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Selective flotation of scheelite from calcite using Al-Na_2SiO_3 polymer as depressant and Pb-BHA complexes as collector

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ABSTRACT

In previous studies, by regulating the Pb/BHA ratio and pH, lead complexes of benzohydroxamic acid (Pb-BHA) have been proven to be selective for the separation of scheelite from calcium minerals. In this study, sodium silicate (Na_2SiO_3) and Al-Na_2SiO_3 polymer were used as depressants for the further separation of scheelite from calcite. Flotation results indicated that both scheelite and calcite were depressed by Na_2SiO_3, while Al-Na_2SiO_3 polymer gave good selectivity. The depressing ability of Na_2SiO_3 for calcite was significantly improved due to the formation of some Al-Na_2SiO_3 species with aluminum ions, while the reverse was true for scheelite. Zeta potential results indicated that both colloidal Na_2SiO_3 and Al-Na_2SiO_3 particles were negatively charged and difficult to adsorb on the negative scheelite surface through electrostatic attraction, especially for Al-Na_2SiO_3. X-ray photoelectron spectroscopy analysis results showed that the Al-Na_2SiO_3 adsorbed amount on the scheelite surface was less than the Na_2SiO_3 adsorbed amount, while the reverse was true on the calcite surface. Binding energy analysis results indicated that calcium cations of scheelite and calcite surfaces could bond to oxygen atoms of Na_2SiO_3/Al-Na_2SiO_3 through chemisorption. However, compared with Na_2SiO_3, Al-Na_2SiO_3 showed weaker chemisorption on the scheelite surface, but adsorbed more powerfully onto the calcite surface. Therefore, Al-Na_2SiO_3 showed excellent selectivity for scheelite and calcite, which has been successfully applied at the Shizhuyuan mine.

1. Introduction

Scheelite is a principle tungsten mineral that has become the main source of tungsten metal in China. Scheelite is usually associated with other calcium-bearing minerals in ore deposits, from which it almost must be separated by means of flotation (Hu et al., 2012; Shepeta et al., 2012). The flotation separation of scheelite from other calcium-containing minerals, such as fluorite and calcite, is problematic, due to their similar physicochemical characteristics and flotation behavior, and, especially, because they contain the same active Ca^{2+} site for interaction with anionic collectors (Rai et al., 2011; Deng et al., 2016; Ozcan and Bulutcu, 1993; Yongxin and Changgen, 1983).

In previous work, lead complexes of benzohydroxamic acid (Pb-BHA) were found to be selective for the separation of scheelite and calcium minerals by regulating the Pb/BHA ratio and pulp pH range (Han et al., 2017a, 2017b). However, calcite still demonstrated some floatability in the Pb-BHA flotation, which resulted in difficulties in improving the concentrate grade. To obtain a high-quality concentrate, the efficient separation of scheelite from calcite without the addition of a depressant seems impossible. Sodium silicate has commonly been used to depress gangue minerals in the traditional fatty acid flotation process, but also affects the floatability of scheelite to some extent and greatly decreases the recovery with a large sodium silicate dosage (Gao, 2014; Gao et al., 2015a; Bo et al., 2015, Han et al., 2017a). To improve the selectivity of sodium silicate, diverse metal ions, such as Fe^{2+}, Pb^{2+}, Cu^{2+}, Mg^{2+}, and Al^{3+}, have been used to modify sodium silicate in some other mineral flotation processes (Tohry and Dehghani, 2016; Li and Ji, 1981; Zhang and Song, 2003; Wen and Xiang, 1990; Luo et al., 2012). After reaction with metal ions, the selectivity of Na_2SiO_3 for some minerals was obviously improved, but the active species, structures, and adsorption mechanism of metal–Na_2SiO_3 remain undetermined.

In this study, Na_2SiO_3 and Al-Na_2SiO_3 polymer was used as a depressant to separate scheelite from calcite using Pb-BHA complexes as the collector. Flotation experiments of pure minerals were conducted to study the floatability of scheelite and calcite with different depressants and collectors. Furthermore, some industrial applications of Al-Na_2SiO_3 polymer serving as depressant were introduced to validate the test results. Zeta potential measurements and X-ray photoelectron spectroscopy (XPS) were used to provide detailed information of the mineral

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surface to allow the adsorption mechanism to be further understood.

2. Materials and methods

2.1. Experimental minerals and reagents

Pure scheelite, calcite, and fluorite were sourced from Shizhuyuan mine, Hunan, China. Powder X-ray diffraction (XRD) data confirmed that the samples were above 97% purity. The −74 μm fractions of scheelite and fluorite were used for flotation experiments. The −74 μm, −37 μm, and 37–74 μm fractions of calcite were also prepared. Samples further ground to −2 μm in an agate mortar were used for zeta potential measurements.

Analytical grade benzohydroxamic acid (BHA) and lead nitrate were purchased from Guangfu, Tianjin, China. The pH was adjusted using NaOH or HCl stock solutions. Sodium silicate (SS, $Na_2SiO_3{\cdot}9H_2O$) was obtained from Zhuzhou Flotation Reagents Factory, Hunan, China. Analytical grade aluminum sulfate ($Al_2(SO_4)_3$) and terpineol were obtained from Kemiou Chemical Research Institute, Tianjin, China. Deionized water was used throughout pure material flotation experiments.

Table 1 shows the elemental content of the ore from Shizhuyuan mine used in experiments. The tungsten minerals were mainly scheelite and wolframite (in proportions of approx. 2–3:1), which were associated with calcite, fluorite, and garnet.

2.2. Flotation experiment

Pure mineral flotation tests were conducted in an XFG flotation machine at an impeller speed of 1900 rpm, with a plexiglass cell volume of 40 mL. The mineral suspension was prepared by adding 2.0g of minerals to 30 mL of deionized water and agitating for 1 min. Reagents were then added in order at the desired concentration, as shown in Fig. 1. $Pb(NO_3)_2$ was mixed with BHA, and Na_2SiO_3 was mixed with $Al_2(SO_4)_3$ at the mass ratio of 2:1, referred to as Al-Na_2SiO_3, before addition. The pH was adjusted and measured before flotation. After 5 min of flotation, the floated and unfloated particles were collected, dried, and weighed, and the recovery was calculated.

2.3. Zeta potential measurements

Zeta potential measurements were conducted at 20 °C using a zeta potential analyzer (ZetaPlus, Bruker, Germany). The colloid particle suspensions of Na_2SiO_3 and Al-Na_2SiO_3 were prepared by adding desired reagents to 40 mL of KCl background electrolyte (10^{-3} mol/L) and agitating for 3 min. Mineral suspensions containing 0.02 g of solids and 40 mL of KCl background electrolyte (10^{-3} mol/L) were prepared in a beaker at a given pH and a desired reagent concentration. After settling for 10 min, the supernatant liquor was used for zeta potential measurements.

2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Fisher Scientific K-Alpha 1063 X system. The −74 μm fractions of pure scheelite and calcite samples (2.0 g) were conditioned using the same procedure as the flotation tests with and without adding the desired reagents. The prepared samples were stirred for 10 min and then washed twice with 40 mL of distilled water. Finally, the samples were dried in a vacuum oven controlled at below 50 °C.

Table 1
Multi-element analysis results of experimental run-of-mine ore (%).

Elements	WO_3	Mo	Bi	Mn	Fe	S	F
Content	0.38	0.01	0.02	0.31	2.29	0.12	15.10
Elements	Pb	Zn	P	SiO_2	CaO	Al_2O_3	MgO
Content	0.01	0.04	0.01	43.24	20.18	6.83	0.96

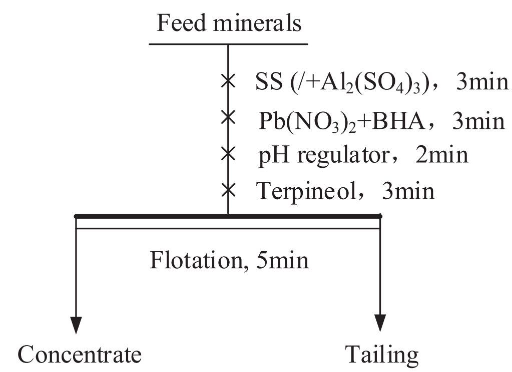

Fig. 1. Flowsheet of pure mineral flotation test.

3. Results and discussions

3.1. Results of single mineral flotation experiment

In previous work, the mixture of $Pb(NO_3)_2$ and BHA showed some selectivity for calcium minerals, with much better separation achieved when the mole ratio of Pb^{2+} to BHA was 2:1 (Han et al., 2017a, 2017b). Fig. 2 shows the differences in floatability of scheelite, calcite, and fluorite using Pb-BHA complexes as collectors, which were consistent with previous reports. Pb-BHA complexes demonstrated a good collecting ability for scheelite and calcite at pH 8–10, with calcite maintaining a high recovery throughout the pH range tested, while fluorite could not be collected. Although the scheelite recovery was better than that of calcite at pH 9.5–10.5, indicating the possibility of separation, it was not different enough for the complete separation of scheelite from calcite without using a depressant.

Depressants Na_2SiO_3 and Al-Na_2SiO_3 polymer were introduced to improve the selective separation. Fig. 3 shows the effects of Na_2SiO_3 and Al-Na_2SiO_3 polymer on the floatability of scheelite and calcite. Interestingly, the scheelite recovery curve showed some peaks as the depressant dosage increased, in contrast to the literature (Gao et al., 2016, 2015a, 2015b; Meng et al., 2015; Bo et al., 2015, Han et al., 2017a). When the dosage of Na_2SiO_3 or Al-Na_2SiO_3 polymer was small,

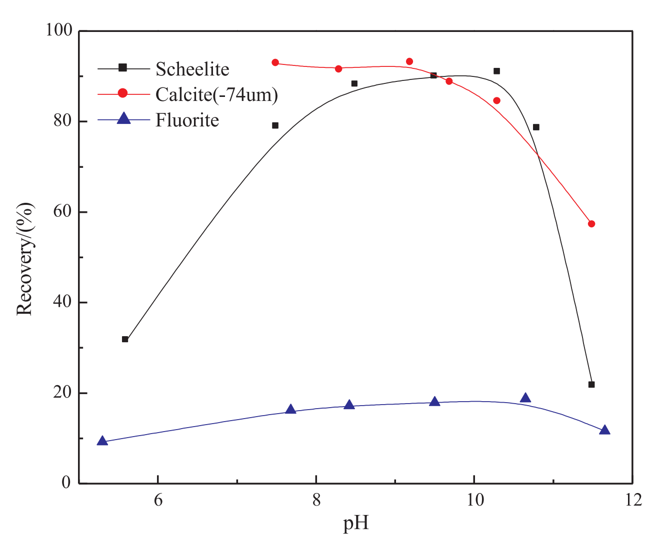

Fig. 2. Floatability of calcium minerals with Pb-BHA as the collector ($C_{(lead\ ion)} = 3 \times 10^{-4}$ mol/L, $C_{(BHA)} = 1.5 \times 10^{-4}$ mol/L, $C_{(terpineol)} = 12.5$ μL/L).