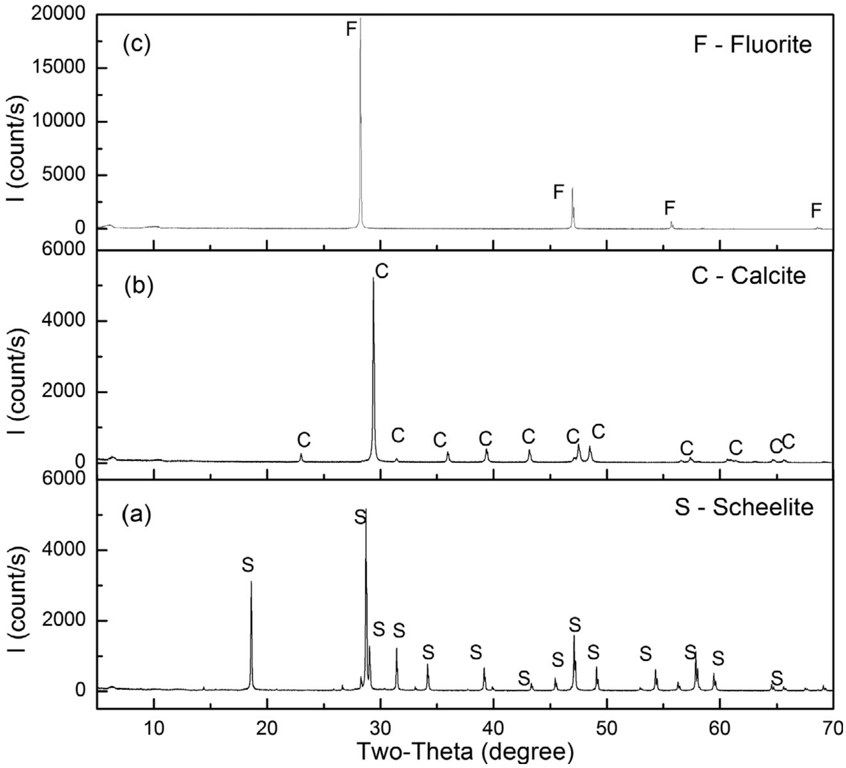

Fig. 1. XRD spectrums of the scheelite (a), calcite (b) and fluorite (c) samples.

with and without treatment of NaAl and NaOl were performed to define the depressant effect mechanism.

2. Experimental

2.1. Mineral samples and reagents

The samples of scheelite, calcite and fluorite were all obtained from Xintianling mine, Hunan, China. Hand-selected crystals of these minerals were crushed to −1 mm by a laboratory roll crusher. The crushed products were then ground in a ceramic ball mill and dry-sieved to obtain the −74 + 38 μm-size fractions for micro-flotation tests. A portion of −38 μm-size fraction particles was further ground to −2 μm for zeta potential measurements and FTIR studies. The purities of these samples were 97.25% (for scheelite), 99.30% (for calcite) and 99.27% (for fluorite) according to their XRD spectrums (Fig. 1) analysis.

Sodium alginate (NaAl) used in this study was purchased from Zhengzhou Taber Trading Co. Ltd, Henan, China. Sodium oleate (NaOl) was bought from Tianjing Kermil Chemical Reagents Development Centre, Tianjin, China. The molecular structure of NaAl and NaOl are shown in Fig. 2. NaAl is a kind of linear polymer ($(C_6H_7NaO_6)_n$) with a Mol. wt. around 50,000. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used as pH regulators. All the reagents used in this paper are of analytical grade. Distilled water was used for all tests.

2.2. Micro-flotation tests

Micro-flotation tests were conducted on a XFGC flotation machine with a 40-mL cell at 1800 rpm. For single mineral flotation test, mineral pulp was prepared through adding 2 g mineral samples into the cell with distilled water and conditioned for 1 min before adding a reagent. Then pulp pH was adjusted to a desired value with HCl or NaOH solutions. After the depressant and collector were added at a designed concentration, the pulp was conditioned for an additional 6 more minutes (3 min for each reagent). The flotation started when air was bubbled into the cell at a flow rate of 0.2 m^3/h. The total flotation time was 4 min. After flotation, the concentrates and tails were collected, filtered, dried, weighed and the recovery was determined based on solid weight distributions between the two products. Each single mineral flotation tests were conducted three times. The average value of recovery and the standard deviation of parallel results were calculated and presented.

For artificial mixed minerals, the mass ratio of scheelite and gangue mineral was 1:1.5 for binary mixture (0.8 g scheelite + 1.2 g calcite or fluorite) and 1:0.75:0.75 for ternary mixture (0.8 g scheelite + 0.6 g calcite + 0.6 g fluorite). The flotation operation was the same as above. After flotation, the concentrates and tails were assayed for W and Ca. The recovery of scheelite was calculated based on $CaWO_4$ distributions between the two products.

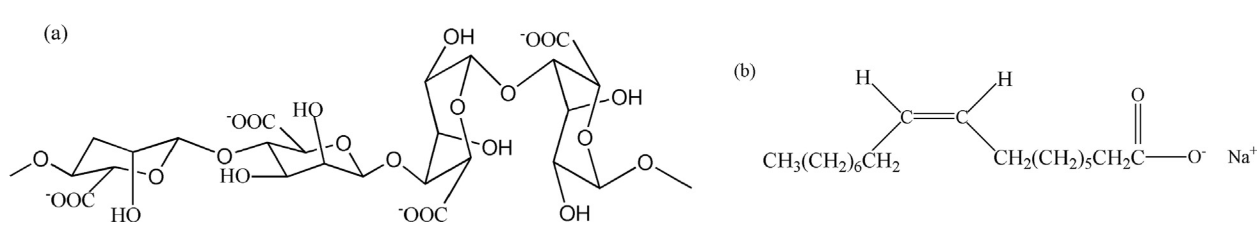

Fig. 2. Molecule structures of NaAl (a) (Treenate and Monvisade, 2017) and NaOl (b).