The separation of chalcopyrite and chalcocite from pyrite in cleaner flotation after regrinding

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ABSTRACT

In this study, the differences between the separation of chalcopyrite and chalcocite from pyrite in cleaner flotation after regrinding were investigated. In the rougher flotation prior to regrinding, high chalcopyrite and chalcocite recovery were obtained in conjunction with high pyrite flotation recovery due to the activation of pyrite by copper ions during primary grinding. The rougher flotation concentrate was reground in a rod mill before cleaner flotation. It was found that chalcopyrite and chalcocite exhibited different flotation behavior and also affected pyrite flotation differently in cleaner flotation. The mechanism underpinning these phenomena was investigated by a range of techniques including the polarization of mineral electrodes, X-ray photoelectron spectroscopy (XPS) analyses and ethylene diamine tetraacetic acid (EDTA) extraction. It was found that the flotation behavior of both copper minerals and their effect on pyrite flotation after regrinding were governed by their electrochemical activities and galvanic coupling with pyrite.

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1. Introduction

Regrinding rougher flotation concentrates is becoming a common practice to improve the recovery and grade of valuable minerals as a result of the need to process low grade and complex ores. The small grain size of the valuable minerals in low grade ores requires much finer grinding to provide sufficient liberation. In some mineral processing plants, the desirable liberation of valuable minerals in low grade ores can only be achieved by regrinding particles to less than 10 μm (Johnson, 2006). Further, the mineralogy of low grade ores is becoming more complex, therefore, the separation of valuable minerals from gangue minerals in downstream processes (e.g., flotation and leaching) is more challenging even though minerals are well liberated.

Regrinding not only reduces particle sizes and liberates valuable minerals from gangue minerals but also provides appropriate surfaces for subsequent flotation. Grinding conditions, including the use of different types of grinding media and pulp chemistry (pH, Eh and dissolved oxygen), have a significant effect on mineral flotation, and this has been well studied and reviewed (Peng et al., 2003a, 2003b; Bradshaw et al., 2006; Bruckard et al., 2011). It has also been found that the flotation of fine and ultra-fine particles is more affected by grinding conditions than the flotation of intermediate and coarse particles (Frew et al., 1994; Johnson, 2006; Grano, 2009; Peng and Grano, 2010). During regrinding, most particles are reduced to fine and ultra-fine fractions. It is therefore anticipated that regrinding conditions have a more significant effect on the subsequent mineral flotation than primary grinding conditions.

Copper sulfide minerals yield most of the copper produced throughout the world, and are often associated with precious minerals. Due to different formation conditions, their compositions vary greatly. Among them, chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S) are the widely floated copper sulfide minerals. Chalcopyrite is usually formed in the primary hydrothermal zone. Chalcocite can also be formed as part of primary mineralization (e.g. iron oxide hosted copper-gold deposit), but more frequently as a secondary enrichment mineral (Anthony et al., 1990). With the depletion of chalcopyrite-dominant copper ores, more and more chalcocite-dominant copper ores with a high pyritic content are treated. There is a general industrial observation that chalcocite-dominant copper ores are more difficult to treat in particular in cleaner flotation after regrinding (Wightman et al., 2011).

The oxidation of copper minerals plays a critical role in copper flotation and also the separation from pyrite. It is well known that chalcopyrite can be recovered by flotation in the absence of collectors under oxidizing conditions, but not under reducing conditions (Heyes and Trahar, 1977). This is because mild oxidation results in the formation of a hydrophobic sulfur-rich surface, due to the dissolution of iron ions (Gardner and Woods, 1979; Buckley and

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Woods, 1984; Zachwieja et al., 1989). However, extensive oxidation produces a high amount of metal and high valency sulfur oxidation species which are hydrophilic and depress the flotation. Compared to chalcopyrite, chalcocite shows weak collectorless flotation, but can be well floated in the presence of xanthate collectors within a certain Eh range (Heyes and Trahar, 1979). The oxidation of chalcocite has been found to decrease its floatability due to the produced copper hydroxide layer on the surface and a decreased number of copper sulfide sites for collector adsorption. However, its flotation can be restored by increasing the collector dosage (Tolley et al., 1996). It is documented that chalcocite is more reactive than chalcopyrite. Fullston et al. (1999) studied the oxidation of different copper minerals using zeta potential measurements, and found that the oxidation of these minerals follows the order: chalcocite > tennantite > enargite > bornite > covellite > chalcopyrite. It is anticipated that chalcocite flotation is more susceptible to an oxidizing grinding condition than chalcopyrite flotation.

Pyrite depression in the cleaner stage plays a critical role in producing a high quality copper flotation product. In copper flotation plants, the current strategy is to maximize the recovery of copper minerals by floating some pyrite at the rougher stage while further rejecting it at the cleaner stage after regrinding (Wills and Napier-Munn, 2006). However, despite the minerals being well liberated by regrinding, the depression of pyrite can be difficult if pyrite surfaces are activated by copper ions dissolved from copper minerals. During regrinding, more copper ions can be released from copper minerals and activate the exposed fresh pyrite surfaces (Chen et al., 2012, 2013). A number of studies have shown that more copper ions can be dissolved from chalcocite than from chalcopyrite (Lascelles and Finch, 2002; Wong et al., 2002). It is expected that chalcopyrite and chalcocite provide a different extent of copper activation on pyrite during regrinding, and therefore pyrite flotation.

Moreover, galvanic interactions occur between the copper mineral and pyrite due to a difference in their rest potential resulting in different electrochemical reactions on both mineral surfaces and different floatability (Nakazawa and Iwasaki, 1985; Yelloji Rao and Natarajan, 1989; Ekmekçi and Demirel, 1997). It has been reported by Huang and Grano (2005) that the galvanic current was increased as the particle size reduced. As a result, the galvanic interaction is stronger during regrinding than during primary grinding with a greater effect on mineral flotation and separation.

The objective of the current study is to understand the different separation of chalcopyrite and chalcocite from pyrite in the cleaner flotation after regrinding. Previous studies emphasized primary grinding and rougher flotation, and limited studies have been undertaken to understand the effect of regrinding on cleaner flotation which is the subject of the current study.

2. Experimental details

2.1. Materials and reagents

Chalcopyrite, chalcocite 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. XRD analysis indicated that the pyrite sample was very pure without detecting any impurity. The chalcocite sample also had a high purity with a minor amount (<2%) of iron sulfide impurity. The purity of the chalcopyrite sample was slightly lower with about 95% chalcopyrite and 5% pyrite. To be consistent with previous studies, the processed samples were sealed in polyethylene bags and then stored in a freezer at a temperature of −20 °C to avoid further surface oxidation (Chen et al., 2012, 2013).

Potassium amyl xanthate (PAX) and Interfroth 56 were used as a collector and frother, respectively. Collector and frother were of industry grade and used as received. Other chemicals were of AR grade. The pH was adjusted by the addition of a NaOH solution instead of lime used at plants to eliminate the effect of Ca^{2+} on flotation and surface analyses by XPS (Hu et al., 2000). De-ionized water was used in all experiments. All chemical solutions were made fresh daily.

2.2. Grinding, regrinding and flotation

This study focused on regrinding of rougher flotation concentrates with high sulfide concentrations and therefore pure sulfide minerals were used. Crushed chalcopyrite or chalcocite single mineral (100 g), or the mixture of chalcopyrite or chalcocite (50 g) and pyrite (50 g) was combined with 150 g deionized water, and ground in a stainless steel rod mill using 4 stainless steel rods (3750 g) to achieve a P_{80} = 75 μm determined by traditional sieving. A 2.5% sodium hydroxide solution was added during grinding to achieve pH 9.0 in a primary grinding discharge.

After grinding, the pulp was transferred to a 1.5 dm³ steel flotation cell and conditioned with potassium amyl xanthate (160 g/t) and Interfroth 56 (200 g/t). 2 min was allowed for the conditioning of each reagent. During flotation, pH was fixed at 9.0 by adding a sodium hydroxide solution. Flotation concentrate was collected every 10 s, and four concentrates were collected after cumulative times of 0.5, 2.0, 4.0 and 8.0 min. The air flow rate was 1.5 dm³/min during the first 0.5 min flotation, and then increased to 3.0 dm³/min from the second concentrate.

The four flotation concentrates were combined and reground in a rod mill with stainless steel grinding media. The total weight of grinding media was about 10.3 kg. Particle size P_{80} = 20 μm was achieved by adjusting the grinding time. The size distribution was determined by Laser Diffraction with a Malvern MasterSizer (Malvern Instrument Ltd., U.K.) in line with the laboratory and plant practice where a laser sizer has been routinely used to control the grind size smaller than 38 μm. A sodium hydroxide solution was added to achieve pH 9.0 in the regrind discharge. The specific surface area of regrinding feeds and products was measured by the BET method and is shown in Table 1.

After regrinding, the pulp was transferred to a 1.5 dm³ flotation cell. The solid percentage was slightly lower in cleaner flotation than in rougher flotation with more than 90% recovery was achieved in rougher flotation. In cleaner flotation, different dosages of collector were added in flotation while 200 g/t Interfroth was added. The operational procedure was the same as used in rougher flotation after primary grinding.

2.3. Surface analysis

Samples for surface analyses (about 10 ml of slurry) were collected from mill discharges and also flotation products. These samples were frozen in liquid nitrogen to avoid surface oxidation.

2.3.1. EDTA extraction
EDTA extraction was used in this study to determine the amount of oxidation species from minerals and grinding media. A

Table 1
Specific surface area of regrinding feeds and products (m²/g).

Sample	Regrinding feed	Regrinding product
Chalcopyrite	0.686	1.392
Chalcocite	0.192	1.317
Pyrite/chalcopyrite	0.760	1.340
Pyrite/chalcocite	0.144	1.272