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Tune surface physicochemical property of fluorite particles by regulating the exposure degree of crystal surfaces

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ABSTRACT

Grinding for mineral liberation is a prerequisite for a successful flotation separation and different grinding media produce mineral particles with different morphologies and surface properties. In this paper, a systematic investigation was carried out on surface physicochemical properties of fluorite particles produced by ball and rod mills through such methods as single mineral flotation experiment, wettability measurement, X-ray diffraction (XRD) test and scanning electron microscopy (SEM) observations. XRD and SEM observations indicate that the predominant surfaces exposed for both mill particles follow the order of {1 1 1} > {1 1 0} > {3 1 0} > {1 0 0} surfaces. The difference lies in that the rod mill particles possess a higher exposure of more reactive {1 1 0} and {3 1 0} surfaces of higher calcium-atom reactivity, which show a stronger interaction with the collector and hence a higher monolayer coverage degree. This difference also leads to a higher elongation and lower roundness values of rod mill particles that are beneficial to the particle-bubble attachment by shortening the induction time. The results of wettability and flotation show that when treated with the collector solution, the particles produced by rod mill possess a lower critical surface tension and greater hydrophobicity, hence exhibiting a higher flotation recovery. This study signifies the importance of the exposure of crystal surfaces in determining the shape factors and reactivity of mineral particles, which will help to guide the optimization of flotation separation and particle surface modification.

1. Introduction

Fluorite (CaF_2) is the most important basic resource mineral for F-based chemicals and materials that are widely used in industrial, environmental, and medical fields (Kobayashi et al., 2013; Nazabal et al., 2013). There are two types of fluorite mineral occurrences in ore deposit. As for the first type, fluorite mainly coexists with calcite ($CaCO_3$), quartz (SiO_2) and other gangue minerals. And due to their similar density and fine-grained dissemination in ore deposit, ball mill grinding has been widely applied to the production of relatively fine particles before flotation separation (Oja and Tuunila, 2000). As for the second type, fluorite is often associated with other valuable minerals with higher relative density such as scheelite ($CaWO_4$) and cassiterite (SnO_2). Due to their obvious density difference and coarse-grained distribution in ore deposit, rod mill grinding prior to gravity separation has been widely used in producing more uniform particles and avoiding over-grinding (Abouzeid and Fuerstenau, 2012; Heyes et al., 1973; Tavares et al., 2012). After gravity separation, flotation separation is also employed to beneficiate the fluorite (Cooper and de Leeuw, 2004).

The grinding methods of different breakage mechanisms can produce particles with different shapes and flotation performances (Moosakazemi et al., 2017). In recent years, several studies led by Yekeler from Cumhuriyet University have shown that different mineral particles (coal, sulfide, oxide and salt-type minerals) produced by different mills exhibit different values of shape factors. The rod mill ground particles with larger elongation and smoother surface display a better flotation performance (Hiçyilmaz et al., 2004; Ulusoy et al., 2004, 2003; Yekeler et al., 2004). Moreover, the coverage of the collector on the irregular particles produced by rod mill is conducive to the stability of the three-phrase contact line, thus increasing the flotation recovery (Koh et al., 2009; Verrelli et al., 2014; Xia, 2017). Xia (2017) concluded that the particle shape also affects the gravity separation by changing the setting rate of minerals. For example, compared with rounded particles, the setting rate of flaky particles with similar density and size is relatively low.

Given the above reports, the shape factor of mineral particles exerts

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obvious influence on mineral flotation, and the difference in shape factors can explain the different flotation behavior of mineral particles produced by different grinding media. Our previous reports showed that the mineral flotation behavior is always governed by the physicochemical properties of exposed crystal surfaces of the mineral (Gao et al., 2016a, 2018a, 2015; Hu et al., 2012; Jiang et al., 2018; Li and Gao, 2017; Wang et al., 2018; Tian et al., 2018; 2017). It can be inferred that the different flotation behavior is also related to the different exposure of crystal surfaces in mineral particles produced by different grinding media. In addition, the shape factors seem to be directly related to the proportion of crystal surfaces exposed in mineral particles.

In terms of selective separation of fluorite, the collector also plays an important role in modifying the wettability of fluorite. In recent years, some new collectors have been tested in laboratory. Jiang et al (2018) found that the benzohydroxamic acid (hydroxamate types) performs well in separating fluorite from calcite. Hu and Xu (2003) used the α-benzol amino benzyl phosphoric acid to separate fluorite from calcite by controlling pH levels. Besides, collector mixtures such as anionic-cationic and anionic-nonionic also exert synergistic effects on the flotation of fluorite (Filippova et al., 2014; Helbig et al., 1998). However, long chain fatty acids and their derivatives are still used in industry as collectors for fluorite flotation (Keqing et al., 2003; Mielczarski et al., 1999; Pugh, 1986; Sivamohan et al., 1990).

In this study, fluorite particles sized $-74 + 38\,\mu m$ were firstly prepared by both ball and rod mills. Then X-ray diffraction (XRD) test and scanning electron microscopy (SEM) observation were employed to investigate shape factors and exposed crystal surfaces in fluorite particles. And wettability measurement and flotation experiment were conducted to study the collector adsorption and flotation behavior of fluorite particles when treated with oleate collector. These results will help to establish the correlation between the percentage of Miller index crystal surfaces and particle shape factors, hence providing a meaningful guidance for both flotation separation optimization and surface modification.

2. Materials and methods

2.1. Materials

Representative samples of pure green fluorite crystals were collected from Huili mine, Sichuan, China. Chemical analysis showed that the purity of these fluorite samples was 98.64%.

Chemically pure sodium oleate (NaOL, $C_{18}H_{33}O_2Na$) and methanol were provided by Baisaiqin Chemical Technology co., Ltd., Shanghai, China. The pH value was adjusted using dilute sodium hydroxide (NaOH) or hydrochloric acid (HCl) stock solutions. Deionized (DI) water with resistivity of over $18\,M\Omega \times cm$ was used throughout the experiments.

2.2. Methods

2.2.1. Grinding tests

The JC6 jaw crusher (Beijing Grinder Instrument Equipment Co., Ltd.) was firstly used to reduce the size of the pure fluorite crystal (Fig. 1a) from 40 mm to 5 mm in diameter. Then, dry grinding tests were conducted in a 146 mm × 200 mm laboratory size mill (Fig. 1b). As for the rod mill, corundum rods of 15 mm and 11 mm in diameter and 15 cm in length (Fig. 1c) were used as the grinding media. Whereas in the ball mill, corundum balls with a diameter of 21, 16 and 12 mm (Fig. 1d) were used as the grinding media.

During the grinding tests, 200 g of fluorite samples were firstly fed into the mill and ground, running for 30 s each time to prevent overgrinding. After a run, the ground particles were sieved using a standard screen with a pore size of 74 μm (200 mesh). Oversized particles were returned to the mill for a next run, while the particles under the screen were collected for further sieving to obtain particles in the size fraction of $-74 + 38\,\mu m$. Samples with a required size were rinsed with DI water and dried at the temperature of 60 °C.

The size distribution of both ball and rod mill particles were measured by Mastersizer2000 (Malvern Panalytical Ltd., UK), and the results were shown in Fig. 2. The results indicate that there is no significant difference in particle size distribution between the two mill fluorite particles. Then, the specific surface area values of ball and rod grinding particles were determined by the surface area measurement (BET) as 0.052 and 0.037 m^2/g, respectively.

2.2.2. Particle shape characterization by SEM

As for the shape characterization description of milled particles, the fluorite particles were firstly imaged by JSM-6490LV SEM instrument (JEOL Ltd., Japan) before they were calculated using the CorelDraw × 4 software with an assumption that the projection of the particles had an ellipse-like shape (Yekeler et al., 2004).

As shown in Fig. 3, particles that were not overlapped with each other nor bordered out of the picture were chosen and the mean value of five liner lengths and widths were calculated as the real length (L) and width (W) for each particle, respectively (Hiçyilmaz et al., 2004; Yekeler et al., 2004). As for the particle group, more than 200 particles were measured, and the L and W of particle group were calculated by averaging the values of all chosen particles. Based on the ellipse-like shape assumption, Eqs. (1) and (2) were used to calculate the area (A) and perimeter (P), respectively.

$$A \approx \frac{\pi LW}{4} \tag{1}$$

$$P \approx \frac{1}{2}\pi\left[\frac{3}{2}(L + W) - (LW)^{1/2}\right] \tag{2}$$

With values of L, W, A and P, two important shape factors namely the roundness (Ro) and elongation (E), were calculated by Eqs. (3) and (4). It should be noted that the maximum roundness value is 1.0 for a circle.

$$Ro = \frac{4\pi A}{P^2} \tag{3}$$

$$E = \frac{L}{W} \tag{4}$$

2.2.3. X-ray diffraction (XRD) measurement

X-ray diffractometer (D8-ADVANCE, Bruker-AKS, Germany) was run in the reflection mode with Cu Kα radiation (λ = 1.5406, tube potential of 40 mV, and tube current of 40 mA) at a goniometer speed of 4°/min. Random orientation of the sample was very important in sample preparation. Coning and quartering procedure (4 cycles) was used to ensure the representativeness of the measured samples.

2.2.4. Micro-flotation test

Micro-flotation tests were carried out in an XFG flotation machine with a 40 mL plexiglass cell at an impeller speed of 1650 rpm (Gao et al. 2016a). The mineral suspension was prepared by adding 2.0 g minerals and 36 mL DI water to the flotation cell and stirring it for 2 min. The pH value of the mineral suspension was adjusted by adding NaOH or HCl for 2 min before adding a certain concentration of sodium oleate for another 3 min. The stable pH value was recorded prior to the flotation which lasted for 3 min before the flotation products were collected, filtered, dried and weighted. The flotation recovery was calculated using dry product weight.

2.2.5. Wettability measurement

For the measurement of the wettability of nubby samples, sessile drop technique (Rupp et al., 2014) and the captive bubble method (Baek et al., 2012) were widely used. Whereas for the powder samples, the Washburn method (Galet et al., 2010) and the flotation method