EFFECTS OF VARIABILITY IN GRINDING MEDIA AND BALL SIZE ON PULP CHEMISTRY

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ABSTRACT

Grinding ore is an important step in the flotation process. Not only does grinding reduce particle size and liberate minerals, it also creates conditions for reactions to occur on particle surfaces that can aide or inhibit flotation. There have been numerous studies examining various grinding regiments and the effect on flotation pulp chemistry, including autogenous grinding and using media of variable composition. There have been however, few studies looking at the effect of variability in grinding media size on pulp chemistry and subsequent flotation. This study attempts to link changes in pulp chemistry in response to variations in grinding media size to flotation recovery. It uses probes mounted in the grinding chamber (pH, Eh, DO, and conductivity) to monitor pulp chemistry changes during grinding of a Cu-Zn ore. Surface chemistry analysis by ToF-SIMS was performed on sphalerite from the mill discharge. Activator and depressant species were monitored on the mineral surfaces and their presence was evaluated in the context of variability in pulp chemistry linked to differences in grinding media and its ball size.

KEYWORDS

Ball mill, Grinding media, Ball size, Surface chemistry

INTRODUCTION

It has been widely recognised that not only does grinding reduce particle size and liberate minerals but the grinding environment has a large effect on the flotation of sulphide minerals. This effect is attributed to Eh change, iron hydroxide coating on surfaces, oxygen reduction, precipitation from solution and galvanic coupling (Grano, 2009). As early as 1960, it was reported that after grinding the ores in an iron mill the natural floatability of sphalerite was reduced significantly (Rey and Formanek, 1960). Kocabag and Smith (1985) studied on the industrial circuits showing that the depression of sulphides flotation in a steel mill is possibly due to the coating of iron oxidation products. Peng, Grano, Fornasiero, and Ralston (2003a, 2003b) found that iron contamination from grinding media plays a dominant role in depressing galena and chalcopyrite flotation. Huang, Grano, and Skinner (2006) reported the same observation in the flotation of arsenopyrite.

There have been numerous studies examining various grinding regiments and the effect on flotation pulp chemistry, including using media of variable composition. It was found that with high chromium alloy steel medium the grinding increased galena and chalcopyrite recovery and rate constant compared to grinding with high carbon steel (mild steel) medium (Cullinan, Grano, Greet, Johnson, & Ralston, 1999; Peng, Grano, Fornasiero, & Ralston, 2003a, 2003b). When particle size is considered, Peng and Grano (2010) identified that fine particles flotation is more susceptible to iron contamination from grinding media than its intermediate sized counterpart. Similar examples can be found from other publications (Grano, Wong, Skinner, Johnson, & Ralston, 1994; Huang, Grano, & Skinner, 2006). There have been, however, few studies looking at the effect of variability in grinding media size on pulp chemistry and subsequent flotation. Grinding medium size, in particular, is known to impact mill efficiency and the energy consumption (McIvor, 1997). Spherical balls are generally used in ball mills, while the size and shape changes continuously due to impact breakage and wear, which can lead to a reduction in sphericity and the production of exposed cavities (Vermeulen & Howat, 1989). It may also affect the subsequent sulphide processing considerably.

This study attempts to link changes in pulp chemistry and surface chemistry in response to variations in grinding media size. It uses probes mounted in the grinding chamber (pH, Eh, DO, and conductivity) to monitor pulp chemistry changes during grinding of a Cu-Zn ore along. Surface chemistry analysis by ToF-SIMS was performed on sphalerite particles from the mill discharge. Activator and depressant species were monitored on the mineral surfaces and their presence was evaluated in the context of variability in pulp chemistry linked to differences in grinding media and the ball size.

METHODOLOGY

Grinding was performed in a horizontal, cylindrical, rubber-lined laboratory ball mill, which has probes mounted in the grinding chamber to monitor pulp chemistry changes (pH, Eh, DO, and conductivity) during grinding. The grinding pulp density is 25%.

Sample ore was obtained from the Matagami mines (Glencore Xtrata Canada Inc). It was crushed to 1.7 mm, homogenized, split, sealed and frozen prior to use. 200 g of homogenized sample was ground to 80% passing 75 μm with either mild steel or stainless steel balls. There are two different sizes of each grinding medium, the big (1 inch) and the small (1/2 inch). For each grinding testing, whatever the grinding medium and its size, the same weights of grinding medium was kept resulting in the same grinding efficiency. Table 1 shows the experiments performed and their parameters. After grinding, the sample of pulp was immediately purged of oxygen using argon and frozen by liquid nitrogen.

Table 1 – Experimental parameters of each grinding testing. The pulp chemistry in all cases was measured for pH, Eh, DO, and conductivity.

Test No.	Grinding medium	Cr (%)	Size of balls	Total surface area of grinding medium (cm^2)
1	Mild steel	0	Big (1 inch)	5837
2	Mild steel	0	Small (0.5 inch)	11644
3	Mild steel	0	1:1 mix (wt%)	8740
4	Stainless steel	18.44	Big (1 inch)	5837
5	Stainless steel	18.44	Small (0.5 inch)	11644
6	Stainless steel	18.44	1:1 mix (wt%)	8740

Surface chemistry analysis by ToF-SIMS was performed on sphalerite from the mill discharge. To analyze the outer-most layer of samples, an ION-TOF, TOF SIMS IV™ secondary ion mass spectrometer was used. This technique allows for the analysis of the outermost 1–3 atomic layers of a surface by mass spectrometry. Each sample was mounted on indium foil, introduced into the instrument, pumped down in the vacuum and analysed. From six regions on each sample, a minimum of six grains of each mineralogical type were examined, therefore for each sample more than 36 grains were identified and analyzed. This analysis provides a comprehensive survey of the surface species on the mineral grains in the various samples.

The intensity of selected species detected on the grain surfaces as positive or negative ions are plotted in vertical box plots and illustrate relative changes in surface species abundance for the mineral grain examined in the sample. In the vertical box plots, the median is plotted as the solid line across the box, whereas the mean is plotted as the dashed line (Figure 1). All TOF-SIMS data presented (counts) are normalized by the total ion intensity (counts of the recorded total mass spectrum) for the region of interest.

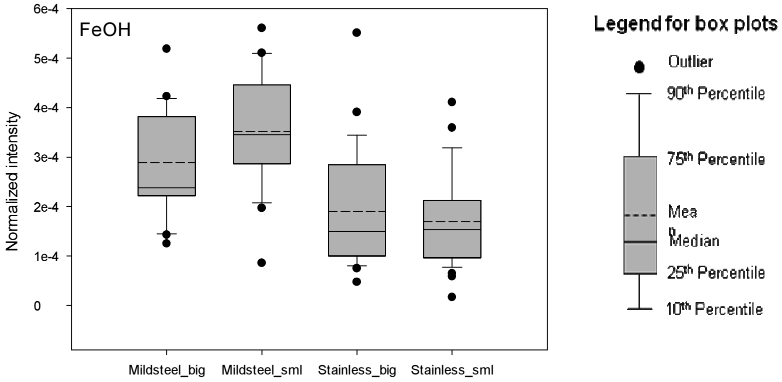

Figure 1 – Box plot showing the various components

In order to identify collector #3418A which was used in flotation, a sample of #3418A was deposited on a silicon substrate and analysed by TOF-SIMS to generate the spectral fingerprints. Dominant peak positions for 3418A examined were used to identify their presence and assess variations in loading between different grains in each of the four samples investigated. Normalized intensities for mass positions identified as collector 3418A are given in Figure 2.

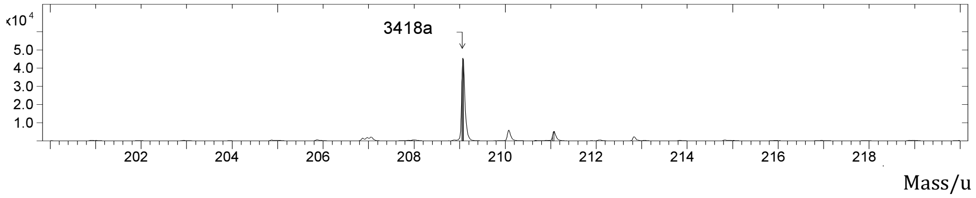

Figure 2 – Normalized intensities for mass positions identified as collector 3418A

RESULTS AND DISCUSSION

Pulp Chemistry

Pulp chemistry changes of pulp pH, oxidation reduction potential (Eh), dissolved oxygen (DO), and conductivity were monitored during grinding. The changes of DO content in grinding tests by using the two different grinding medium was recorded in Figures 3a and 3b separately. It reveals that oxygen level in the slurry is decreasing during grinding regardless whatever the grinding media was employed. It is also noted that the various grinding medium size from big balls to 1:1 mixed balls and then to the small balls shows a significant effect on the DO content. For testing with stainless steel balls, as shown in Figure 3a, in the test with the small balls, the DO drops rapidly from more than 6 to 1.75 mg/L in the first 20 minutes then falls from 1.75 to 0 mg/L in the 20 to 40 minute interval. In contrast, in the test with the big balls the DO content only drops from at around 6 to 5.5 mg/L in the first 20 minutes then declines at a gradual rate from 5.5 to 2.65 mg/L over the 20 to 40 minutes grinding interval. The DO content in the test with a mixture of the big and small balls falls directly between the data from the other two testing. When the grinding medium was substituted to mild steel balls, as shown in Figure 3b, the decrease of DO content is much faster than by using stainless steel balls. For the testing with small size of mild steel balls, DO content drops extremely rapid from more than 6 to almost zero in the first 20 minutes. While for the big balls, DO decreasing from more than 6 to 0 mg/L takes more than 30 minutes. The mixture of big and small balls behaves similar to small balls when grinding with a mild steel medium (Figure 1b). The data show that with an increase in surface area of balls, oxygen consumption rate is increased.

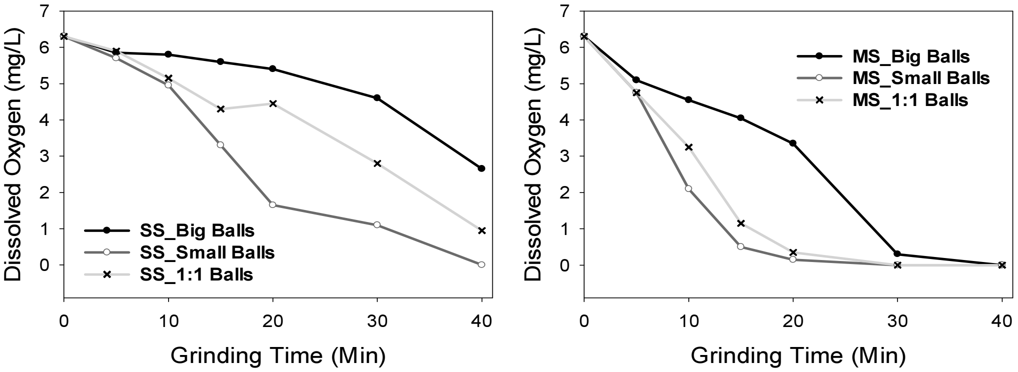

Figure 3 – Measurement of dissolved oxygen in the slurry during milling of a Cu-Zn ore using different types of grinding medium (a) Stainless steel balls; (b) Mild steel balls

Pulp pH was recorded in Figure 4 during grinding. It shows that the pulp pH increases rapidly in the first 20 minutes and then the pH curves become relatively stable in the 20 to 40 minute interval at last gradually achieving from 6.8 to more than 8.0. The ball sizes have a significant effect on the pulp pH. Both grinding medium, the stainless steel and the mild steel balls, reveal the same distribution that small size of balls could lead to a higher pulp pH after grinding relative to the big size of balls. The mixture of big and small size of balls behaves almost the same as the small balls. The pulp pH data indicates that with an increase in surface area of balls, pulp pH is increased. Moreover, the small balls has dominated control to the changes of pulp pH. In comparison of the two different material, in general, the testing with mild steel balls has a higher pulp pH after grinding than using the stainless steel balls.

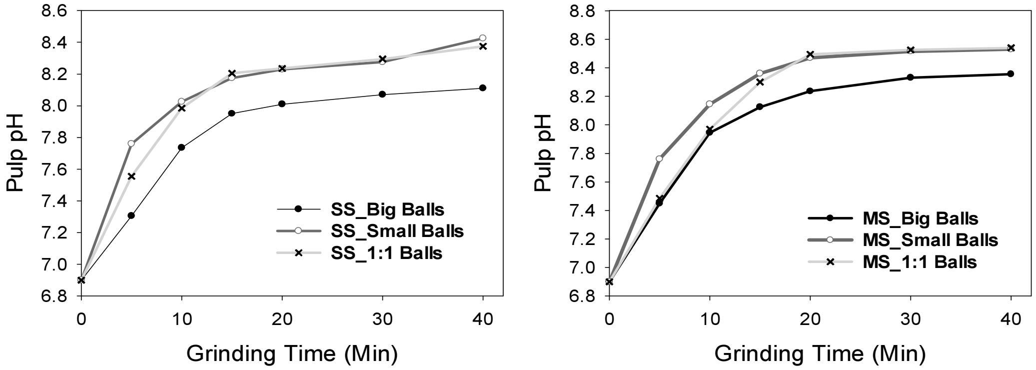

Figure 4 – Measurement of pulp pH during milling of a Cu-Zn ore using different types of grinding medium (a) Stainless steel balls; (b) Mild steel balls

Figure 5 shows the ORP data changed with the various grinding media and the size of the balls during milling. ORP data drops very fast in the first 15 minutes, after that it decreases gradually. It is obvious that the testing with mild steel balls results in the lower ORP relative to the stainless steel balls, and the small size of balls testing has lower ORP that the testing using the big balls. The data shows an identical distribution with the DO content.

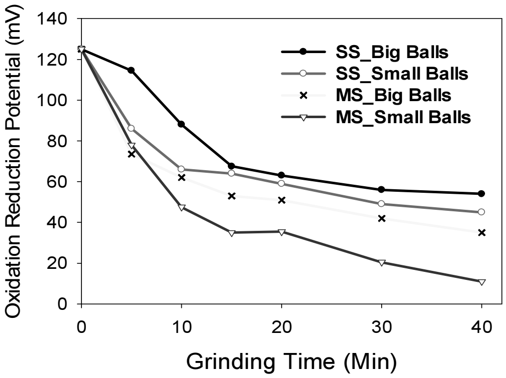

Figure 5 – Measurement of oxidation reduction potential (ORP) during milling of a Cu-Zn ore by using different types of grinding medium

The data in Figure 6 indicate the changes of conductivity by varying the grinding medium and the size of balls. The conductivity was measured at 30 minutes since start grinding. The higher conductivity may indicate the higher of Fe ions in the slurry. In comparison to the stainless steel balls, the mild steel balls is much more active in the pulp and should have generated more Fe ions in the slurry. A significant lower conductivity, however, is shown in Figure 6 using mild steel balls. This suggests the Fe(OH) precipitated in the pulp so having lower Fe ions.

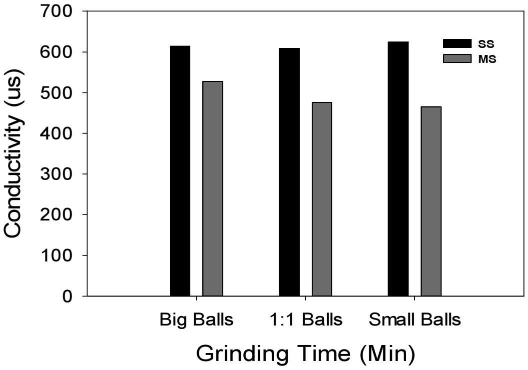

Figure 6 – Measurement of conductivity during milling of a Cu-Zn ore using various types grinding medium at 30 minute

Surface Chemistry

Owing to the changes of pulp chemistry during grinding testing by using the difference grinding medium and the different size of the balls, the grinding discharge of each testing was analysed by ToF-SIMS to show the surface chemistry information.

From Figure 7, we can see an obvious enrichment of Cu on the surface of sphalerite in the testing using stainless steel balls during milling. This indicates that the sphalerite grains from that testing are attached by dissolution of Cu ions from complex sulphide ores resulting in its activation. Figure 8 reveals a higher degree of Fe, FeO, FeOH and FeOOH on the sphalerite surface for the testing with mild steel balls during milling relative to stainless steel balls. It would be related to the pulp chemistry data as the mild steel balls are more readily supply ferrous ions during grinding so the consumption of oxygen for mild steel balls is much more rapid than using stainless steel balls; the pulp pH is slightly higher for mild steel balls testing relative to stainless steel balls; the ORP is much lower for mild steel testing and the conductivity indicates the generation of iron hydroxides in the slurry. As for the ball size, it reveals that grinding with smaller balls (larger surface area) also increases oxygen consumption, resulting in slightly higher pulp pH and the lower ORP and conductivity.

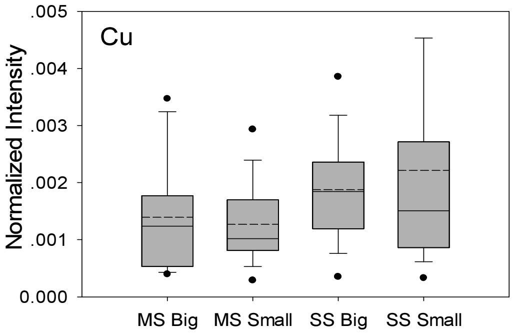

Figure 7 – Normalized intensity of Cu on the sphalerite surface

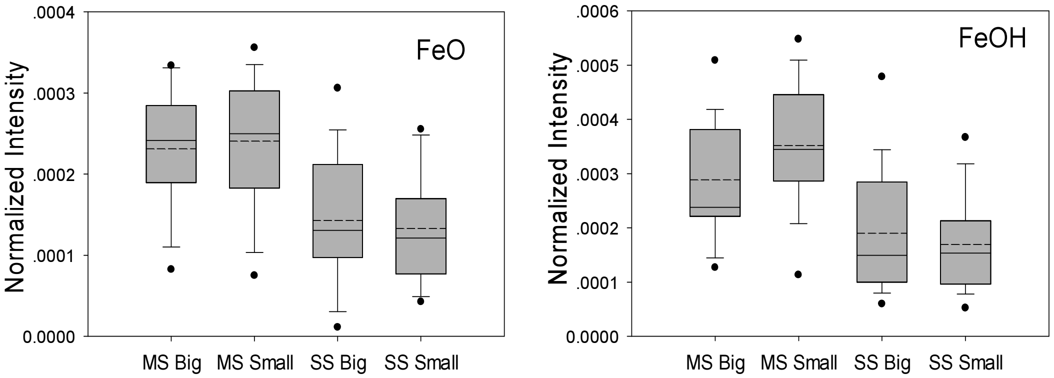

Figure 8 – Normalized intensity of FeO and iron oxyhydroxide species on sphalerite surfaces

Adam and Iwasaki (1984) supplied one of the models of galvanic reactions (electron transfer) between grinding media and minerals. i) Steel media serves as an anode in the steel-sulfide mineral system, which supplies the electrons to the sulfide mineral; ii) Steel grinding media will corrode and consume dissolved oxygen, then lead to the formation of hydroxyl ions in the pulp; iii) A stable coating of metal hydroxides reduces on the mineral surface (Martin, McIvor, Finch, & Rao, 1991). It is reveals that mild steel balls have stronger galvanic reactions than the stainless steel balls in a steel-sulphide minerals grinding environment. From the discussion above, we can see the ball size also has effect on the galvanic reactions between grinding media and the minerals, as the smaller balls provide a larger surface area of the grinding media and there would be greater quantity of ferrous ions allowing for the formation of more iron oxidized components on the surface of sphalerite.

CONCLUSIONS

It is evident from this study that the material of grinding medium and the size of grinding balls both have significant effect on the pulp chemistry and the surface chemistry of sphalerite. It is concluded that mild steel balls and the smaller balls could generate more ferrous ions during grinding. The Fe ions may react with oxygen producing a greater quantity of iron hydroxides resulting in a significant decrease of DO content, a slightly higher pulp pH after grinding and a relatively low ORP. The iron hydroxides precipitated on the sphalerite surface as a decreasing conductivity was measured and a higher normalized intensity of iron hydroxide species was revealed by ToF-SIMS analysis when using the mild steel balls.

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