MECHANISM OF SPHALERITE DEPRESSION IN AN OPEN CU/ZN FLOTATION SEPARATION CIRCUIT

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ABSTRACT

Plant and laboratory test work was performed in order to optimize a copper/zinc flotation separation circuit at Matagami concentrator, Canada. The testing identified a significant difference between the laboratory testing and the plant flotation, particularly for the sphalerite recovery in the rougher copper concentrate. Tests indicate that sphalerite recovery of the flotation concentrate in the laboratory testing was significantly higher than in the plant. The ToF-SIMS surface analysis identifies surface species responsible for the discrepancy in Zn recovery. It shows that sphalerite flotation is in response to the collector attachment and a significant enrichment of Cu on the surface of sphalerite grains. A comparative surface chemical analysis was performed on both sphalerite and chalcopyrite grains from the plant flotation and laboratory testing in order to identify surface species variability between the two testing. Two significant observations were revealed. First, there is considerably more hydrophilic iron oxyhydroxide on sphalerite surface from the plant flotation sample relative to those from the lab testing. The secondary coating likely completely or partially passivates sphalerite surfaces, reducing Cu enrichment and hence sphalerite floatability. Secondly, comparing the surface chemistry on sphalerite and chalcopyrite, the hydrophilic iron oxyhydroxide species have preference for the sphalerite grains relative to chalcopyrite. Despite numerous studies on the effect of galvanic coupling during grinding, there is limited documented evidence on the effect of the milling environment on the flotation and plant operations. This observation suggests that interaction between sulphide minerals and grinding media have a significant influence on subsequent flotation. This paper discusses the results of a detailed surface chemical evaluation of sphalerite grains from both the plant and laboratory testing in the context of grinding environments and pulp chemistry.

KEYWORDS

Galvanic interaction, Grinding, Sphalerite, Surface chemistry, Copper/zinc separation

INTRODUCTION

The Matagami Mining Camp in Quebec Canada is a world-class mining district that has 18 known volcanogenic massive sulphide deposits. Historically the area has produced on the order of 8.6 billion pounds of zinc and 853 million pounds of copper (Mills, 2012; "Technical report", 1997). Following an extensive Electro Magnetic (EM) survey flown over the camp in 1999, the region has been experiencing an unprecedented interest in new developments. Glencore Xstrata's Perseverance mine became the 11th deposit put into production in mid 2008 however it was closed in 2013. Following the close of the Perseverance deposit the Bracemac-Mcleod base metal mine, Mine Matagami-Une Compagnie Glencore, became the 12th producer in the region. As of 2013, the proven and probable reserves include 3.7 million tonnes of ore grading at 9.60% Zn, 1.26% Cu, 28.25 g/t Ag and 0.43 g/t Au. There is also an inferred resource of 2.6 million tonnes at 8.79% Zn, 1.31% Cu, 38.84 g/t Ag and 1.06 g/t Au (Canadian Mining Journal 2013). Approximately 3000 t/d of the ore is processed at the Matagami Mill.

In 2012, Matagami commenced a laboratory flotation program representing the first 12 months of production to confirm: reagent dosages identified in the feasibility study, metallurgical response, process optimization and to obtain a better understanding of the precious metal recoveries. Samples for the flotation program, generated from drill core, were crushed to 1.7 mm, homogenized, split, sealed and frozen prior to further testing. For the flotation tests, the samples were ground to 80% passing 50 microns; the grinding media used in the flotation testing were 100% stainless steel. After grinding, the slurry was transferred into a 4.3 L flotation cell, conditioned with lime (1100g/t), the collector 3418A (30g/t in total) and frother MIBC (70 µL). Each reagent was conditioned for 0.5 minutes, for the flotation, the air flow was set at 2.4L/min and pH was maintained at 10.5. The total rougher copper flotation time was 7.5min. The laboratory flotation testing results are shown in Table 1.

Table 1 – Laboratory flotation testing results

Samples	Weight	Mass rec.	Grade (%)		Recovery (%)	
	(g)	(%)	Cu	Zn	Cu	Zn
Rougher Conc.	194.60	9.76	13.52	10.56	95.31	9.91
Rougher Tailing	1798.40	90.24	0.07	10.39	4.69	90.09
Feed	1993.00	100.00	1.39	10.41	100.00	100.00

During the various testing programs there has been significant variation in Zn recovery to the Cu concentrates. The feasibility study did not show a significant amount of Zn reporting to the Cu concentrate, likely due to the Cu circuit not being fully optimized for Cu recovery thereby unintentionally reducing the Zn content. On the other hand, during flotation testing programs, activation of sphalerite was indeed indicated as Zn recoveries to the Cu concentrate were too high to be explained by entrainment or liberation; >9% Zn in the lab Cu concentrate, Table 1. Furthermore depressant testing also resulted in lower Zn recoveries, supporting the idea that sphalerite recoveries to the Cu concentrate were through activation and flotation. The metallurgists at Matagami were well aware that sphalerite was being activated during flotation however the mechanism was not clear given that no secondary Cu minerals have been identified.

Following laboratory testing, Matagami commenced a plant flotation program using the strategy developed during the feasibility and laboratory testing program. Figure 1 illustrates the current grinding and Cu flotation circuits. The grinding media in the mill is variable and consists of forged mild steel balls in BROY 4 and in the three subsequent mills; the ball composition is a cast, high chromium alloy, consisting of 18% Cr.

Analyses of the Cu rougher concentrate from the Mill scale-up program revealed that there is considerably less Zn (sphalerite) reporting to the roughers relative to that reported in the laboratory testing

program. Data from the mill in 2013 showed that the Zn recovery to the Cu rougher circuit was 3.02% whereas that from the flotation tests was on the order of 10%. This big disparity in Zn recovery to the Cu concentrates suggests that there is some surface chemical control operating in the mill that was not apparent in the previous testing.
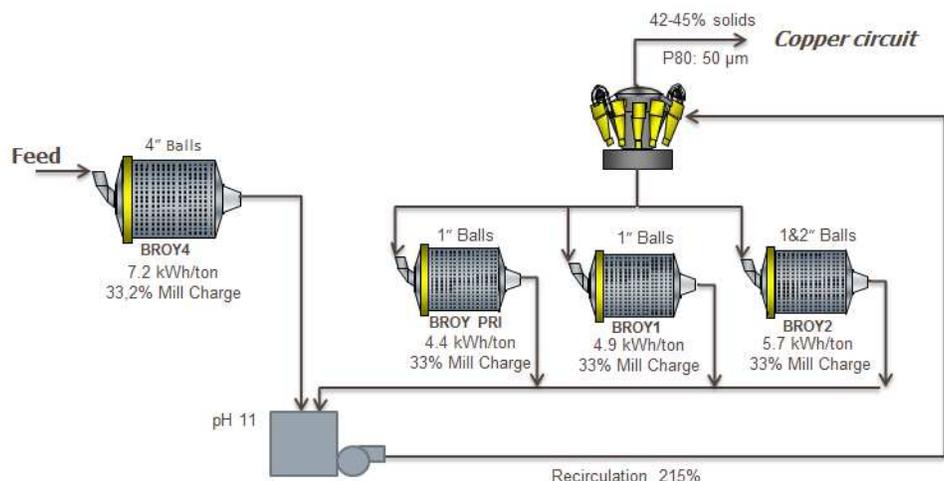
Figure 1 – An illustration of the current Glencore-Matagami plant grinding

Inadvertent activation of sphalerite by dissolution of copper ions from complex sulphide ores has been been reported in many instances (Chandra and Gerson, 2009). For the most part however, it is most common in ores containing secondary sulphides, for example chalcocite and bornite, which easily oxidize, contributing Cu ions to solution which are then readily adsorbed by sphalerite. Given the lack of these minerals, the activation of the sphalerite was somewhat surprising but more importantly the difference in Zn recovery between the lab tests and the mill was more significant.

Selective activation or depression of sphalerite can be evaluated by understanding the surface chemistry while relating these observations to pulp chemistry which is linked to differences in grinding and flotation schemes. In order to evaluate mineral surface chemistry the Time of flight secondary ion mass spectrometry (ToF-SIMS) technique has been used measure various surface features, for example collector adsorption, mineral dissolution, mineral activation and mineral oxidation (Chehreh&Hart, 2014; Xia, Hart, &Loshusan, 2015). ToF-SIMS provides elemental and molecular information on surface species at monolayer depths of analysis (Laajalehto, Kartio, &Suoninen, 1997; Smart, Jasiieniak, Prince, &Skinner, 2000; Nagaraj& Brinen, 2001) and can be used as a statistical measure of the hydrophobic/hydrophyllic balance of the mineral surface (Piantadosi, Jasiieniak, Skinner, &Smart, 2000; Piantadosi&Smart, 2002). In this paper we discuss the surface chemical differences of sphalerite grains reporting to the Cu concentrates from the laboratory tests and those collected from the Glencore mine Matagami -Une Campagnie Glencore. These analyses will identify potential factors controlling sphalerite stream partitioning in the lab tests and mill.

MATERIALS AND METHODS

Surface Analysis Samples

In order to provide process relevant results, surface chemical analysis were performed on samples of the same starting material (plant feed) and from the same location for both laboratory testing and the plant flotation: mill discharge samples and Cu rougher concentrates. Samples for analyses were collected according to Smart (1991) which is designed to remove dissolved oxygen and snap-freeze the sample to stop further surface reaction. For this paper the surface of sphalerite grains were analysed from 4 samples:

- laboratory mill discharge sample (feed to the lab Cu rougher): Lab Cond Dis
- laboratory Cu rougher concentrate: Lab Ro Conc
- Cu flotation feed: Mill Cu Feed
- Cu Rougher Flotation Concentrate: Mill Ro Con

ToF-SIMS Surface Analysis

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, +36 grains in total were analysed. This analysis provides a comprehensive survey of the surface species on the mineral grains in the various samples. The analytical approach was to conduct comparative surface analyses of the lab flotation test samples and the plant flotation samples in order to determine statistically significant differences in the surface species.

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 specie 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 (Fig.2). 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.

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 a spectral fingerprint. 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.
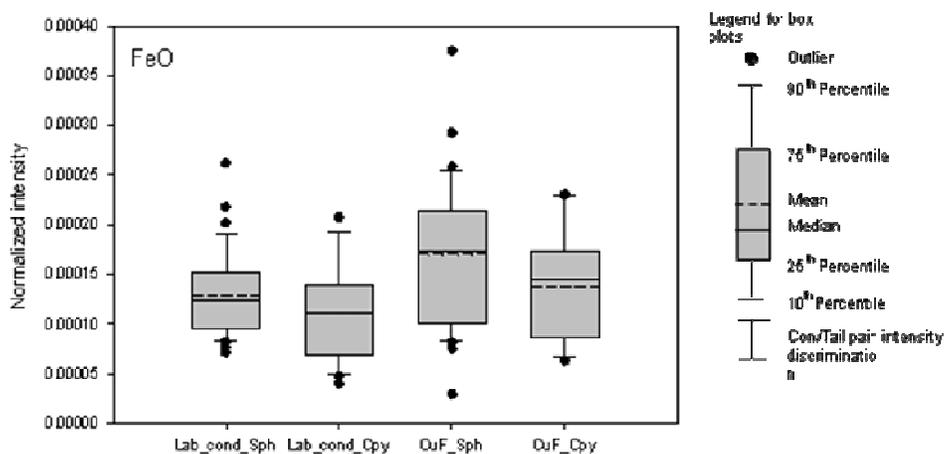
Figure 2 – An illustration of a box plot showing the various components

RESULTS AND DISCUSSION

A detailed surface chemical evaluation by ToF-SIMS was performed in order to potentially identify factors promoting stream partitioning in relation to the Zn depression control. The data was processed following the method outlined by Hart (2006). 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. Normalized intensities for mass positions identified as collector 3418A are given in Fig. 3.
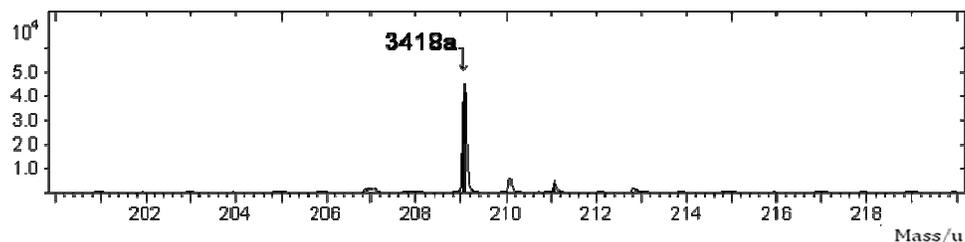
Figure 3 – Normalized intensities for mass positions identified as collector 3418A

Flotation Feed *vs* Flotation Concentrates

Normalized intensities for collector 3418A and PO_x, species related to the collector, are given in Fig.4. It reveals that higher normalized intensities for collector are reported on the surface of sphalerite grains in the Cu concentrate. From Fig.5, the normalized intensities of Cu, CuS and CuHS are significantly higher on sphalerite grains from the flotation concentrate relative to the flotation feed. The data confirms that sphalerite flotation is in response to collector attachment likely facilitated by Cu adsorption. The presence of Cu is likely from dissolution of Cu sulphides in the sulphide ore. The data in Fig.6 shows that the intensities for FeO and FeOH are very low on the grains reporting to flotation concentrates relative to flotation feed in both laboratory and plant samples. This distribution is also seen for the species O, OH and SO_3 (Fig.7). These data suggest that the surface species FeOH, OH and SO_3 are contributing to sphalerite depression and indicate that there is some difference in the degree of surface oxidation exhibited on sphalerite grain surfaces between the lab tests and the mill samples.
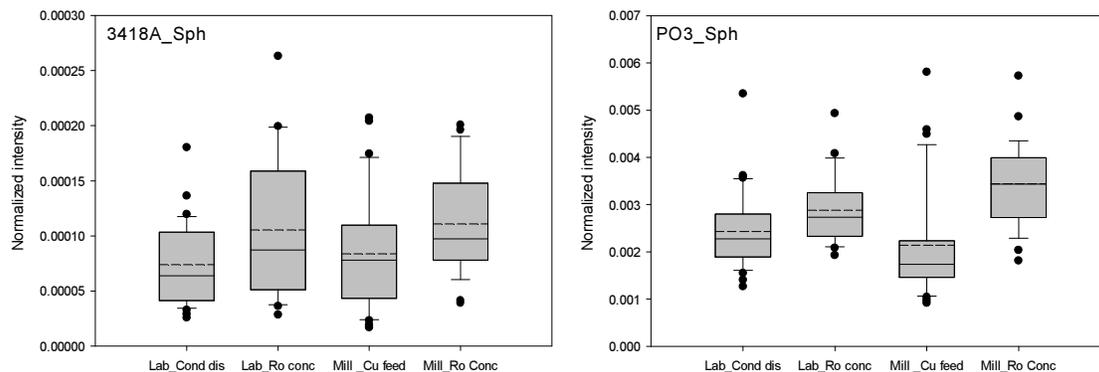
Figure 4 – Normalized intensity of collector 3418A and PO_3 on sphalerite surfaces
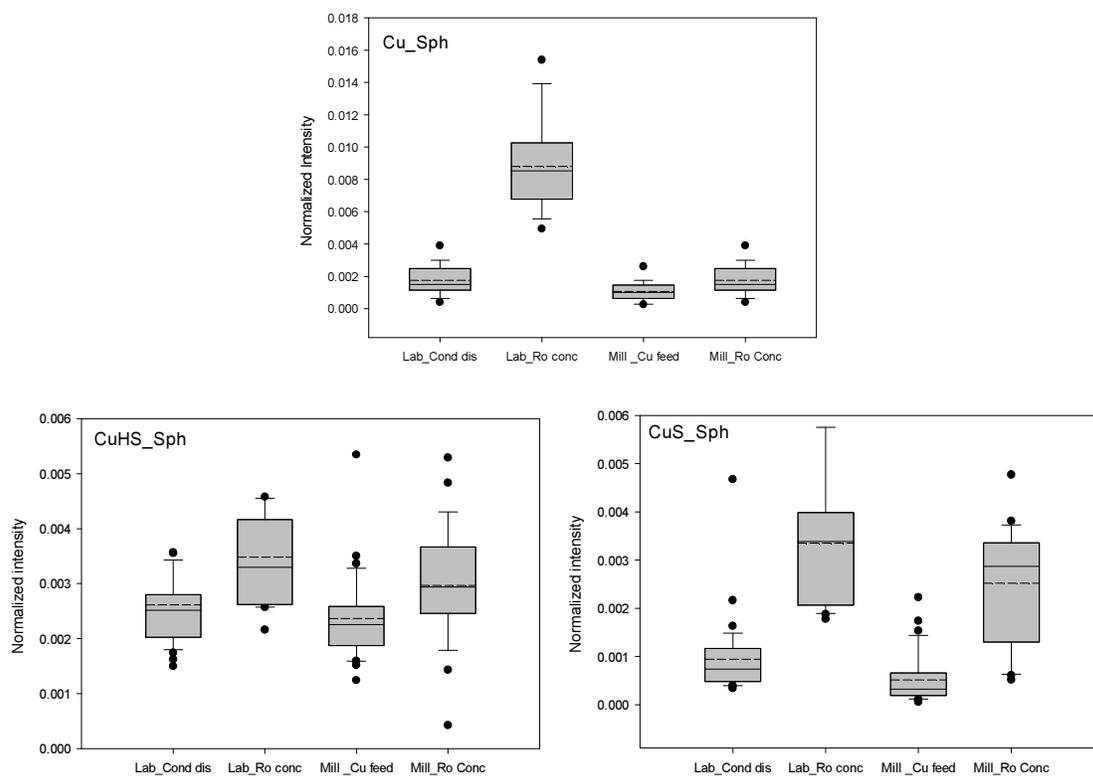
Figure 5 – Normalized intensity of Cu positive and negative species on sphalerite surfaces
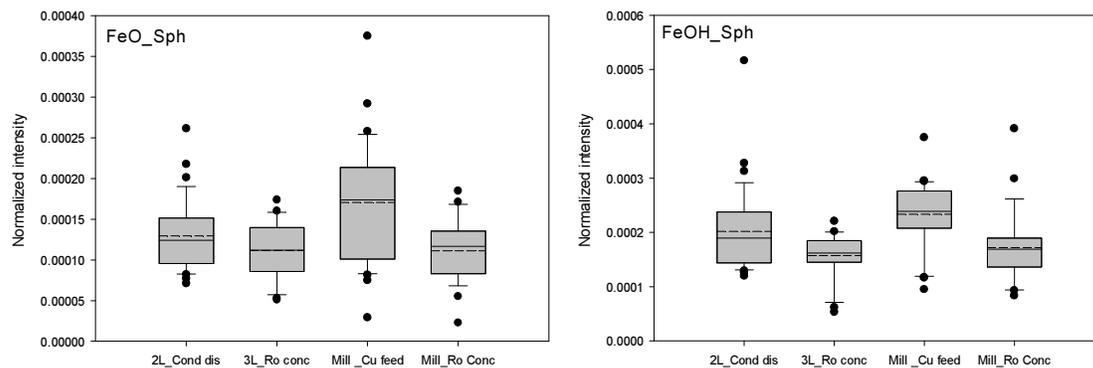
Figure 6 – Normalized intensity of iron oxyhydroxide species on sphalerite surfaces
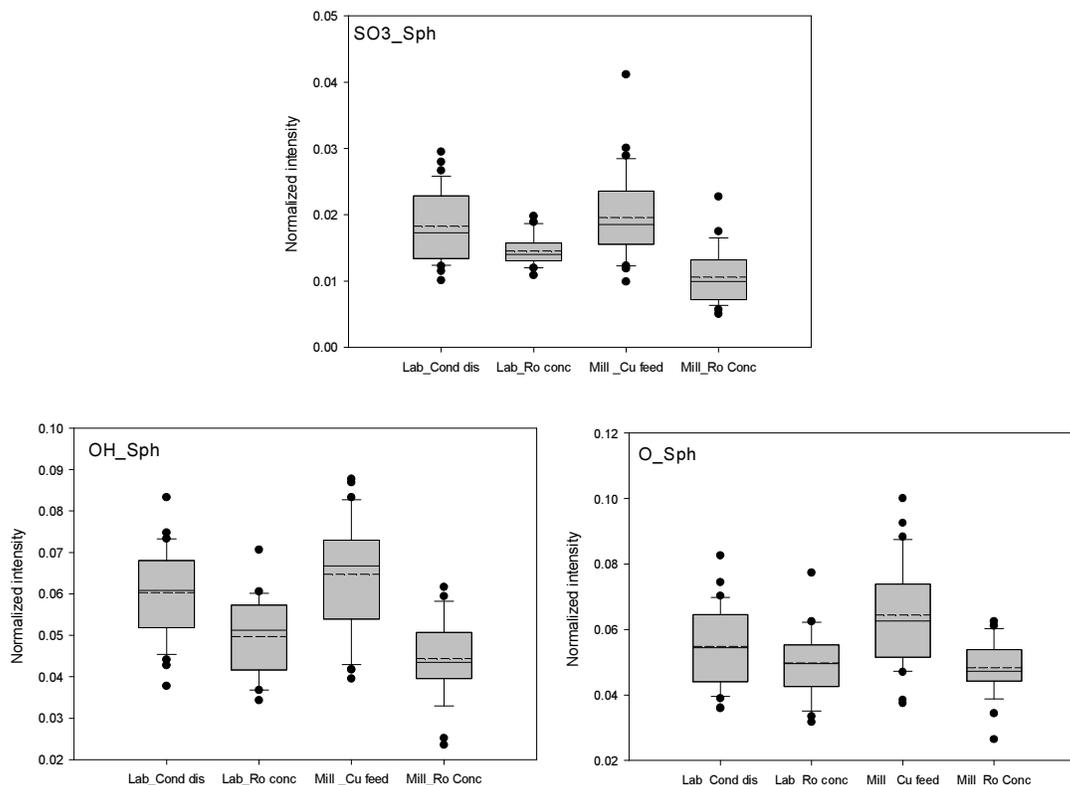
Figure 7 – Normalized intensity of O, OH and sulphate species on sphalerite surfaces

Samples from Laboratory *vs* Plant Flotation

It was reported that Zn (sphalerite) recovery to the Cu concentrate was significantly less that that reported for the laboratory test samples. Zinc recovery in the plant Cu concentrate was ~3% whereas for the Cu concentrate in tha laboratory testing the Zn recovery was on the order of 10%. In order to identify potential factors leading to this disparity, a comparative surface analysis was carried out on flotation feed samples from the laboratory testing and the plant. The data in Fig.8 shows an obvious higher intensity for FeO &FeOH on the surface of sphalerite grains from the Cu circuit feed relative to the mill discharge sample in the laboratory testing. The similar distribution is observed for O and OH. The significant difference in surface species between the two samples then reflects variations in the oxidation-reduction environment during grinding. It has been widely accepted that the grinding environment of sulphides has a pronounced effect on the downstream flotation recovery and selectivity (Martin, McIvor Finch and Rao 1991). Due to sulphide mineral electrical conductivity contact between mineral(s) and the grinding media results in a galvanic couple, the results of the surface oxidation/reduction reactions are manifest on the grinding media and various minerals within the pulp. The following electrochemical reactions may be occurring: (Natarajan 1996; Pavlica and Iwasaki 1982; Cheng and Iwasaki 1992; Nataranjan, Riemer and Iwasaki 1984).

Cathodic reaction on cathodic mineral surface:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
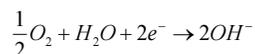
Anodic reactions on grinding media surface:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
$$Fe \rightarrow Fe^{3+} + 3e^{-}$$

Precipitation:

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$$
$$Fe(OH)_2 + OH^{-} \leftrightarrow Fe(OH)_3 + e^{-}$$
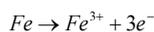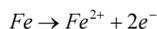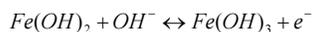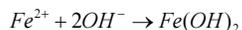
During sulphide ore grinding, galvanic interaction may happen among two sulphide minerals and the grinding media. In the case of the Matagami ore pyrite (most nobel) acts as cathode and the grinding media (the least nobel) the anode. Chalcopyrite and sphalerite with lower rest potentials less than pyrite but higher than the grinding media may develop an intermediate anodic reaction on their surface (Azizi, Shafaei, Noaparast and Karamoozian 2013). The reaction on the anodic mineral surface:

$$MS \leftrightarrow M^{2+} + S + 2e^{-}$$
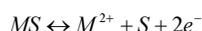
Although galvanic current was not monitored in the mill or lab tests, the ToF-SIMS data suggests that there appears to have been a greater proportion of ferrous ions in the pulp of the plant mill relative to the laboratory mill. The high level of ferrous Fe in the pulp feeding the Cu circuit in the plant was likely related to the oxidative dissolution of the grinding media. The result was the precipitation FeOH, (FeOOH, FeO; Fe-O$_x$ species) on the surface of sphalerite likely leading to a degree of partial depression. Fig. 9 shows no significant difference in the normalized intensity of S$_2$, HS and SO$_3$ on sphalerite surfaces from either sample. The implication here, is that surface oxidation of the sulphide grains is not particularly evident and that this would further confirm that the development of Fe oxidative species on the surface of sphalerite particularly in the plant is related to grinding media composition: stainless steel in the laboratory tests, mixed forged and high chrome steel in the plant. In the case of the later, the flow of electrons from the grinding media to sulphide minerals increases the oxidation of grinding media, leading to more oxidized iron species in the slurry.

The normalized intensity of Cu, CuS and CuHS is significantly higher on the sphalerite grains from the lab test samples relative to the plant samples, Fig.10. From the data collected, it is apparent that copper transfer occurred in both samples, but it is clear that copper activation of sphalerite in the plant samples is significantly less than that in the lab tests. The reduction in Cu loading and greater Fe-O$_x$ species on sphalerite from the plant suggests a competitive adsorption between iron oxyhydroxide and copper, and where the pulp has an overabundance of ferrous ions, Fe-O$_x$ species precipitate, inhibit Cu and collector attachment resulting sphalerite depression.
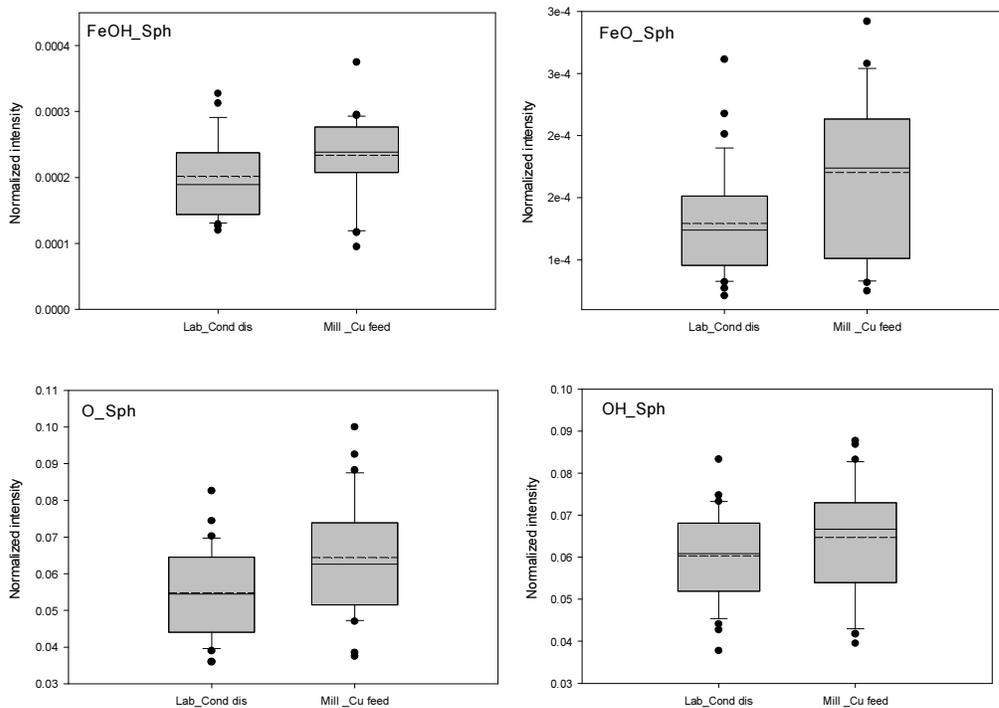
Figure 8 – Normalized intensity of O, OH and iron oxyhydroxide species on sphalerite surfaces from the two types of flotation testing
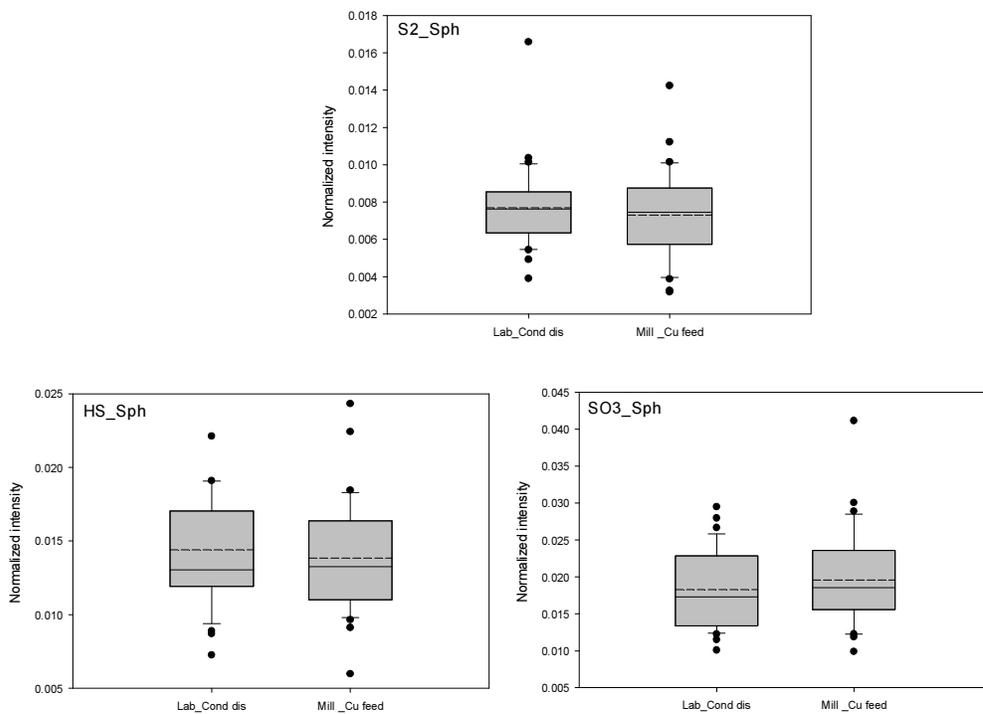
Figure 9 – Normalized intensity of S, HS &SO_3 species on sphalerite surfaces from the two types of flotation testing
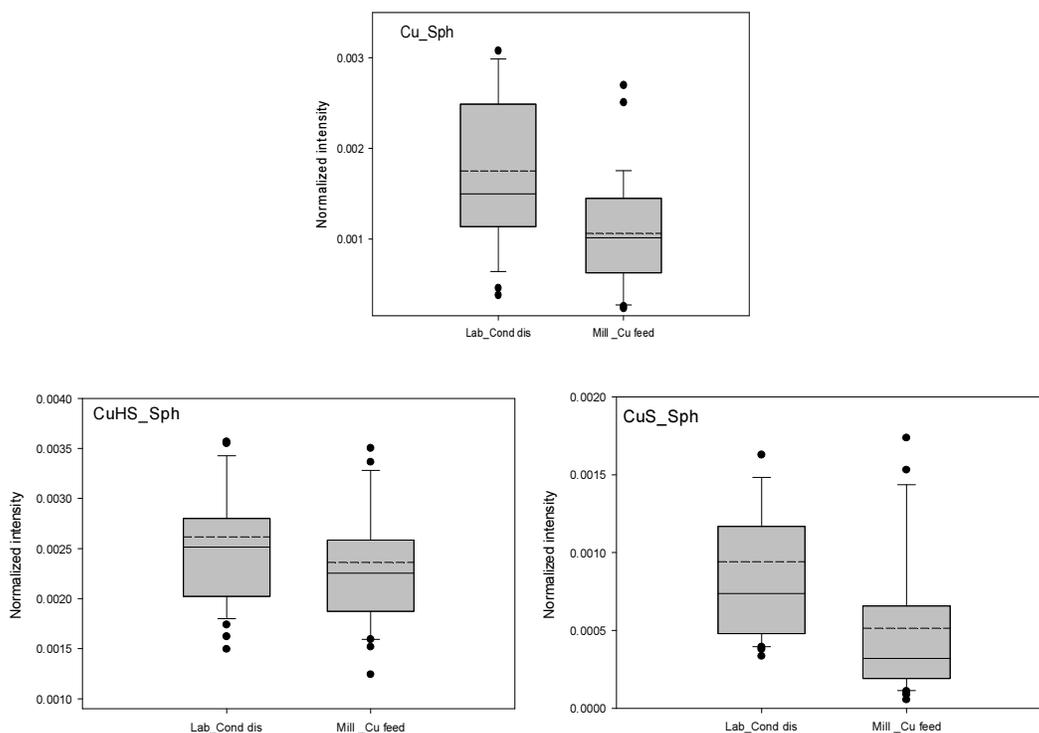
Figure 10 – Normalized intensity of copper species on sphalerite surfaces from the two types of flotation testing

Comparison of Sphalerite *vs* Chalcopyrite

During grinding, sphalerite and chalcopyrite are in contact each other but the recovery data showed a significantly selective depression for sphalerite. The surface of sphalerite and chalcopyrite grains was examined from both the lab sample and the Cu feed sample. The normalized intensity of the iron oxy-hydroxide species on sphalerite and chalcopyrite from the 2 samples are given in Fig. 11. The data show that FeO & FeOH have a preference for sphalerite relative to chalcopyrite in both samples, and overall the loading of these species is slightly higher on both minerals in the plant samples.
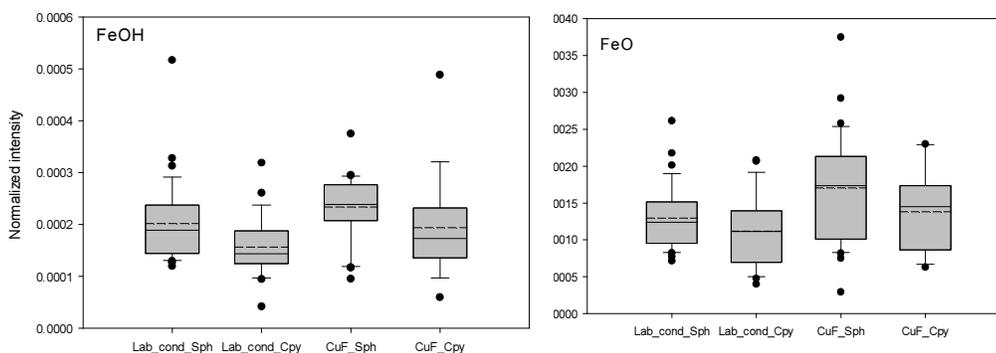
Figure 11 – Normalized intensity of iron oxyhydroxide species and OH on sphalerite and chalcopyrite surfaces from the two types of flotation testing

CONCLUSIONS

Surface chemical analyses of sphalerite grains was performed to determine the factors controlling differences in sphalerite recovery to the Cu rougher concentrates between laboratory flotation tests and mill start-up samples using the same ore and reagent schemes. Zinc recovery data for the laboratory tests was significantly higher than for the mill samples. The data showed that in both cases Zn recovery to the rougher concentrates is in response to Cu activation and collector attachment. However sphalerite grains from the mill Cu feed had a significantly higher proportion of iron oxy-hydroxide species on their surface relative to the laboratory Cu feed. Copper and collector attachment on sphalerite grains lead to Zn recovery, while the precipitation iron oxy-hydroxide, and possibly various other hydroxide specie,s limit the potential for development of surface hydrophobicity and sphalerite floatability. By comparison of the surface chemistry of the two samples and, evaluating the differences between the mill and plant testing parameters it is concluded that the difference in surface chemistry is a result of galvanic interactions within the mill and the anodic dissolution of iron from the grinding media. From these analyses the reduction in Zn reporting to the Cu rougher concentrate in the mill is linked to inhibiting Cu attachment through the precipitation of Fe oxide/oxyhydroxide species which is directly related to grinding media chemistry. The laboratory tests were performed with stainless steel grinding media whereas milling in the plant is accomplished with mixed forged and high chrome steel media, the later providing the source for ferrous to the pulp.

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