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Selective adsorption of benzhydroxamic acid on fluorite rendering selective separation of fluorite/calcite

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ABSTRACT

Fluorite, a chief source of fluorine in the nature, usually coexists with calcite mineral in ore deposits. Worldwide, flotation techniques with a selective collector and/or a selective depressant are commonly preferred for the separation of fluorite from calcite. In the present study, an attempt was made to use benzhydroxamic acid (BHA) as a collector for the selective separation of fluorite from calcite without using any depressant. Results obtained from the flotation experiments for single mineral and mixed binary minerals revealed that the BHA has a good selective collecting ability for the fluorite when 50 mg/L of BHA was used at pH of 9. The results from the zeta potential and X-ray photoelectron spectroscopy (XPS) indicated that the BHA easily chemisorbs onto the fluorite as compared to calcite. Crystal chemistry calculations showed the larger Ca density and the higher Ca activity on fluorite surface mainly account for the selective adsorption of BHA on fluorite, leading to the selective separation of fluorite from calcite. Moreover, a stronger hydrogen bonding with BHA and the weaker electrostatic repulsion with BHA$^-$ also contribute to the stronger interaction of BHA species with fluorite surface.

1. Introduction

Fluorite (CaF_2), which is a major source of fluorine in the Earth, has been considered as an important strategic mineral in recent years [1]. In natural ore deposits, fluorite is mostly associated with calcite ($CaCO_3$) mineral [2]. Around the world, froth flotation method is commonly used for the separation of fluorite from calcite. Conventional collectors, like fatty acids and their salts, are mainly utilized for the flotation of fluorite ores [3]. Pugh and Stenius showed that the maximum flotation response for calcite and fluorite with sodium oleate as a collector can be correlated directly with the minimum interfacial tension of the air/solution interface based on solution chemistry calculations [4]. Marinakis and Shergold found that sodium silicate can depress fluorite and calcite by preventing oleate species from reacting with surface sites [5]. Gao et al. recently reported a novel reagent schedule including sulfoleic acid (SOA) as a collector, citric acid (CA) as a depressant and sodium fluoride (NaF) as a regulator to achieve the selective separation of calcite from fluorite [2]. It should be noted that the separation of fluorite from calcite by flotation technique is quite difficult due to

their similar surface properties, and hence similar interactions with fatty acid collectors [6–8].

Some efforts were made to sort out some new selective collectors to achieve the selective separation of calcite and fluorite, as fatty acid collectors possess poor selectivity and low water-solubility at a low temperature. Filippova et al. stated that the sulpho-succinamate or alkyl hydroxamate can perform moderate collecting difference in the flotation behaviour of fluorite and calcite [9]. Schubert et al. utilized oleyl sarcosine as a collector and quebracho as a depressant to achieve effective separation of fluorite from calcite [10]. Xu et al. showed that cyclohexene formic acid as a collector and water glass as a depressant could achieve the satisfactory separation [11]. However, the extremely high dosage of quebracho or water glass for the separation may cause the fine particles to well disperse in the tailing pond, and thus cause a serious problem for wastewater treatment.

Some researchers have tried to use the mixture of collectors, such as anionic-cationic or anionic-nonionic, for the separation of fluorite from calcite. Helbig et al. indicated that anionic-cationic mixing collectors of sodium N-dodecanoyl sarcosine and dodecy-lammonium chloride can improve the floatability of fluorite, however the selectivity of the collector was not clearly elaborated [12]. Filippova et al. found that two combinations of anionic/nonionic reagents (di-2-ethylhexyl phosphoric acid/octylphenol ethoxylate and alkyl hydroxamate/iso-tridecanol) at pH 8 can float fluorite

effectively while calcite was not floated by these collectors [9]. However, it's a pity that they had not investigate further the separation performance of those collectors for mixed binary minerals and/or run-of-mine.

In recent years, hydroxamate types of collectors have attracted more and more attention for their better selectivity and moderate collecting power. Deng et al. conducted the pure mineral flotation tests at pH 10 and found that N-(6-(hydroxyamino)-6-oxohexyl) decanamide (one kind of amide hydroxamate) exhibits a superior affinity to scheelite against calcite [13]. Recently, benzhydroxamic acid (BHA) has been used widely as a collector for the cassiterite [14] and tungsten minerals (scheelite and wolframite) [15] flotation in the presence of activator Pb^{2+} both in the laboratory and in dressing plants. It is interesting to note that in either cassiterite or tungsten mineral flotation systems, calcite is the main gangue mineral. These reports have proved that BHA have a weak interaction with calcite, and it might be served as a better candidate collector for the separation of fluorite/calcite.

In this work, BHA was utilized as a collector to separate the fluorite from calcite through flotation tests using single mineral and mixed binary minerals. The mechanism of the selective separation was analysed through zeta potential measurements, X-ray photoelectron spectroscopy (XPS) detections and crystal chemistry analysis.

2. Materials and methods

2.1. Samples and reagents

Representative samples of fluorite and calcite were collected through hand picking from the Shizhuyuan Mine, Chenzhou, Hunan, China. The received samples were analysed through the X-ray diffraction (XRD) for their purity. The XRD results revealed that the purity of fluorite and calcite is greater than 97%, as shown in Fig. 1.

After that, samples were ground in a pottery ball mill, in order to obtain $-75+38\,\mu m$ size fraction for the micro-flotation. The received undersize fraction (i.e. $-38\,\mu m$) was further ground in an agate mortar to obtain particles with size less than $5\,\mu m$ for zeta potential and XPS measurements.

BHA with 98% grade was obtained from Tokyo Chemical Industry. Pine oil was provided by Qingdao Ruchang Mining Industry Co., Ltd. The pH was adjusted with hydrochloric (HCl) and sodium hydroxide (NaOH) solutions. Deionized (DI) water with a resistivity of more than $18\,M\Omega * cm$ was used throughout the experiments.

2.2. Flotation experiments

The XFG Flotation machine (Exploring Machinery Plant, Changchun, China) with a 40 mL plexiglass cell was used for flotation tests. The impeller speed was set at l650 r/min, since the flotation results showed that the speed from 1250 to 2000 r/min exerts slight influence on the flotation response for two minerals. The XFG machine configuration has been reported in previous publication [2]. For single mineral, the flotation suspension was prepared by adding 2 g of single mineral, while for mixed binary minerals, the suspension was made by mixing fluorite and calcite at a certain mass ratio into 35 mL of DI water. The pulp was conditioned for 2 min followed by 3 min conditioning after adjusting the suspension pH to a desired value. After conditioning, the collector was added and agitated for 3 min. After that, Pine oil (0.1 μL) was added and conditioned for 1 min. Finally, the froth collection was performed for 5 min.

For single mineral flotation, the products were collected, dried, weighed and the recovery was determined. For mixed minerals
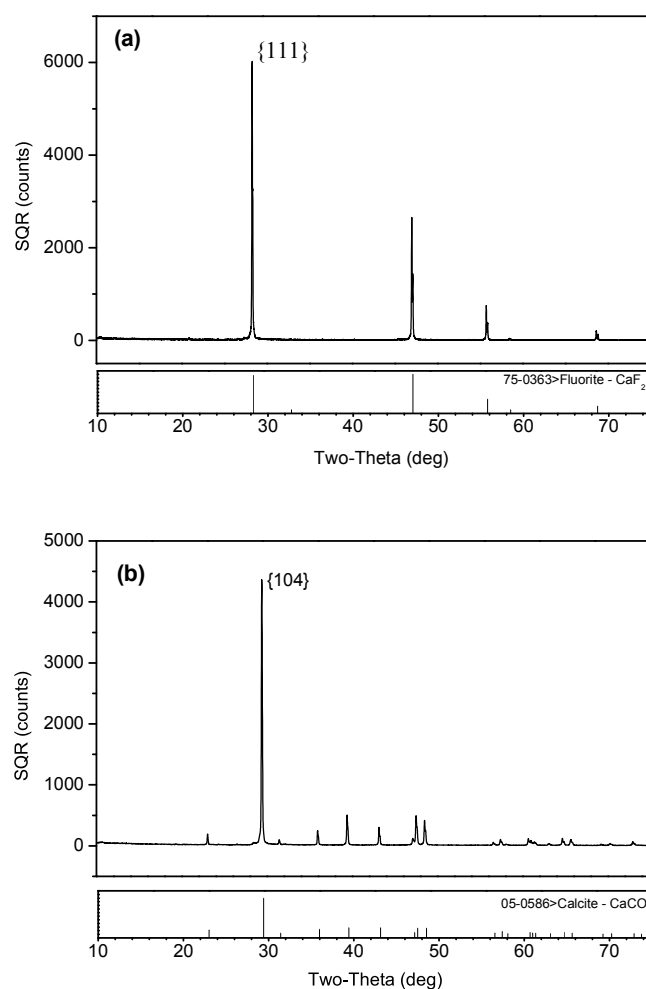

Fig. 1. XRD spectrums of powdered fluorite (a) and calcite (b) minerals used for flotation tests.

flotation, the concentrate and tail were assayed for CaF_2 and $CaCO_3$ content. The average recovery and standard deviation were also calculated and reported.

2.3. Zeta potential measurements

Zeta potential measurements were carried out at a temperature of 20 °C by using a Nano-ZS90 zeta potential analyzer (Malvern Instruments, UK). The suspension was prepared by adding 0.02 g of mineral samples into 40 mL KCl (0.01 mol/L) solution. Then BHA was added and the pH was adjusted and measured. The suspension was continuously agitated by magnetic stir for 10 min. After that, the supernatant liquid was sucked out and used for other tests. At least 3 measurements were made for a certain experimental condition, and the average value of zeta potential was determined simultaneously.

2.4. XPS measurements

In present study, VG ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA) was used for the determination of XPS spectra of fluorite and calcite powders for both untreated and treated with BHA as a collector. The Al Kα X-rays meter with an energy of 20 eV for narrow scans was employed for observations. The pressure in the analysis chamber was more than 5×10^{-10} mbar. Samples having particle size less than $5\,\mu m$ were conditioned in BHA solution at pH of 9. The mineral suspension was than magnet-