

The role of sodium sulfide in the flotation of pyrite depressed in chalcopyrite flotation



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ABSTRACT

In copper-gold flotation plants, pyrite which is depressed in copper flotation is often floated subsequently with the addition of sodium sulfide (Na_2S) to recover the associated gold. For the first time, this study investigated the role of Na_2S responsible for the flotation of pyrite depressed in chalcopyrite flotation through flotation tests and Cyro-XPS (X-ray photoelectron spectroscopy) analyses. It was found that the application of Na_2S improved pyrite flotation to the same extent as the application of PAX and the combination of Na_2S and PAX further increased pyrite recovery. It is interesting that PAX and Na_2S promoted pyrite flotation through different mechanisms. PAX reduced the hydrophilic metal oxidation species and adsorbed on pyrite surface, resulting in the flotation of depressed pyrite. Unlike PAX, Na_2S increased the hydrophobicity of pyrite and pyrite flotation by forming elemental sulfur and polysulfide on pyrite surface. The application of PAX and Na_2S at the same time further enhanced the hydrophobicity of pyrite and pyrite flotation as a result of the combined actions of PAX and Na_2S .

1. Introduction

In porphyry copper-gold ores, gold is commonly present as free gold, copper-associated gold and pyrite-associated gold which are recovered through gravity separation, copper flotation and pyrite flotation, respectively (Burns et al., 2014; Seaman et al., 2012a; Zheng et al., 2010). In copper flotation, gold is floated with copper minerals, while pyrite is depressed in order to produce a saleable copper-gold concentrate. Then, the depressed pyrite is activated and floated to recover the remaining gold associated with pyrite (Zheng and Manton, 2010).

Lime is the most commonly used pH modifier to depress pyrite in copper flotation (Mu et al., 2016a,b). The depression mechanism of pyrite by lime is attributed to the formation of hydrophilic species such as $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and CaSO_4 (Hu et al., 2000). The stability of these hydrophilic oxidation products increase with the increase of pH (Moslemi and Gharabaghi, 2017). Li et al. (2012) reported that the presence of calcium hydroxyl on pyrite surface provided electrons to pyrite and caused electron accumulation on pyrite surface, which inhibited the reaction of xanthate with pyrite and therefore reduced pyrite flotation. This finding was confirmed by Zhang et al. (2011) who demonstrated that the resistance of pyrite surface increased from $48.2 \Omega/\text{cm}^2$ at pH 12 adjusted with NaOH to $232.6 \Omega/\text{cm}^2$ at the same pH but adjusted with lime.

To float pyrite depressed in copper flotation, sodium sulfide or sodium hydrosulfide is normally used to activate pyrite. Seaman et al.

(2012b) found that in order to obtain 70% pyrite recovery, the dosage of sodium sulfide was required to be as high as 460 g/t in a copper-gold flotation plant. The activation mechanism of Na_2S on the flotation of pyrite depressed in copper flotation is unknown.

In fact, sodium sulfide or sodium hydrosulfide is commonly used as a sulfidizer of oxidized sulfide minerals (Becker et al., 2014; Clark et al., 2000; Newell and Bradshaw, 2007; Newell et al., 2006, 2007), base-metal oxide minerals (Castro et al., 1974a,b; Corin et al., 2017; Ejtemaei et al., 2014) and cerussite (Herrera-Urbina et al., 1999). Different mechanisms have been proposed to explain the sulfidization process on mineral surfaces. Castro et al. (1974b) proposed an anionic exchange of sulfidization on oxidized chalcopyrite. A covellite-like surface formed under less intense sulfidizing conditions while a chalcocite-like surface formed at high hydrosulfide concentrations. Newell et al. (2007) proposed that the sulfidization of oxidized pyrrhotite proceeded through both an anionic exchange mechanism and a direct precipitation reaction to form a pyrrhotite/pyrite-like surface and the sulfidization of oxidized pentlandite was through chemisorption of hydrosulfide ions, followed by a surface reaction with nickel hydroxide to produce a millerite-like surface. In addition, a reasonable quantity of polysulfide and elemental sulfur was found on all the sulfidized mineral surfaces and could well contribute to their hydrophobicity and floatability (Newell and Bradshaw, 2007).

Sodium sulfide was also found to induce the collectorless flotation of sulfide minerals. Yoon (1981) and Luttrell and Yoon (1984)

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demonstrated that chalcopyrite could be floated in the presence of sodium sulfide without the addition of collector and proposed that sodium sulfide acted as a cleaning agent to remove the surface oxidation products, thus restoring the inherent hydrophobicity of chalcopyrite. However, Trahar (1983) argued that chalcopyrite was not inherently hydrophobic and the Na_2S -induced collectorless flotation might be due to the formation of elemental sulfur and polysulfide on chalcopyrite surface through slight oxidation of sulfide ions.

Despite the studies on sulfidization and collectorless flotation with sodium sulfide, few studies have been conducted to understand the role of sodium sulfide in the flotation of pyrite depressed in chalcopyrite flotation which was a subject of this paper. This study provides insights to improve the flotation of gold associated with pyrite.

2. Materials and methods

2.1. Materials and reagents

Chalcopyrite and pyrite single minerals, supplied by GEO Discoveries, were crushed through a jaw crusher and a roll crusher, and then screened to collect +0.71–3.35 mm particle size fractions. The elemental content of iron and sulfur of the pyrite sample was 45.4 wt% and 50.5 wt%, respectively. XRD analysis of the sample revealed a composition of 96.0 wt% pyrite with minor quartz, galena and copper minerals. The chalcopyrite sample contains about 95.0 wt% chalcopyrite and 5.0 wt% pyrite. The processed samples were sealed in polyethylene bags and then stored in a freezer at a temperature of $-20\text{ }^\circ\text{C}$ to reduce surface oxidation.

RTD11A (a dithiocarbamate type collector), potassium amyl xanthate (PAX) and DSF004 were used as the chalcopyrite collector, pyrite collector and frother, respectively. They were of industry grade and used as received. Other chemicals were of AR grade. Deionized water was used in all experiments. Fresh chemical solutions were prepared daily for flotation tests.

2.2. Methods

2.2.1. Flotation procedure

The mixture of chalcopyrite (20 g) and pyrite (80 g) was combined with 100 mL water and ground with 3.6 kg of stainless steel grinding media in a laboratory stainless steel rod mill for 4.4 min so that 80 wt% of the particles were less than 106 μm . The pulp was then transferred to a 1.5 L Agitair flotation cell and agitated at 600 rpm. Lime was added to adjust the pH to 9.5. 18 g/t RTD11A and 30 g/t DSF004 were added and conditioned for 2 min for each reagent. Four chalcopyrite flotation concentrates were then collected after cumulative times of 1, 3, 6 and 10 min at an air flow rate of 6 L/min with a scrapping time interval of 10 s. After chalcopyrite flotation, Na_2S (if needed), PAX (if needed) and DSF004 (30 g/t) were added to the tailing and conditioned for 2 min for each reagent. Then, pyrite flotation was carried out. Four pyrite flotation concentrates were collected after cumulative times of 1, 3, 6 and 10 min. All the concentrates and tailings were filtered, weighted and assayed to calculate chalcopyrite and pyrite recoveries.

2.2.2. Cryo-XPS analyses

The feeds to pyrite flotation under different conditions were taken from the flotation cell and frozen immediately in liquid nitrogen ($-196\text{ }^\circ\text{C}$) before the analyses by Cryo-XPS.

XPS data was acquired using a Kratos Axis ULTRA X-ray photoelectron spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al $K\alpha$ X-rays (1486.6 eV) at 150 W (15 kV, 15 mA). Survey (wide) scans were taken at a pass energy of 160 eV, and multiplex (narrow) high resolution scans were taken at 20 eV. Survey scans were carried out over the 1200–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and

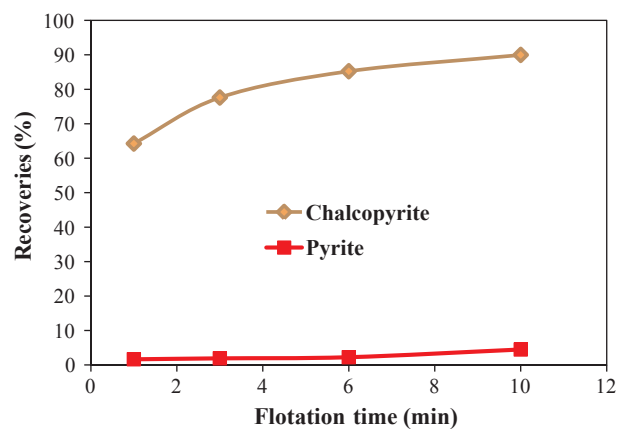


Fig. 1. Recoveries of chalcopyrite and pyrite as a function of flotation time in copper flotation (pH adjusted to 9.5 by lime; 15 g/t RTD11A; 30 g/t DSF004).

250 ms dwell time. Base pressure in the analysis chamber was 1.0×10^{-9} Torr, and during sample analysis was 1.0×10^{-8} Torr.

To avoid the sublimation of elemental sulfur or other volatile compounds formed on mineral surfaces under the ultra-high vacuum condition, samples for Cryo-XPS analyses were cooled in the loading chamber to $-160\text{ }^\circ\text{C}$ before evacuation and maintained at that temperature during the sample analysis using liquid nitrogen. The resulting spectra were charge-corrected using C 1s as a reference with a binding energy of 284.8 eV. Data processing and fitting were carried out using CasaXPS.

3. Results and discussion

3.1. Flotation

Fig. 1 shows the recoveries of chalcopyrite and pyrite as a function of flotation time in copper flotation. Lime was used to increase pH to 9.5 in flotation to depress pyrite. It can be seen that chalcopyrite was selectively floated from pyrite with about 90% chalcopyrite recovery and only 4% pyrite recovery. The depression of pyrite might be caused by the formation of hydrophilic $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and CaSO_4 species on pyrite surface, thus preventing the adsorption of collector (Li et al., 2012). Moreover, RTD11A is a dithiocarbamate type collector and has an excellent selectivity for chalcopyrite against pyrite (Mu et al., 2016b), which assisted in rejecting pyrite in copper flotation.

After chalcopyrite flotation, pyrite flotation was conducted to recover the depressed pyrite. Fig. 2 shows pyrite recovery as a function of

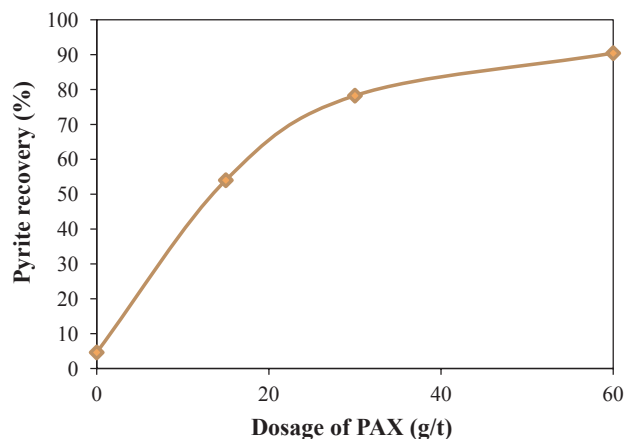


Fig. 2. Pyrite recovery as a function of PAX dosage in the absence of Na_2S in pyrite flotation (pH 8.5; 30 g/t DSF004).

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