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The flotation separation of scheelite from calcite and fluorite using dextran sulfate sodium as depressant

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ABSTRACT

This paper introduced dextran sulfate sodium, a medical intermediate rich in sulfate group, as a potential depressant for calcite and fluorite in scheelite flotation. The flotation behaviors of scheelite, calcite and fluorite under different pulp pH with dextran sulfate sodium acting as depressant and sodium oleate acting as collector were studied through micro-flotation tests. The results showed that when sodium oleate was used alone, the three minerals floated well and were difficult to separate. Dextran sulfate sodium exhibited a selective depressant effect on calcite and fluorite flotation when it was added before sodium oleate. Using dextran sulfate sodium as depressant could achieve the preferential flotation separation of scheelite from calcite and fluorite by control of pulp pH at 7.0. The selective depressant effect of dextran sulfate sodium on calcite and fluorite was explored through surface analyses including zeta potential measurements, contact angle measurements and FTIR studies on mineral samples treated with dextran sulfate sodium and/or sodium oleate. On the basis of the surface analyses, a selective adsorption model of dextran sulfate sodium on calcite and fluorite was proposed.

1. Introduction

Scheelite ($CaWO_4$) is a typical tungstate mineral and usually coexists with other calcium-containing minerals, such as calcite ($CaCO_3$) and fluorite (CaF_2) in deposit. By now, flotation is the most commonly used technique to separate scheelite from calcite and fluorite. Long chain carboxylic acids, such as fatty acids and their derivatives, are the most typical collectors in the flotation of scheelite. However, due to the same Ca^{2+} species on the cleavage (Pradip et al., 2002), these calcium minerals exhibit similar surface reactivity to the carboxylic acids collectors in flotation practice (Hanumantha Rao and Forssberg, 1991). It has been widely demonstrated that the carboxylic acids collectors can collect these calcium-bearing minerals by forming calcium dicarboxylates on the mineral surface through chemisorption between the calcium ion and the carboxyl (Atademir et al., 1981; Rao et al., 1990; Rao and Forssberg, 1991). Therefore, it is very necessary to add flotation modifiers in flotation process to realize the depression of calcite and fluorite when carboxylic acids are used as collectors.

The depressant effect of the flotation modifiers (commonly termed depressants) on the calcium-bearing gangue minerals is usually realized through the interactions between the calcium ions on mineral surface and the functional groups in their molecules. Common functional groups in depressants are —SiO_3, —OH, COO— and —PO_4, which are known to strongly interact with Ca^{2+} and have the potential to get adsorbed on the mineral surface. Water glass (sodium silicate solutions) and water glass mixed with inorganic salt ions are traditional flotation modifiers that utilize —SiO_3 to depress the flotation of calcite and fluorite (Marinakis and Shergold, 1985; Rao et al., 1990). They are widely used in flotation plants in the form of water glass (Haisheng et al., 2017), acidified water glass (Bo et al., 2015) and salinized water glass (Bo et al., 2017), though they have inevitable depressant effect on scheelite flotation. Depressants rich in functional groups —OH and COO—, such as quebracho (Castro and Hoces, 1993; Ozcan and Bulutcu, 1993), sodium polyacrylate (Zhang et al., 2017), carboxymethyl cellulose (Tian et al., 2017), alginate (Chen et al., 2017) and tannin (Liu et al., 2016) are reported to exhibit limited depressant effect on flotation of calcite and fluorite. Polyphosphates, such as $Na_4P_2O_7$ and $(NaPO_3)_6$, are also reported effective inhibitors in separating scheelite from calcite and fluorite (Yongxin and Changgen, 1983). But the polyphosphates are easy to decompose to sodium phosphate (Na_3PO_4) in solutions, which is detrimental for scheelite flotation (Changgen and Yongxin, 1983). At the present time, the efficient separation of scheelite from calcite and fluorite remains a problem, as the depressants reported above also show a certain degree of negative effect on flotation of scheelite. New depressant that can depress the flotation of calcium gangue minerals but exhibits none negative effect on scheelite flotation is urgently required in scheelite flotation.

Dextran sulfate sodium (DSS) is a medical intermediate widely used in clinical experiment (Wang et al., 2017). Dextran is a complex

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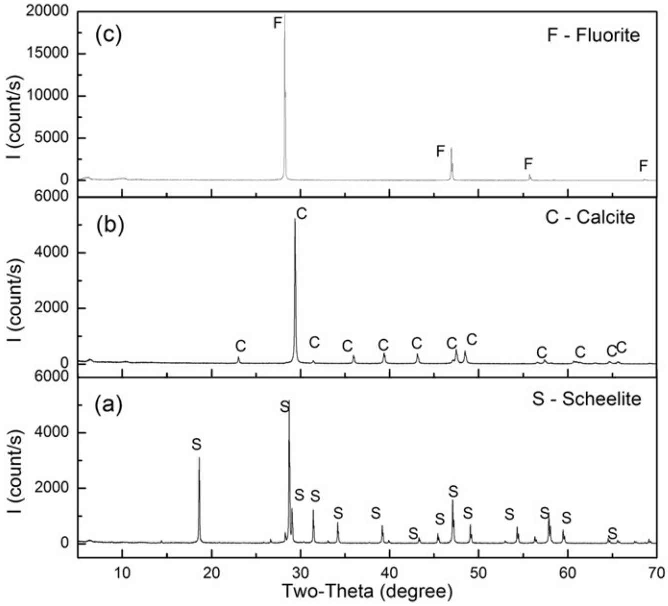

Fig. 1. X-ray diffraction (XRD) spectra of single scheelite (a), calcite (b) and fluorite (c) samples used in the research.

polymer of glucose, which is made of straight and branched chains, with highly variable molecular weight (range from 5000 to 1.4 million Da) (Hu et al., 2017). DSS is polyanionic derivative of dextran, produced by esterification with chlorosulphonic acid. It is rich in —SO_4 group, which is able to interact with Ca^{2+} on the calcium mineral surface. Therefore, DSS also has the potential to act as a depressant for calcite and fluorite in scheelite flotation. However, there are little published papers referring to utilizing the functional group in DSS in flotation field, especially in the separation of scheelite from calcite and fluorite.

In this research, DSS was introduced as a flotation modifier to separate scheelite from calcite and fluorite. Sodium oleate (NaOl), a kind of carboxylic acid, was used as collector. Micro-flotation tests on single minerals were conducted to show its depressant effect on calcite and fluorite. The depressant effect was analyzed by zeta potential measurements, contact angle measurements and FTIR studies. Based on the surface analyses, a possible adsorption model of DSS on calcite and fluorite was proposed.

2. Materials and methods

2.1. Mineral samples and reagents

The samples of scheelite, calcite and fluorite were all obtained from Xintianling mine, Hunan, China. Large, pure mineral crystals with fresh cleavage surface were carefully selected for contact angle measurement. Powder samples for flotation tests (+38–74 μm) were prepared by crushing, grinding and dry sieving the hand-selected crystals. A portion of the −38 μm size fraction particles was further ground to −2 μm for zeta potential measurements and FTIR spectra studies. The purities of the mineral samples were 97.25% (for scheelite), 99.30% (for calcite) and 99.27% (for fluorite) according to their X-ray diffraction spectra analysis in Fig. 1.

DSS used in this study was purchased from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. It is water-soluble powder with a molecular formula $(C_6H_7Na_3O_{14}S_3)_n$ and an average molecular weight of 500,000. NaOl was bought from Tianjing Kermil Chemical Reagents Development Centre, Tianjin, China. The molecular structures of DSS and NaOl are shown in Fig. 2. HCl and NaOH were used as pH regulators. All reagents were of analytical grade. Distilled water was used for all tests.

2.2. Micro-flotation test

Micro-flotation tests were conducted on a XFG flotation machine at 1800 rpm with a 40 mL cell (Gao et al., 2016). Mineral pulp was prepared by adding 2 g mineral samples to the cell with distilled water. PH was adjusted by HCl or NaOH solutions in 3 min. Depressant (if needed) and collector were added at a designed concentration. Conditioning time for each reagent was 3 min and flotation time was 4 min. After flotation, the concentrate and tailing were collected, filtered, dried, weighed and the recovery was determined based on solid weight distributions between the two products. All flotation tests were repeated at least three times. The average value of recovery and the standard deviation were calculated and presented.

2.3. Zeta potential measurement

Mineral pulp for zeta potential measurement was prepared by adding 0.03 g single mineral (−2 μm) to 1×10^{-2} mol/L KCl solution. The pH was adjusted to 7.0 and then flotation reagent was added and conditioned for 10 min. After a standing of 5 min, the supernatant liquid was sucked out for measurement. Zeta potential measurements were conducted on a Coulter Delsa440sx Zeta analyzer instrument at 25 °C. Each measurement was repeated 3 times. The average value and the standard deviation were calculated.

2.4. Contact angle measurement

In this paper, contact angle was used to characterize the hydrophobicity of mineral surface. The contact angle of mineral surface sample before and after flotation reagent treatment under different pH was measured with goniometry technique with a JY-82C video based contact angle measuring device. The flat surface of mineral crystals for contact angle measurement was prepared by grinding the crystals with a diamond disk subsequent by 0.05 μm alumina powder solutions on a "selected silk" polishing cloth. The prepared mineral surface was first immersed in flotation reagent solution with desired concentration and pulp pH. The reagent solution was gently stirred to let the reagent react with the fresh mineral surface. The stirring time for each reagent was 20 min. After the stirring, the surface sample was gently washed by water with the same pH as the reagent solution. Then the surface sample was vacuum dried at 30 °C. Finally, a 0.016 mL water drop was

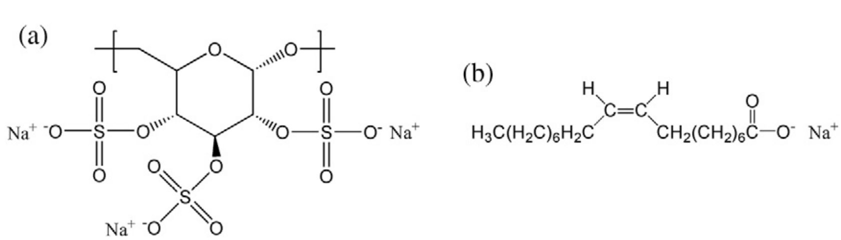

Fig. 2. Molecular structure of DSS (a) and NaOl (b).