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The influence of pyrite content on the flotation of chalcopyrite/pyrite mixtures



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1. Introduction

The most abundant mineral resource of copper is the sulphide minerals. Examples of such minerals include chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄), chalcocite (Cu₂S) and covellite (CuS). In recent times, it is very rare to find copper deposits with head grade averaging more than 2% Cu (Davenport et al., 2002). In both porphyry and skarn ores, the copper grade is lowered by the presence of other sulphide and non-sulphide gangue minerals such as pyrite (FeS₂), sphalerite (ZnS), and quartz (SiO₂) (Aplan and Chander, 1988; Kydros et al., 1994). Chalcopyrite, a major resource for copper production, is not exceptional; it is often found in association with iron sulphides, particularly pyrite, and minor amounts of sphalerite and molybdenite (Habashi, 1978; Wang and Forssberg, 1991). Recent studies indicate that selective separation of chalcopyrite from pyrite is very difficult due to several electrochemical interactions that occur at the minerals surfaces during the grinding and conditioning processes (Finkelstein, 1997). For instance, galvanic interactions between pyrite and chalcopyrite surfaces prior to flotation may lead to the oxidation and dissolution of the chalcopyrite and copper activation of the pyrite. The formation of hydrophilic surface coatings of iron hydroxide which depress chalcopyrite flotation may also occur. Copper activation of pyrite favours collector adsorption on to the surface, enhancing its floatability and subsequently lowering the overall chalcopyrite grade (Xu et al., 1995; Peng et al., 2003). To improve mineral liberation and increase chalcopyrite flotation recovery and grade,

ABSTRACT

In the flotation of copper ores, several processing plants report that copper recovery is affected by the proportion and reactivity of pyrite in the ore, with the effect becoming more intense when the feed particles are finer as a result of regrinding. In this work, a mixed model mineral system consisting of chalcopyrite (CuFeS₂) and pyrite (FeS₂) with varying pyrite content (20–80 wt.%) was used to investigate the effect of pyrite on the pulp chemistry and chalcopyrite recovery. Flotation tests showed that chalcopyrite flotation rate, recovery and grade, as well as the pulp oxidation potential, decreased with increasing pyrite content whilst pyrite recovery increased. Surface analysis (XPS, ToF-SIMS and EDTA) indicated that copper activation of pyrite increased with increasing pyrite content, facilitating pyrite recovery. The decrease in chalcopyrite recovery can be attributed to increased surface oxidation.

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regrinding to very small particle size is commonly performed (Gaudin, 1939; Sutherland, 1989). However, in most cases, an increase in valuable mineral recovery is not observed upon regrinding, implying that size and liberation changes are not the only key influential factors determining the flotation performance (Frew et al., 1994). Ye et al., 2010 showed that the surface chemistry of minerals (which impacts on the optimum mineral separation) may change significantly after regrinding, depending upon the type of mill and grinding media used. The effect of grinding media and environment on chalcopyrite flotation has been reported in previous studies (Van Deventer et al., 1991; Grano, 2009; Bruckard et al., 2011; Peng and Grano, 2010). These studies revealed that grinding with mild steel media yields lower chalcopyrite flotation recovery compared with stainless steel, which is attributed to an increase in the formation of iron hydroxide species on the chalcopyrite surface. Arguably, it is difficult to deconvolute the effect of pyrite and steel grinding media on chalcopyrite as both serve as sources of iron ions released into the pulp solution. Recently, Pease et al. (2006) showed that when fully inert ceramic medium is used in the regrinding of the ore, the effect of iron contamination was noticeably reduced, improving the selectivity against sulphide gangue minerals and increasing chalcopyrite flotation recovery. Recent reports from various processing plants show that chalcopyrite flotation recovery after regrinding is affected by the proportion and type of pyrite in the ore, the effect becoming more pronounced when the feed ore particles are fine (<20 µm). Therefore, the aim of this work is to extract the exact influence of pyrite content on the chalcopyrite recovery, grade, and selectivity after regrinding using an IsaMill with fully inert ceramic medium. Model mineral systems comprising of pyrite



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and chalcopyrite in different proportions (20–80 wt.%) are used for the study. Surface species formed on the mineral surfaces during grinding and flotation were determined using ToF-SIMS, XPS and EDTA extraction to provide fundamental understanding on the species responsible for the flotation performance of the two minerals.

2. Experimental

2.1. Materials and reagents

Chalcopyrite (Cp) (Mannum minerals) and pyrite (Py) (Peruvian mine) minerals of particle size ranges $400-2000 \,\mu\text{m}$ and $600-2000 \,\mu\text{m}$, respectively were used for this study. The chemical composition of the two samples is reported in Table 1. It is noted that, from stoichiometric calculations, the Cp sample contains about 75% Cp, 4% Si and about 9% of non-sulphide iron minerals. The Py sample contains about 97% Py and virtually no copper sulphide. Blends of the two samples, in different ratios, have been used in this study.

Ceramic beads (Ø 3.5 mm) (Xstrata Technology, Australia) were employed as the regrinding media for the IsaMill. Sodium isopropyl xanthate (SIPX) and Dowfroth 250 (polypropylene glycol) were used as a collector and a frother, respectively. Analytical reagent grade lime and demineralised water were used throughout the whole experiment for pH/pulp conditioning and grinding purposes, unless otherwise stated.

2.2. Experimental procedures

2.2.1. Mineral grinding and flotation

Samples of 200 g of Cp single mineral or Cp/Py mixtures comprising different proportions of Py and Cp (20, 50 and 80 wt.% Py addition) were mixed with 0.3 dm³ of demineralised water and lime and ground with grinding medium (stainless steel rods, 10×22 mm and 6×16 mm) in a Galigher laboratory mill to obtain a d_{80} of 105 μ m at pH 10. The mill product was transferred into a 1.5 dm³ flotation cell (Agitair Model LA-500R), pH adjusted to 10.5 with lime and conditioned with xanthate collector (200 g/t SIPX) for 2 min. The conditioned pulp was reground to a d_{80} of 20 μ m in a 1 dm³ laboratory attrition mill (IsaMill). After regrinding, the ground pulp was quickly removed from the mill and transferred back into the 1.5 dm³ Agitair flotation cell (in order to retain the pulp potential and the dissolved oxygen level at or close to the value in the mill) and pH adjusted to 10.5. The pulp was then conditioned with 50 g/t of SIPX and frother (25 g/t Dowfroth 250) for 2 and 1 min, respectively. A schematic diagram of the flotation procedure is presented in Fig. 1. Four concentrates were collected at time intervals of 1, 2, 3 and 4 min. The dry masses of the four concentrates and tailings were determined and chemical assays were undertaken for determination of their elemental compositions.

The impeller speed (1000 rpm), pH (10.5) and air flow rate (2.5 dm³ min⁻¹) were maintained during conditioning and flotation in all experiments. Pulp oxidation potential (Eh) and dissolved oxygen level (DO) after IsaMilling prior to collector addition were measured at room temperature using a TPS 90-FLMV meter (Fig. 1). The pulp pH was maintained at 10.5 to mimic plant

| ladie I | | | | | | |
|-------------|--------------|----------------|------------|---------|----------|------------|
| Chemical co | omposition o | f chalcopyrite | and pyrite | samples | used for | the study. |

.....

| Mineral | | Elements (mass %) | | | | | | | | |
|---------|------------------------|-------------------|--------------|--------------|--------------|--------------|------------|--------------|--------------|--------------|
| _ | | Zn | Fe | S | Ca | Cu | Si | Pb | Mn | Mg |
| | Chalcopyrite Pyrite | 0.01 0.18 | 28.9 44.9 | 29.0 53.5 | 1.76 0.44 | 26.4 0.13 | 4.2 0.7 | 0.34 0.02 | 0.02 0.02 | 0.68 0.08 |

conditions. The pulp Eh was expressed relative to the standard hydrogen electrode (SHE). In some tests the amount of collector added was kept constant regardless of the amount of Cp in the mineral mixture (200 g/t after primary grinding and 50 g/t after regrinding), while in other tests, it was scaled to the amount of Cp in the mixture, (200 g/t of Cp after primary grinding and 50 g/t to Cp after regrinding). This is discussed further below.

2.2.2. Flotation data analysis

After chemical analysis, the elemental assays for Cu and Fe for each sample were converted into mineral compositions using the following mathematical relations based on the stoichiometric compositions of Cp and Py:

$$(\%Cp) = \%Cu \times (183.3/63.5)$$
 (Chalcopyrite) (1)

%Fe^{*} = %Fe - %Cu × (55.8/63.5) (Iron present as pyrite) (2)

$$\%$$
Py = $\%$ Fe^{*} × (1119.8/55.8) (Pyrite in sample) (3)

The metallurgical balance of each test was also performed with respect to Cp and Py, and recovery versus time data were fitted to a first order rate equation:

$$R = R_{\max}(1 - e^{-kt}) \tag{4}$$

where *R* is the recovery at time *t*, R_{max} is the maximum recovery at infinite time and *k* is flotation rate constant. From Eq. (4), R_{max} and *k* were inferred for the two minerals.

2.2.3. Subtraction of entrainment

In this work, mineral particles recovered by true flotation and entrainment were determined using the method developed by Ross (1991). A simplified solution of the method developed by Ross can be obtained by dividing the total flotation time in time intervals (corresponding to the collection of the four concentrates). In a short time interval Δt , the recovery by entrainment, as a percentage of the feed, can be written as:

$$Ei_{\Delta t} = X(\Delta t) \times R_W(\Delta t) \times \frac{Mi(\Delta t)}{Mi_{feed}}$$
(5)

where $R_W(\Delta t)$ is the recovery of water in the time interval, Mi_{feed} is the mass of mineral in the flotation feed and $\overline{Mi}(\Delta t)$ is the average mass of mineral in the cell during the time interval. $X(\Delta t)$ is a transfer or entrainment factor, which is particle size dependent (Ross and Van Deventer, 1988). The entrainment factor was estimated from Eq. (5) with the assumption that the recovery of the hydrophilic mineral (which in this study is pyrite) in the last concentrate (i.e. the last Δt) is purely by entrainment, $E_{Py}(\Delta t) = R_{Py}(\Delta t)$. This method is a discretisation of the method developed by Ross (1991), which would require numerical solution. It has been tested and proved to show negligible differences from the Ross method. Recovery by entrainment was subtracted from the chalcopyrite and pyrite recovery data to give the recovery by true flotation.

2.3. Techniques

2.3.1. EDTA extraction

Ethylenediamine tetra acetic acid disodium salt (EDTA) extraction followed by inductive coupled plasma (ICP) analysis was performed to measure the amount of extractable metal oxide/hydroxide Cu and Fe at the mineral particle surface. A volume of 190 cm³ of a 3 wt.% solution of AR grade EDTA was prepared and the pH was adjusted to 7.5 using AR grade sodium hydroxide solution. The solution was then placed in a continuously-stirred reaction vessel and purged with nitrogen for 10 min. 10 cm³ of slurry was collected immediately after

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