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The flotation separation of scheelite from calcite using acidified sodium silicate as depressant



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1. Introduction

Tungsten has wide application in industry such as high temperature technology, chemical industry, lighting, X-ray technology, machine construction owing to its low vapor pressure, high melting point, good electrical and thermal conductivities, high density, high-elastic modulus, high wear resistance and good X-ray performance (Ilhan et al., 2013; Rao, 1996). It is one of the strategic metals identified for stockpiling in many countries. Scheelite is the principle mineral of tungsten and usually associated with other calcium-bearing minerals in ore deposits, from which it shall be separated by means of flotation (Hu et al., 2012; Shepeta et al., 2012).

Flotation separation of scheelite from calcite is difficult to be realized because of the existence of the same cation in the minerals and similar physicochemical characteristics such as solubility, hardness, specific gravity and PZC (point of zero charge) (Hu et al., 2011; Ozcan and Bulutcu, 1993). The conventional collectors used in the flotation of scheelite ores are generally fatty acids or fatty acid derivatives (Li and Lu 1983; Lu and Li, 1983; Yin et al., 2014). The adsorption mechanism of these collectors occurs through chemisorption of the oleate ion onto the mineral surface (Atademir et al., 1981; Rao and Forssberg, 1991a, 1991b).

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ABSTRACT

The flotation separation of scheelite from calcite using sodium oleate as collector and acidified sodium silicate as depressant has been studied. The results show that sodium oleate has collecting ability to both scheelite and calcite and the flotation separation of scheelite from calcite cannot be realized if collector is used only. The depressant acidified sodium silicate has selective depression effect on calcite and the optimum ratio of sodium silicate to oxalic is 3:1. The use of acidified sodium silicate as depressant can achieve the flotation separation of scheelite from calcite. Infrared studies and zeta potential measurements showed that the pre-adsorption of acidified sodium silicate interferes with the adsorption of sodium oleate on calcite surface while does not interfere with its adsorption on scheelite surface.

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Therefore, it is almost impossible to separate scheelite from calcite by fatty acid without using depressant (Ozcan and Bulutcu, 1993).

Unfortunately, depressants used for this purpose such as quebracho, organic colloids, hydrosols and sodium phosphates (Hernáinz and Calero, 1993; Hicyilmaz et al., 1993) also depress scheelite to a large extent. Although recent studies are focused on the development of selective depressants for calcite, the separation of scheelite from calcitic ores is still a big problem (Ozcan et al., 1994).

The aim of this study is to show the selective flotation of scheelite from calcite using acidified sodium silicate as depressant. Zeta potential measurements and infrared studies of pure scheelite and calcite conditioned with sodium oleate as collector and acidified sodium silicate as modifier were conducted to define the depression mechanism.

2. Materials and methods

2.1. Pure minerals and reagents

The Huangpodi mine is located in Jiangxi province. The valuable mineral in Huangpodi tungsten ore is mainly scheelite and the ore head grade is 0.5% WO₃. The dominant gangue minerals are calcite, quartz and fluorite. Hand-picked pure scheelite and calcite from Huangpodi mine were crushed to -1 mm in a laboratory jaw crusher and a laboratory roll crusher, then they were concentrated on a concentrating table and with a high-intensity magnetic separator several times to remove the heavy minerals and the magnetic



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minerals. The non-magnetic products were ground in a porcelain mill. The ground samples were wet-sieved and the $-74 \,\mu m$ size fraction (with a D90 value of 75.9 μm for scheelite and 70.3 μm for calcite) were collected and used in flotation tests. Samples further ground to D90 value less than 2 μm in an agate mortar were used for zeta potential measurements and FTIR studies.

An X-Ray diffractometer D8-ADVANCE with rotating Cu anode was used for mineral phase identification. The X-ray tube was set at 40 kV and 40 mA. X'pert Quantify and X'Pert High Score software were used for data acquisition and phase analysis, respectively. The chemical analysis was done in the chemical analysis laboratory. They use atomic absorption spectroscopy and chemical titration analysis to analyze the chemical composition of sample.

X-ray diffraction measurements on the scheelite and calcite samples showed that there were no other tungsten minerals in scheelite and trace silicate in calcite (see Fig. 1). Chemical analysis of the samples showed that the scheelite sample contained 79.85% WO_3 , representing a high purity of 99.2% scheelite, and that calcite contained 55.47% CaO, indicating a purity of 99.0% calcite (see Table 1).

The sample of sodium oleate used in this study was obtained from Tianjing Kermil Chemical Reagents Development Centre, Tianjin, China. The acidified sodium silicate is the mixture of sodium silicate and oxalic acid. The sodium silicate used in this study is a kind of water-soluble silicate with a molecular formula of Na₂SiO₃·9H₂O. HCl (hydrochloric acid) and NaOH (Sodium hydroxide) were used as pH regulators. Distilled water was used for all tests.

2.2. Flotation tests

Flotation tests of individual minerals and artificially mixed minerals were both conducted. Flotation tests were carried out in a mechanical agitation flotation machine (Fig. 2). The volume of the cell is 50 ml. The mineral suspension was prepared by adding 2 g of minerals to 40 ml of solutions. The pH of the mineral suspension was adjusted to a desired value by adding NaOH or HCl stock solutions. The prepared acidified sodium silicate and sodium oleate solution was added at a desired concentration and conditioned for 3 min. Each flotation test was carried out for a total of 4 min.

For individual mineral flotation, the floated and unfloated particles were collected, filtered and dried. The flotation recovery was calculated based on solid weight distributions between the two products. For mixed minerals flotation, the WO₃ contents of the concentrates and tailings were analyzed, and the recovery and

Table 1

The chemical composition of scheelite and calcite.

Sample	W0 ₃	Fe	SiO ₂	Al_2O_3	CaO
Scheelite	79.85	/	/	/	19.72
Calcite	/	0.21	0.52	0.22	55.47



Fig. 2. Schematic of flotation machine.

content of scheelite were calculate based on the theoretical content of WO_3 in pure scheelite mineral.

2.3. FTIR study

For the infrared studies, 2 g pure scheelite and calcite were individually suspended in 200 ml of reagents solutions for 25 min at pH 7. The pulps were then centrifuged and washed at least three times with distilled water and dried in a vacuum oven at 40 °C. The infrared spectra of minerals were recorded using a Model Nexus 670 series Fourier transform infrared spectrometer in the range 4000–450 cm⁻¹.

2.4. Zeta potential measurements

Isoelectric points (iep) of mineral samples were determined by measuring the electrophoretic mobility of aqueous dispersions as a function of pH in a zeta potential meter. For these measurements, a dilute mineral suspension was prepared by adding 0.03 g mineral



Fig. 1. XRD diagrams of scheelite and calcite.

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