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Investigating the role of pulp chemistry on the floatability of a Cu–Ni sulfide ore

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ABSTRACT

This study investigated the effect of the pulp chemistry conditions during milling on the flotation performance of an Nkomati ore. The results have shown that there was approximately 10% increase in Ni recovery, when the ore was ground at dissolved oxygen (DO) concentration of 0 ppm in comparison to a condition where oxygen was allowed to access the slurry during the grinding stage. However, when the pH was changed from 9 to 11, the presence of oxygen resulted in a 20% decrease in the Ni recovery as compared to only 5% decrease in the Ni recovery at DO = 0 ppm. A noteworthy observation is that controlling a combination of DO and pH during grinding can have a significant effect on selectivity in the flotation of such ores. It was shown that grinding at lower DO levels/redox potentials (Eh) in the presence of xanthate significantly improved the recoveries of pentlandite and pyrrhotite.

1. Introduction

Grinding is a process used to prepare an ore for downstream processing such as flotation and hence plays a crucial role in influencing the surface properties of the mill product particles. Nevertheless given the enormous amount of research rightly dedicated to developing more efficient comminution processes the effect of pulp chemistry during grinding is often overlooked. It is believed that the surface properties of the minerals can be adjusted during flotation rather than during grinding. However, recent developments in surface analytical techniques (e.g. TOF-SIMS, XPS, AES, etc.) have shown, for example, that the hydrophilic iron hydroxides formed at the mineral surface during grinding make it difficult for effective collector adsorption, which may result in poor grades and recoveries of the valuable minerals.

A number of researchers have found that the presence of oxygen is essential for electrochemical reactions to occur on sulfide mineral surfaces. Oxygen starts playing its role through the weathering of sulfide ores during the mining and material handling stage. As soon as the ore enters the grinding circuit, galvanic interactions between mineral/mineral and mineral/media need to be considered. It is well established in the literature that oxygen reduction is a key reduction reaction for galvanic interactions. Based on electrochemical theory, the reduction of oxygen affects the following: the oxidation of sulfide minerals, mineral/mineral, mineral/media galvanic interaction as well as the mineral/collector interactions. However, the mineral/collector interactions have a pronounced influence on the flotation behavior of sulfide minerals.

Kelebek et al. (1996) suggested that there is a strong correlation between the oxidation of the surface after grinding and its influence on the grade and recovery of pentlandite (Pn). In 2007, Kelebek and Nanthakumar (Kelebek and Nanthakumar, 2007) investigated the impact of oxidation on flotation of a complex Cu–Ni massive sulfide ore. They considered the effect of oxidation, showed that oxidation before, and after grinding, produced an inferior quality Pn grade-recovery. However, when oxidation occurred after grinding a Pn recovery loss of up to 25% was seen as compared to a maximum of 3.5% recovery loss in oxidation before grinding. The reason may be the fresh surfaces generated after grinding, which were not previously exposed to atmosphere, being able to oxidize.

Nickel producers have been using a number of different strategies, sometimes in combination, to reject Po from Pn. These include raising the pH of flotation to partially suppress Po floatability (Klymowsky, 1968) and introducing separate Po rejection circuits, which largely also exploit the fact that Po floats poorly in alkaline solutions. Magnetic separation has also been used in some plants to remove the magnetic Po from feed or concentrate streams (Klymowsky, 1968). However, none of these techniques is entirely satisfactory, as high levels of Po rejection are invariably accompanied by unacceptable Pn losses due to similarity in the structure and surface properties of the Pn and Po.

In 2005, Legrand et al. (Legrand et al., 2005a) performed the surface analysis of a pyrrhotite (Po)/pentlandite (Pn) system and noted that the separation of Pn from Po via flotation was inefficient unless either they are exposed to the flotation reagents prior to oxidation, or their FeOOH over layer is removed in some way. Therefore, the study of pulp oxygen control at the grinding stage might be an efficient way to better understand the process. However, there is little published work which has quantified the significant effect of oxygen on flotation considering all of oxidation, xanthate adsorption and galvanic interactions. The scarcity of such literature might be because

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of the non-availability of a system, where oxygen content may be controlled simultaneously to fresh surface generation and reagent addition. The Magotteaux Mill® (Greet et al., 2004) offers the opportunity to understand the combined system.

The conditions under which grinding occurs have a marked effect on the pulp potential of the slurry which in turn affects the flotation response of the sulfide minerals. Greet et al. (2010) showed the effects of changing the grinding media type on the sulfide recoveries at Perilya Broken Hill; they also investigated the addition of collector at various points in the circuit and concluded that addition of collector to the mill proved beneficial to the performance of the circuit. Rao and Finch (1988) and Ralston et al. (2007) have suggested that galvanic interactions may be weakened by purging the pulp with nitrogen during grinding; this was confirmed by further studies (Yelloji Rao and Natarajan, 1988; Peng et al., 2003a). Purging the pulp with oxygen allows for oxidation to take place at both the mineral and grinding media surfaces. The iron oxides and hydroxides generated are available to deposit onto the surfaces of the minerals (Ralston et al., 2007; Huang and Grano, 2006; Natarajan and Iwasaki, 1984) and inhibit the adsorption of the collector (Forssberg et al., 1988), thus impacting negatively on the flotation outcomes (Peng et al., 2003a,b). Considering Taggart's hypothesis, metal ions, generated through oxidation of mineral surfaces, may also be able to dissolve into the solution and reside in the flotation pulp from where they are able to form metal xanthates on contact with collectors and deposit onto mineral surfaces allowing for flotation (Rao, 2004). Extensive research has proven that 21% Cr grinding media may give optimum plant performance when compared to other grinding media types (Cullinan et al., 1999; Greet et al., 2004; Huang and Grano, 2006; Huang et al., 2006). The objective of this study was to use 21% Cr grinding media and manipulate the grinding environment in order to investigate the effect of grinding pulp chemistry (DO and/or pH) on the flotation performance.

2. Experimental

In order to control the dissolved oxygen (DO) level and pH of the pulp the Magotteaux Mill® has been used. The Magotteaux Mill® is a device that allows for the measurement of in-situ pulp chemistry. This mill allows for the simultaneous monitoring of the following electrochemical parameters: redox potential (Eh), DO, pH and temperature. The detailed operating procedure can be found in the relevant operating manuals (E.J.B., 2009).

An ore typical of the Nkomati MMZ reef was acquired from Nkomati. The major sulfides in this ore were chalcopyrite, pentlandite and pyrrhotite. The bulk sample was crushed, blended, riffled, and split using a rotary splitter into 2 kg portions. The mill was charged with 20 kg of 21% Cr grinding media, a 2 kg sample of ore and 1.5 L of synthetic plant water constituted of ions typical of processed water used in such concentrators (Wiese, 2009). The ionic strength of this water was 0.0213 M. The DO level in the mill was maintained at either 0 or 5.5–6.5 ppm by constantly purging the mill with either nitrogen or air respectively. The pH of the pulp was varied between ~9 and 11 by using lime in the milling stage. The natural pH of the slurry was ~9. It was found that in order to raise the pH from 9 to 10 the amount of lime added should be 16 g and from 9 to 11 it should be 32 g into the mill at the beginning of the milling. After grinding the slurry to 80% passing 75 μm, the slurry was transferred into a bucket. The sample was then transferred into a 5 L Magotteaux flotation cell (bottom driven). The impeller speed was kept at 1200 rpm. For all the tests, sodium isobutyl xanthate (SIBX) collector was added to the mill as it was believed this would allow for better adsorption onto the freshly cleaved mineral surfaces. DOW200 frother was added to the float cell. Dosages of both collector and frother were maintained at 20 g/t. The air supply to the flotation cell was regulated to a flow rate of 10 L/min. The froth height was maintained manually at 2 cm throughout the batch flotation test-work. Four concentrates were collected at 2, 6, 12 and 20 min of flotation time by scraping the froth into a collection pan at 15 second intervals. After transfer of the slury from the mill to the flotation cell the DO value increased. Typically after milling at DO = 0 ppm the DO concentration in the cell was about 0.5 ppm. The pH in the mill was sustained into the flotation cell. It should be noted that the Eh values shown in Table 1 are those measured in the mill. After transfer to the flotation cell the Eh value increased by ~300 mv at DO = 0 ppm and ~200 mv at DO = 6.5 ppm. The amount of wash water used was monitored and recorded for all tests. Feed concentrates and tails were filtered, dried, and weighed before assay analysis. All tests were conducted in duplicate for reproducibility. Copper and total nickel analysis of all samples was done using a Bruker S4 Explorer XRF Spectrophotometer. Sulfur analysis was carried out using a LECO DR 423 sulfur analyzer. It is assumed that the chalcopyrite and pentlandite are present in the form of $CuFeS_2$ and (FeNi)S respectively. The recovery therefore of pyrrhotite was determined by the sulfur and iron elemental balances (Corin et al., 2011; Becker et al., 2009).

3. Results

All test conditions used in this study are given in Table 1.

The final mass of solids and water recoveries obtained from flotation under the different DO conditions are shown in Fig. 1. It can be seen from Fig. 1, that there was a substantial increase in the mass of solids recovered at a DO concentration of 0 ppm as opposed to the other test conditions. This figure also shows that even a small amount of oxygen, i.e. DO = 1 ppm, gave the same mass and water recoveries as that of DO = 6.5 ppm.

The effect of oxygen concentration during the grinding stage is shown in Fig. 2. It can be seen that the Cu recovery and grade were more or less independent of Eh or pulp DO concentration during the grinding stage. However, the presence of oxygen during the grinding stage resulted in significant decreases in the pentlandite and pyrrhotite recovery and a significant increase in the Eh value measured. The grade of pentlandite did not change very much, but the grade of pyrrhotite significantly decreased as DO and Eh increased even though the mass of solids recovered decreased as the DO concentration increased at equivalent water recoveries. This decrease in grade may be due to the much greater decrease in pyrrhotite recovered.

It should be noted that a slightly higher pH was recorded when the ore was ground at a DO concentration of 0 ppm as compared to a DO concentration of 5.5 ppm. Fig. 3 shows the mass of solids and water recovered at different pH values at a DO concentration of 0 ppm. This figure indicates that as the pH is increased above 9, the mass of solids recovered decreased at equivalent water recoveries. The total mass of water recovered did not change very much between pH 9 and pH 10 but there was a significant decrease in total water recovery at pH 11.

Table 1
Pulp chemistry conditions in the mill for the various tests carried out.

Dissolved oxygen (ppm)	pH	Recorded pH	Recorded Eh mV (SHE)
0	9.2	9.2–9.3	−160 to −180
1	9.2	9.0–9.2	170 to 145
6.5	9.2	9.0–9.2	230 to 245
0	10	10.2–10.4	−180 to −205
0	11	11.2–11.6	−205 to −230
5.5	9.2	9.0–9.2	220 to 230
5.5	10	9.9–10.1	195 to 190
5.5	11	10.9–11.2	150 to 140