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Oxidative weathering of a copper sulphide ore and its influence on pulp chemistry and flotation

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ABSTRACT

The influence of grinding chemistry on the flotation behaviour of sulphides minerals has been widely studied. However, its influence on partially oxidised sulphide ores is not well documented. Various oxidation events can affect a sulphide ore, either during in situ weathering of an ore body or during the different extraction and processing stages (mining operations, stockpiling, crushing, milling and flotation). In this study, a hypogene copper sulphide ore was artificially oxidised to various lengths of time by percolating a small quantity of acidic ferric sulphate solution inoculated with a mixed bacterial culture through packed columns. For each time interval a series of grinding-flotation tests using different grinding media alloys was completed. The grinding and flotation chemistry were compared and linked to the flotation behaviour of the ore samples.

The results reveal that as oxidation progressed the copper metallurgy deteriorated. However, the deleterious effects of oxidation could be partially overcome through the application of the right grinding chemistry.

1. Introduction

The importance of pulp chemistry in sulphide mineral flotation and its role in the selective flotation of chalcopyrite against pyrite has been well documented. Pulp chemical conditions and especially the electrochemistry play an important role in mineral collector interactions and in the nature and composition of the species present at the mineral surface (Tolley et al., 1996; Woods 2003, 2010; Ekmekçi et al., 2005). More specifically, the grinding chemistry through electrochemical interactions between grinding media and sulphide minerals is known to markedly affect the subsequent sulphide flotation. A great number of works on this subject are reported in the literature (Adam et al., 1984; Bruckward et al., 2011; Gonçalves et al., 2003; Greet et al., 2004; Huang and Grano, 2005a, 2005b; Ekmekçi et al., 2005; Grano, 2009). Carbon steel grinding media, through galvanic interactions and oxidation-reductive reactions, are responsible for the precipitation of iron oxyhydroxy species at the sulphide surfaces, along with pulp dissolved oxygen (DO) scavenging and lowering of pulp electrochemical potential (Eh), leading to poor sulphide floatability.

The use of less electrochemically active grinding media (such as high chromium alloys) can counteract the deleterious effects of more electrochemically active grinding media (such as forged steel media) on sulphide flotation. They can reduce the quantity of iron oxidation products and increase the pulp electrochemical potential and oxygen content, improving the collector-sulphide interactions. Bruckward et al. (2011) reported that the pulp chemical environment, ore composition, properties and type of grinding media, pre-conditioning stages and reagent addition during grinding could influence the subsequent flotation process.

Surface oxidation of sulphide minerals is known to adversely affect the flotation and separation of chalcopyrite from pyrite since sulphide flotation depends on the proportion of hydrophobic and hydrophilic species covering the surfaces (Smart, 1991; Guy and Trahar, 1985). Due to their electrochemical properties, the surfaces of the sulphide minerals start oxidising as soon as they are in contact with oxygen or water, due to electrochemical interactions that occur between sulphide minerals or solution species, affecting their subsequent recovery (Ralston et al., 2007; Peng and Zhao, 2011; Owusu et al., 2014). Various oxidation events can affect a sulphide ore, either during in situ weathering of an ore body or during the different extraction and processing stages (mining operations, stockpiling, crushing, milling and flotation) (Clark et al., 2000). Chalcopyrite surface oxidation leads to, in the first instance,

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dissolution of Cu and Fe ions from the mineral surface leaving a metal deficient layer enriched in sulphur on the surface, with some metal hydroxide present in alkaline conditions (Owusu et al., 2014; Peng et al., 2003; Todd et al., 2003; Peng and Zhao, 2011). Since collectorless flotation is attributed to the presence of sulphur rich species such as polysulphide or elemental sulphide (Lutrell and Yoon, 1984a,b; Barzyk et al., 1981; Walker et al., 1986), slight surface oxidation may enhance the flotation performance of the sulphide mineral (Buckley and Woods, 1984; Smart, 1991; Smart et al., 1998; Vaughan et al., 1995). However, the presence of dissolved Cu ions also promotes pyrite flotation through Cu adsorption on their surface (i.e. copper activation of pyrite (Von Oertzen et al., 2007; Chandra and Gerson, 2009; Lascelles and Finch, 2002), adversely affecting the selectivity of chalcopyrite flotation against pyrite and decreasing the copper concentrate grade. Further oxidation leads to precipitation of a higher quantity of iron hydroxides (in alkaline conditions) covering the metal deficient sulphur rich surface, decreasing the flotation response of the sulphide minerals. Indeed increasing the amount of hydrophilic metal hydroxides decreases the hydrophobicity of the mineral and alters the collector adsorption making it less selective toward the various sulphide minerals (Senior and Trahar, 1991; Clarke et al., 1995).

In this study, a copper sulphide ore has been artificially oxidised for varying lengths of time and a series of grinding and flotation tests under several grinding environments were completed at each time interval to study the combined effect of ore oxidation and grinding pulp chemistry. The results highlight the importance of matching the right grinding environment to the oxidation degree of the ore.

2. Experimental

2.1. Materials

A sample of approximately 600 kg of copper sulphide ore was sourced from the plant feed conveyor from an Australian copper mine. Mineralogical analysis of the ore revealed that copper was present as chalcopyrite only. Pyrite was the main iron sulphide mineral with small amounts of pyrrhotite. The ore was received as a mixture of coarse and fine material. Once received it was crushed to 100% passing to 2 mm. A total of seven representative samples were prepared. One (T0) was kept aside as the baseline, while the other six were packed into the columns. Initially the columns were moistened by hosing the top of the column with water until water escaped from the bottom of the column. Then, they were artificially oxidised for varying lengths of time (15 days, 1, 2, 4, 8 and 16 months) by percolating 70 ml per day of acidic ferric sulphate (9 g/l of ferric Fe) solution inoculated with a mixed bacterial culture through packed columns. Bacteria were used, mainly to catalyse the conversion of ferrous into ferric ions, but also because of their possible direct implication in sulphide oxidation (Watling, 2006; Boon, 2001). This effectively oxidised the ore and produced increasingly more oxidising conditions as the treatment time increased. Holes were drilled at the bottom of each column to allow excess solution to escape. The excess solution was regularly assayed to control the quantity of iron and copper that was being leached into the solution. The temperature of the entire equipment was maintained at 35 °C in a closed room.

The sample identification, oxidation time and head assay are presented in Table 1. Once oxidised, each sample was thoroughly mixed and split into 2.2 kg lots. Each sub-sample was placed in a plastic bag, sealed and stored in a freezer prior to use to minimise any further oxidation. The charge weight was chosen to achieve the target percent solids for rougher flotation.

Table 1
Sample identification, oxidation time and head assay.

Sample ID	Oxidation time	Head assays,%				
		Cu	Fe	S	IS	NSG
T0	0	0.47	11.56	2.14	3.13	95.5
T1	15 days	0.48	11.22	2.10	3.02	95.6
T2	1 month	0.46	11.20	2.06	2.98	95.6
T3	2 months	0.47	11.30	2.04	2.93	95.7
T4	4 months	0.47	11.47	2.01	2.88	95.7
T5	8 months	0.45	10.80	1.97	2.83	95.8
T6	16 months	0.48	10.75	2.04	2.92	95.7

2.2. Grinding and flotation tests

A series of grinding and flotation tests under several grinding environments were completed for each sample. The test procedure was the same for all samples tested. Grinding was completed using the Magotteaux Mill® which allows the control and monitoring of the pulp chemistry during grinding (Greet et al., 2004). A 2200 g sample of ore was ground with 2 L of tap water and 10 kg of the desired grinding media to achieve a P_{80} of 185 μm. The mill speed was adjusted for the seven ores as well as for each alloy tested to keep the particle distribution the same for each condition. The Magotteaux Mill® discharge pulp chemistry was calibrated with forged steel media and the fresh ore sample (T0) and the grinding procedure then kept constant for all media and ores tested. After grinding, the pulp was transferred into a 5 L Magotteaux flotation cell and homogenised during two minutes. The pH was then adjusted to 10.3 with lime. The pulp was conditioned for 1 min with 10 g/t of Aero3418A collector, followed by 5 drops of MIBC frother for 1 min. Following conditioning, four timed copper rougher concentrates were collected for 0.5, 1.5, 3 and 5 min, for a total flotation time of 10 min. The froth was hand scraped every 10 s. Tap water was added during the flotation to maintain the pulp level in the flotation cell. The pulp chemistry (Eh, pH, DO and Temperature) was recorded using a 90 MLF TPS meter during grinding, before and after flotation. All tests were completed in triplicate to obtain confidence in the data produced. The reproducibility was examined for each condition and tests repeated if necessary.

2.3. Chemical analysis

All liquid and solid samples were assayed at Bureau Veritas chemical laboratory in Adelaide, Australia. Liquids were assayed for copper and iron. All solid samples were assayed for copper, iron and sulphur. Iron sulphide (IS) and non-sulphide gangue (NSG) were deducted from the elemental assays using the following equations:

$$\%\text{Cp (Chalcopyrite)} = \%\text{Cu} \times (183.3/63.5) \tag{1}$$

$$\%\text{IS (Iron Sulphide)} = (\%\text{S} - (2 \times 32.06/183.3) \times \%\text{Cp}) \times (119.85/2 \times 32.06) \tag{2}$$

$$\%\text{NSG (Non-sulphide Gangue)} = 100 - \%\text{IS} - \%\text{Cp} \tag{3}$$

2.4. EDTA extraction

Ethylenediamine tetra acetic acid disodium salt (EDTA) extractions were performed for each test to measure the quantity of the Cu and Fe oxidation products present in the slurry and on the mineral surfaces. A sample of 25 ml of flotation feed was stirred under nitrogen for 5 min with a w/w 3% solution of EDTA adjusted to a pH