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Flotation of heavily oxidized pyrite in the presence of fine digenite particles

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ABSTRACT

The ease or complexity of the selective separation of copper sulphur minerals during sulphide flotation is always dominated by the level of surface oxidation. The interaction between oxidized pyrite and other base metal sulphides is important for the flotation process. In this study, the effects of fine digenite particles on the flotation of heavily oxidized pyrite in the presence of sodium butyl xanthate were investigated. The micro-flotation results showed that the floatability of pyrite declined sharply once it was over-oxidized. However, the addition of fine digenite significantly restored the floatability and flotation rate of pyrite, even in strong alkaline solutions. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) of the flotation products indicated no copper ions on the pyrite surface. This restoration can be attributed to fine digenite particles adsorbing on the surface of coarse pyrite particles and removing a large number of fine pyrite particles covering the pyrite surface in the presence of sodium butyl xanthate. The extended Derjaguin–Landau–Verwey–Overbeek theory based on zeta potential measurements and contact angle measurements was used to calculate the interaction energy between mineral particles. The calculation results showed good agreement with the flotation and SEM-EDS analysis results and explained the mechanism of particle interaction.

1. Introduction

Froth flotation is widely used for the treatment of base metal sulphides, and relies on the differences in surface chemistry between valuable sulphide minerals and gangue minerals (Xian et al., 2015b; Ejtemaei and Nguyen, 2017). Pyrite (FeS_2) and other sulphide minerals are closely associated with each other in most copper ores, and their selective separation is a very complicated process because the base metal sulphides are highly oxidized. The oxidation of pyrite occurs more easily during in situ weathering of an ore body, mining stockpiling, crushing, milling, and flotation. Many previous reports in literature have identified the importance of studying the flotation of pyrite after the oxidation (Guy and Trahar, 1985; Wang and Hu, 1989; Smart, 1991; Xian et al., 2015b; Jacques et al., 2016).

Moderate surface oxidation of pyrite is known to be beneficial for the adsorption of collectors and formation of a hydrophobic surface. However, once pyrite is heavily oxidized, the floatability declines sharply, and xanthates cannot effectively collect pyrite unless the dosage is significantly increased. Based on this, many researchers have attempted to depress pyrite in sulphide flotation by oxidation. For example, lime can depress pyrite by accelerating the oxidation of pyrite in alkaline solutions, and is widely used in traditional practices. However, the results of selective separation are unsatisfactory in many cases, particularly when obtaining high-grade copper concentrate. On the one hand, metal ions like copper ions also exist in the flotation pulp, and they can activate pyrite flotation through Cu adsorption on the surface above a certain concentration (Voigt et al., 1994; Zhang et al., 1997; Weisener and Gerson, 2000). On the other hand, lattice defects in the pyrite crystal change the electrochemical properties and floatability of pyrite; this is responsible for the varying pyrite oxidation during ore formation (Abraitis et al., 2004; Li et al., 2011; Xian et al., 2015a, 2015b). However, there has been little research on the interaction between the particles of copper sulphur minerals. As the oxidization proceeds, the attraction or repulsion between particles may happen during flotation. This may be another reason for the unsatisfactory separation results.

Low/high temperature thermal oxidation (Richardson and Vaughan, 1989; Newell et al., 2006) and air oxidation at ambient temperatures (Mycroft et al., 1995; Legrand et al., 1998) are widely employed methods for forming oxidized layers on a sulphide mineral surface. However, the latter method is much closer to the natural oxidation of pyrite, and may better represent the actual surface characteristics after the oxidation.

Digenite is a type of secondary copper-bearing ore. In the present study, the flotation of natural, heavily oxidized pyrite in the presence of fine digenite was investigated by the micro-flotation, zeta potential, and scanning electron microscopy–energy dispersive spectrometry (SEM-EDS) analysis. The interaction results were verified by the calculations

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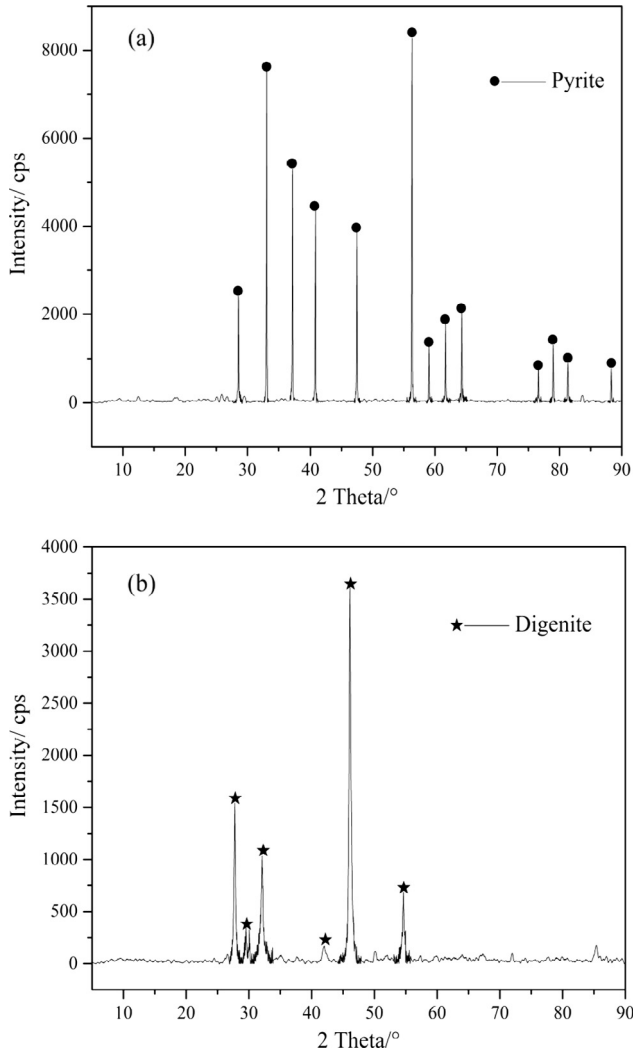

Fig. 1. X-ray diffraction patterns of pyrite (a) and digenite (b).

based on the extended Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. The findings of this study will help in understanding the selective separation of heavily oxidized pyrite and fine digenite. Fine digenite may be used as an activating agent to restore the floatability of heavily oxidized pyrite.

2. Experimental

2.1. Materials and reagents

Lump pyrite and digenite samples were obtained from Zijin Mining (Fujian Province, China). The ore samples were carefully crushed, handpicked, dry-ground with a porcelain ball mill, and finally dry-sieved to obtain size fractions of −74 + 38 μm for the pure mineral flotation tests. The −5 μm fraction of pyrite and digenite was obtained by the elutriation method, and used for the artificial mineral flotation tests, contact angle measurements, and zeta potential measurements. The samples were exposed to air during the preparation for less than 2 h (Newell et al., 2006). The minerals were stored in a desiccator with a nitrogen atmosphere and floated within 2 weeks of preparation. The results of the X-ray diffraction (XRD) shown in Fig. 1 and chemical element analyses showed that, within the assay error, the purities of pyrite and digenite were 99.72% and 98.52%, respectively.

For the oxidation experiments, the samples were left on glass dishes and exposed to air. In order to make the results comparable, the temperature and relative humidity of the laboratory were controlled at approximately 25 °C and 60%, respectively, during the course of the experiments.

Sodium butyl xanthate (SBX) obtained from Tieling, China had 95% purity, and was employed as the collector for the micro-flotation experiments. Analytical-grade HCl and NaOH were used as the pH regulators. Ferric chloride was used as an activating agent. Terpenic oil was employed as a frother. Deionized water (DI water) with a resistivity of 18.3 MΩ·cm was employed in all experiments.

2.2. Micro-flotation experiments

The micro-flotation experiments were performed with a $XFGC_{II}$ laboratory flotation machine which is a kind of air-inlet hanged through cell built by Jilin Prospecting Machinery Plant in China at an impeller speed of 1800 rpm. A PHS-3C acidometer built by Shanghai Leici Company (Shanghai, China) was used to measure the pH value. During the flotation test, 5.0 g of a single mineral (−74 + 38 μm) or an artificial mixture of 5.0 g of heavily oxidized pyrite (−74 + 38 μm) and a proportional amount of digenite (−5 μm) were mixed with 50 mL DI water in the flotation cell, and mixed for 3 min. HCl or NaOH was added as desired to regulate the pH of the suspension. Then, the suspension was conditioned with SBX for 3 min, and terpenic oil for 1 min. In the micro-flotation experiments, the dosage of SBX and terpenic oil was fixed at 1×10^{-4} mol/L and 40 mg/L, respectively. Finally, the froth and sink products were obtained, filtered, dried in a vacuum oven, weighed, and analysed. Before each micro-flotation experiment, ultrasonication/decantation was carried out to clean the sample surfaces for three cycles. For each cycle, the dosage of DI water was fixed at 50 mL, and the ultrasonic treatment time was fixed at 4 min. Each flotation experiment was repeated at least three times, and the average flotation recovery value was calculated. The error of the recovery was found to be within 3.0%.

2.3. Zeta potential measurements

A Malvern Instruments Nano-ZS90 zeta potential analyser was used to determine the zeta potential values of −5 μm pyrite and digenite particles. After 20 mg of a sample was added to 50 mL of DI water, the pulp was stirred with a magnetic stirrer for 5 min. Then, the pulp pH was adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH to the desired value in the presence or absence of SBX. The pulp was stirred for additional 5 min, and left to stand for another 10 min in order to settle down the coarse particles. Then, the supernatant was injected through a syringe into the test electrophoresis tube for the measurement. To ensure the accuracy of the results, the zeta potential measurements were performed at least five times for each pH value, and the average value was calculated. The measurements were performed at room temperature (25 °C), and the error was found to be within 5 mV.

2.4. SEM-EDS studies

An SU1510 scanning electron microscope built by the Hitachi Company in Japan and equipped with an energy dispersive X-ray spectrometer was used to observe the surface profile of the mineral particles, and obtain the elemental composition of the surface. The operating voltage of the scanning electron microscope was 15 kV.

2.5. Contact angle measurements

The contact angles of pyrite after the oxidation and digenite in the presence of SBX were measured with the JC2000A contact angle apparatus. Lamellar samples with a highly smooth surface were prepared by using the compression method. The samples were placed in a rectangular glass chamber, and a liquid drop with a base diameter of 3–4 mm was introduced onto the surface through a micro-syringe.