

Full Length Article

Effect of acidified water glass on the flotation separation of scheelite from calcite using mixed cationic/anionic collectors

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ABSTRACT

In this paper, the effect of acidified water glass (AWG) on the flotation separation of scheelite from calcite using mixed collector of dodecylamine (DDA) and sodium oleate (NaOL) was investigated. The flotation results show that AWG could selectively depress the flotation of calcite at pH 7. A series of mechanism experiments confirm that the chemisorption of AWG on calcite surface is more intense than scheelite. Although the chemisorption of NaOL on calcite surface is almost unaffected by the presence of AWG, the chemisorption of AWG hinders the adsorption of DDA on calcite surface.

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1. Introduction

As an important tungsten-bearing mineral, scheelite (CaWO_4) is often associated with other calcium-containing minerals such as calcite (CaCO_3) and fluorite (CaF_2) [1,2]. As the most common method, flotation is receiving more and more attention in the separation of scheelite from other calcium-containing gangue minerals [3,4]. However, these calcium-bearing minerals often exhibit similar surface properties and floatability due to the similar crystal structure and Ca active sites exposed on the mineral surface [5,6], resulting in inefficient flotation separation of scheelite from calcium-containing gangue minerals. This often leads to a low grade of scheelite concentrate. The flotation process of scheelite is affected by many factors, such as selective reagent scheme (collectors, depressants, modifiers, etc.), selective methods, efficient selective equipment, etc. [7–9]

In flotation, collectors are used to increase the floatability of the target mineral. The most commonly used flotation collectors of scheelite is fatty acid collectors [10], it has been widely recognized that fatty acid collectors can collect these calcium minerals by forming calcium dicarboxylates on the mineral surface through chemisorption [11,12]. Therefore, in the scheelite flotation, the highly selective collectors are often lacking, resulting in inefficient flotation separation of scheelite from calcium-bearing gangue min-

erals [13,14]. Therefore, the separation of scheelite from calcium-containing gangue minerals is often achieved by the use of depressants.

Depressants mainly achieve flotation separation of minerals by reducing the floatability of gangue minerals [15–17]. Depressants for scheelite separation from calcite mainly include inorganic salts and macromolecule depressants [18]. It has been reported that sodium alginate could selectively depress the flotation of calcite [19]. Phosphates, such as sodium phosphate, sodium pyrophosphate and sodium hexametaphosphate also show excellent depression effect on calcite [20,21]. However, they either show relatively weak depression behavior or have a depression effect on target mineral of scheelite. In scheelite flotation, sodium silicate and its inorganic salt solution are often used to depress calcite [21–23] and AWG has been the most popular depressant used in the scheelite flotation due to its strong selective depression behavior on calcite. It has been reported that AWG shows selective depression on calcite using oxidized paraffin soap as collector [24], Feng et al. also studied the depression effect of AWG on calcite using NaOL as a collector [25]. The flotation behavior of minerals and depression mechanism of AWG on calcite from different research groups show some inconsistencies. This is mainly ascribed to the different collectors in flotation and the depressant type (water glass, acidified water glass and salted water glass). It is a pity that they did not investigate its depression behavior on calcite using mixed cationic/anionic collectors, the depression mechanism of AWG on calcite they analyzed is also not sufficient.

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In this study, a mixed collector of DDA and NaOL at a molar ratio was selected as the collector because of the excellent floatability of scheelite. In order to selectively separate scheelite from calcite, AWG was employed as a depressant to achieve a depression effect on calcite. The depression mechanism was revealed by zeta potential measurements, solution chemistry, fourier transform infrared spectroscopy (FTIR) analysis, X-ray photoelectron spectroscopy (XPS) analysis and adsorption amount measurements.

2. Materials and methods

2.1. Pure minerals and reagents

Pure scheelite and calcite were obtained from Guangxi Province, China and Hunan Province, China, respectively. The massive pure minerals were crushed by hand, hand-selected, ground and screened, a sample of -74 to $37\ \mu\text{m}$ fraction was used in the flotation tests and XPS analysis. Part of the samples were further ground to $5\ \mu\text{m}$ for zeta potential tests and FTIR analysis. The samples were analyzed via a chemical method and X-ray diffraction (XRD). Chemical analysis of the samples showed that the scheelite sample contained 77.33% WO_3 , representing a high purity of 96% scheelite, the purity of the prepared calcite was 98.91%. The XRD results were showed in Fig. 1. DDA and NaOL were mixed at different molar ratios to form mixed collectors. The dodecylamine-acetate solution was prepared by mixing equimolar mixtures of dodecylamine and glacial acetic acid. The acidified water glass (AWG) is a mixture of oxalic acid and $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$ at a molar ratio of 1:3. HCl and NaOH were used for pH regulators in the experiments. The water for all experiments was deionized water with a resistivity of more than $18\ \text{M}\Omega \times \text{cm}$.

2.2. Flotation tests

The pure mineral flotation tests were carried out in an XFG flotation machine with a 40 mL plexiglass cell at an impeller speed of 1400 rpm. The pure mineral flotation tests include the following procedures: (1) agitating for 1 min to obtain mineral suspension; (2) adjusting slurry pH by adding HCl or NaOL and agitating for 2 min; (3) adding appropriate amount of depressant AWG for 3 min; (4) adding appropriate collectors for 3 min; (5) collecting the froth products for 3 min. (6) Filter, dry, and weigh froth products and tailings to calculate the recoveries. The flowsheet of pure mineral flotation is shown in Fig. 2.

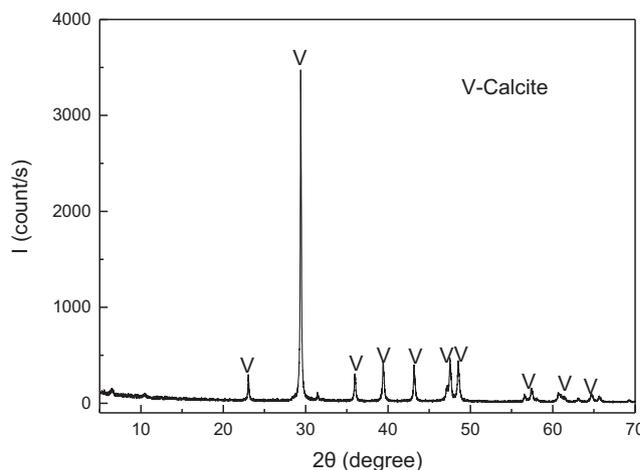
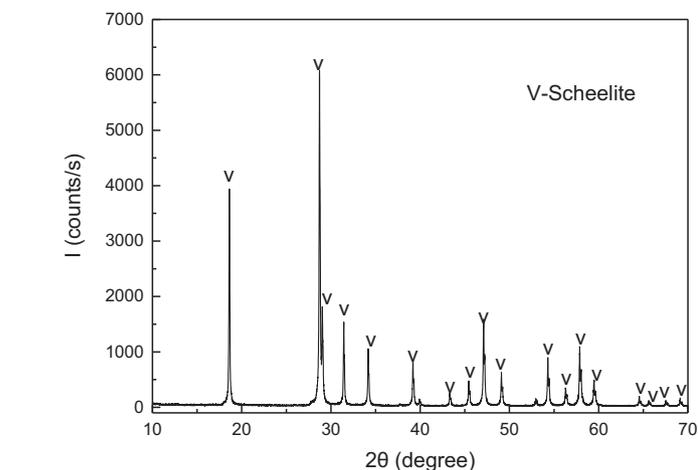


Fig. 1. XRD diagrams of scheelite and calcite.

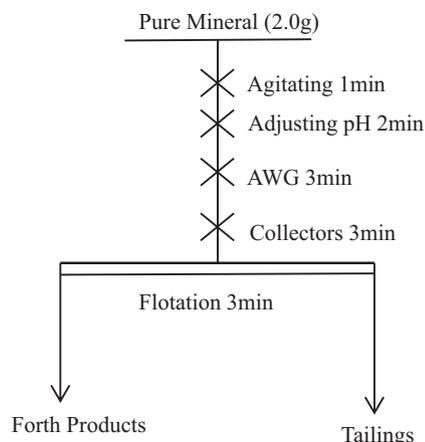


Fig. 2. Flowsheet of pure mineral flotation test.

2.3. Zeta potential measurements

Zeta potential measurements on scheelite and calcite were carried out at $20\ ^\circ\text{C}$ using a zeta potential analyzer. A dilute mineral suspension was prepared by adding 0.03 g of mineral samples to 40 mL KCl ($10^{-3}\ \text{mol/L}$) background electrolyte. Then the desired reagents were added as the same order of flotation experiment and the pH was adjusted and measured. After sedimentation for 5 min, the supernatant liquid was sucked out and used for measurement. The tests were repeated three times and the average value were calculated.

2.4. FTIR measurements

Pure minerals were further ground to $-2\ \mu\text{m}$ in a clean agate mortar. 2.0 g of pure mineral was adding into a 40 mL plexiglass cell then conditioned with the same flotation reagent system and pH for 30 min. After being filtered, the solid phase was washed three times with ultrapure water then vacuum dried at $40\ ^\circ\text{C}$. Samples for spectroscopy measurement were prepared through diluting 1 mg of the dry precipitation to 30 mg potassium bromide powder. The whole process ensured that minerals were not contaminated. The infrared spectra of samples were recorded with a Spectrum One FT-IR (Japan) spectrometer using the diffuse reflection method.

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