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New collectors for the flotation of unactivated marmatite

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ABSTRACT

Three thiophenol collectors were tested for the flotation of marmatite without activation by copper sulfate. Flotation tests showed that marmatite flotation increased according to the following order: 2-fluoro thiophenol < 2-hydroxy thiophenol < 2-amino thiophenol. All these thiophenols exhibited a better flotation property for marmatite than butyl xanthate. Infrared spectra indicated that 2-amino thiophenol and 2-hydroxy thiophenol chemically adsorbed onto the surface of marmatite. 2-Fluoro thiophenol adsorbed physically onto the surface of marmatite. Quantum chemical calculations indicated that the energy of the highest occupied molecular orbital (HOMO) for 2-amino thiophenol was the highest among the tested collectors and we thus determined that its collecting ability should be the strongest. This agreed with the experimentally determined flotation results.

1. Introduction

Marmatite ($Zn_xFe_{1-x}S$) is a type of sphalerite that contains 6–25% ferrous iron and it is an important zinc mineral resource. Marmatite naturally occurs in abundance in China, and China possesses 25% of the total zinc reserves in the world (Tong et al., 2006, 2007). Recently, the beneficiation of marmatite and sphalerite ores and zinc extraction in particular has attracted a great deal of attention because of the booming zinc market. As a consequence, research on collectors has also attracted many researchers.

Collectors of zinc minerals mostly include: xanthates (Chen and Tong, 2007; Girczys and Laskowski, 1972), cationic collectors (Laskowski et al., 2003), chelate collectors (Ackerman et al., 1999; Natarajan et al., 1997; Pradip, 1988) or a combination of these reagents.

Xanthate type reagents are widely accepted and extensively used all over the world by operating mills for the flotation of zinc metal sulfide ores. Copper sulfate is generally used to activate zinc minerals during marmatite and sphalerite flotation (Finkelstein, 1997, 1999). Early in the 1970s it was reported (Pomianowski et al., 1975) that the amount of copper sulfate needed for marmatite flotation depends on the iron content of the mineral. Some mills have to use as much as 1–1.2 kg copper sulfate per metric ton of ore. Copper sulfate is a very corrosive chemical which reduces equipment life and produces a toxic effluent. Laskowski et al. (2003) reported that activated sphalerite could be floated at pH 6–12.5 while quartz was depressed completely at pH > 12 by 12-amine. Due to ores becoming increasingly complex, selective reagents such as non-ionic collectors and especially chelates are receiving plenty of attention.

In 2006, a series of N-arylhydroxamic acids (31 sorts of different N-arylhydroxamic acids) were reported to be able to float zinc minerals without the need for activation by copper sulfate. N-phenyl acetohydroxamic acid and N-phenyl hydrocinnamohydroxamic acid gave the best sphalerite recoveries but pyrite was also floated along with sphalerite (Natarajan and Nirdosh, 2006).

The most significant findings of this work is that thiophenol has the ability to float zinc minerals without activation by copper sulfate and also that thiophenol has a poor collecting property for pyrite.

2. Experimental

2.1. Materials

Marmatite and pyrite samples were supplied by Dachang mine, Guangxi province and Yunfu mine, Guangdong province of China, respectively. Lumps of the samples were crushed and pulverized. The −106 μm size fraction was screened out for the flotation tests and the −38 μm fraction for the FTIR tests. All samples were stored in sealed glass bottles. The purity of pyrite was 94.67%. Element assay indicate that the marmatite samples contain Zn 56.22%, Fe 15.15%, S 27.61%, Pb 1.02%.

Flotation collectors were 2-amino-thiophenol, 2-hydroxy-thiophenol, 2-fluoro-thiophenol (Fig. 1) and butyl xanthate. Butyl xanthate was an industrial grade product from a chemical factory of Zhuzhou. 2# Oil was employed as a frother which was also industrial grade product. Analytical grade sodium hydroxide and hydrochloric acid were used for pH control.

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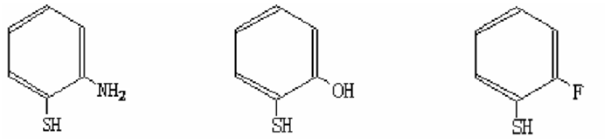

(a) 2-amino-thiophenol (b) 2-hydroxy-thiophenol (c) 2-fluoro-thiophenol

Fig. 1. The molecular structure of thiophenol.

2.2. Methods

Microflotation tests were carried out with hitch groove of a 40 ml flotation cell (Fig. 2) using 2 g of the sample. For each test, 2 g of sample was taken and the surface was cleaned for 10 min using an ultrasonic cleaner to remove any oxide. The sample settled and the upper liquid layer was decanted. The sample was flushed with 40 ml distilled water and the pH value was adjusted upon which the collector and the frother were added. The conditioning time for the collector was 2 min and for the frother it was 1 min. The flotation was performed over 4 min, upon which the floated and non-floated fractions were filtered, dried and weighed for the recovery calculation.

Marmatite samples were put into 25 ml solution at collector concentration 1×10^{-3} mol/L. DRIFT spectra were obtained using a Fourier transform infrared spectrometer NEZUS 470.

Quantum chemical calculations were performed using HyperChem 7.5 software (Makolab, 2002). A molecular model was initially built according to structural parameters and using the Model Builder function to generate a three-dimensional (3D) structure. Geometry optimization was used to generate a molecule for a single point calculation. Molecular orbital energies and the electrostatic potential obtained from single point quantum mechanics calculations may be used to investigate the relative reactivity of different molecular substituents and the regioselectivity of reactions.

Fig. 2. Flotation machine for microflotation test.

3. Results and discussion

3.1. Flotation performance of marmatite and pyrite

Fig. 3 shows the flotation recovery of marmatite with the three thiophenols and butyl xanthate as collectors. Without activation by copper sulfate, marmatite recovery was more than 80% when 2-amino thiophenol and 2-hydroxy thiophenol were used as collectors over a wide pH range, as shown in Fig. 3. It was also found that 2-fluoro thiophenol and xanthate have a weak collecting property for marmatite. Four collectors were tested on marmatite and their effectiveness decreased according to the following: 2-amino thiophenol > 2-hydroxy thiophenol > 2-fluoro thiophenol > butyl xanthate.

Fig. 4 shows the flotation recovery of pyrite with three kinds of thiophenol and butyl xanthate as collectors. The collecting ability of the three thiophenols was found to be poorer than that of butyl xanthate for pyrite flotation. This indicates that thiophenol has good flotation selectivity for marmatite. Thiophenol may thus be used to separate the zinc mineral from pyrite.

3.2. Adsorption of thiophenol on the marmatite surface

The infrared spectrum of the interaction between 2-amino thiophenol and marmatite is shown in Fig. 5. From Fig. 5, the adsorption peak at 1608 cm^{-1} is assigned to overtone and combination bands of NH_2 scissoring and the stretching vibration of C═C (Barbara, 2004). The peak at 817 cm^{-1} is due to the wagging and twisting of NH_2. The peak at 1478 cm^{-1} is assigned to the stretching vibration of C═C groups in the benzene ring. C═C stretching bands of benzene are very sensitive to the electronegativity of substitution groups and electron acceptor groups result in the frequency of C═C stretching bands decreasing from 1500 cm^{-1} to 1480 cm^{-1} (Wang et al., 1982). The peak at 1438 cm^{-1} is also a C═C stretching vibration and the peak at 1309 cm^{-1} is assigned

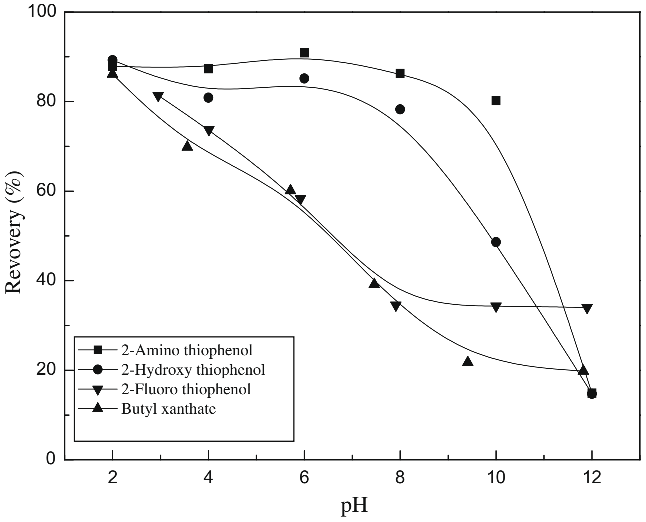

Fig. 3. Flotation recovery of marmatite as a function of pH with a collector concentration of 8×10^{-4} mol/L.