Application of Surface Chemical Analysis to the Industrial Flotation Process of a Complex Sulphide Ore

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ABSTRACT

The objective of this study was to achieve Zn activation control in an industrial Cu flotation circuit treating a complex Cu-Pb-Zn-Au-Ag sulphide ore at the LaRonde Division of Agnico-Eagle Mines Limited (Quebec, Canada). In order to provide process relevant results, a laboratory testing methodology was developed to duplicate plant operational parameters. The action mechanisms of ZnSO₄, TETA (triethylenetetramine) and NaHSO₃ used as depressants in order to limit ZnS activation were examined. Laboratory flotation tests with and without Cu²⁺ ions (the ions responsible for ZnS activation) were performed. All depressants showed equal or better flotation performance relative to baseline tests. For example, in the presence of Cu²⁺, the Zn grade reduced from 32.2% to 17.5% in the copper rougher concentrate after adding 50 g/t ZnSO₄. TOF-SIMS analyses confirmed the relative decrease in surface Cu in the samples treated with ZnSO₄ and TETA. For the case with TETA, this indirectly indicates the formation of a copper TETA complex in solution, thereby reducing available Cu for transfer. The TOF-SIMS and XPS data indicate that the addition of ZnSO₄ and NaHSO₃ resulted in an increase in surface metal hydroxides and SO₃ on ZnS grains inhibiting both Cu and collector attachment. ZnSO₄ was subsequently tested with success in the LaRonde concentrator. The addition of 40 g/t ZnSO₄ at the conditioning (or cleaning) stage led to a 2% reduction in Zn content in the Cu and PM concentrate. Recently, improvements towards the control of copper sulfate addition in the downstream Zn flotation circuit resulted in the reduction of Cu²⁺ in process water. As this “cleaner” water is recycled for Cu and PM flotation, the addition of ZnSO₄ is now used only as required.

Keywords: complex sulphide flotation, inadvertent activation by Cu²⁺ ions, depressant, TETA, zinc sulfate, sodium sulfite, surface chemistry

INTRODUCTION

Complex polysulphide ores are usually difficult to process without incurring inadvertent activation of unwanted minerals, in particular ZnS in a Cu and PM flotation circuit (Alsan 2010). It is well established that the activation of ZnS is linked to the dissolution and transfer of copper and lead sulphides (yielding Cu²⁺ and Pb²⁺) in solution (Pulido 2011, Chen 2010, Mehrabini 2010, Ralston 1980). Ore grinding can influence surface properties and can thus modify the flotation behavior of minerals (Peng 2010, Simpson 2011, Chen 2010, Ye 2010). Such modifications can also occur in flotation cells (Biesinger 2007). COREM’s past experience has shown that process improvement scenarios solely based on laboratory-identified solutions often fall short of expectations. Therefore, duplication of plant operational parameters in the laboratory, while allowing for the monitoring and testing of electrochemical and surface chemical conditions in response to changes in the predefined operational parameters, is the key to the efficient use of a depressant. During the last decade, the understanding of flotation systems has been greatly enhanced by the use of surface characterization techniques like XPS, Auger electron spectroscopy and TOF-SIMS. Knowledge of the surface composition allows establishing a correlation between mineral surface chemistry and flotation.
response. (Peng 2011, Abreu 2011). Unfortunately, the action mechanism of depressants remains partly unknown because of the complexity of sulphide mineralogy and the high cost of surface chemistry techniques.

**EXPERIMENTAL**

**Materials and reagents**

Sample ore was obtained from the LaRonde Division of Agnico-Eagle Mines Limited and prepared as reference material. This sample was crushed to 1.7 mm, homogenized, split, sealed and frozen prior to use. Chemical assaying of resulting sub-samples was done by X-ray fluorescence (XRF). Precious metals (PMs) in samples were analyzed by pyro-analysis and atomic absorption spectrometry. Statistical analysis confirmed no variance between sub-samples in terms of major components and PM contents.

Lime was used to control pH *in situ* during the grinding and flotation steps. Collector (3418A, dithiophosphinate) and frother (MIBC) were obtained from West Paterson NJ Cytec industries Inc.,USA. Copper sulfate (CuSO₄, AR grade) was added to pulp to enhance Cu²⁺ activation of sphalerite. Zinc sulfate (ZnSO₄, AR grade) and sodium sulfite (NaHSO₃, 67.1% in a mixture with sodium metabisulfite, Na₂S₂O₅, AR grade) were used to protect ZnS against inadvertent activation by Cu²⁺. Alternately, TETA (AR grade) was used to complex Cu²⁺ in solution. Deionized water was used throughout the study.

**Grinding and flotation**

Each homogenized sample was ground in a specially instrumented mill to reach a P₈₀ of 75 μm. Milling conditions were controlled to reproduce the same electrochemical/surface conditions as in the plant. The flotation tests were of two types: with and without adding Cu²⁺ ions in the pulp. The addition was to simulate worst conditions at the plant, considering that recirculated process water could be a significant source of Cu²⁺ ions. After grinding, the slurry was transferred in a 2.5L Denver flotation cell, conditioned with the pH modifier, reagent, Cu²⁺ (if planned), collector and frother. For each reagent, 1 minute of conditioning was necessary while Cu²⁺ required 4 minutes. Reagents aiming to control ZnS activation were added before Cu²⁺. Air flow was set at 2.4L/min, pH at 10.0 and temperature (during grinding and flotation) was maintained at 32°C. Five rougher flotation concentrates were collected after 0.5, 1, 2, 3 and 6 minutes.
Surface characterization

Time of flight secondary ions mass spectrometry (TOF-SIMS) analyses

Samples for TOF-SIMS analyses were collected following the sampling methodology of Smart, 1991. The samples were analyzed with an ION-TOF, TOF SIMS IV™ secondary ions mass spectrometer. The secondary ions generated by rastering a $^{209}$Bi$^{+3}$ primary ion beam over the sample surface were extracted and mass analyzed using a time-of-flight mass spectrometer. The data was processed following the method outlined by Hart et al., 2006.

X-ray photoelectron spectroscopy (XPS) analyses

The XPS analyses were carried out with a Kratos AXIS Nova spectrometer using a monochromatic Al Kα source (15mA, 14kV). Binding energy accuracy was ±0.025eV. Survey spectra were collected with a pass energy of 160eV; high-resolution spectra were obtained using either a 20eV or 40eV pass energy. Spectra were analyzed using the Casa XPS software (version 2.2.107). XPS imaging was employed to identify and analyze specific grain(s) in spot mode as per the method outlined by Biesinger et al., 2007.

A bench test was performed in order to examine the potential mechanism related to sphalerite depression in response to ZnSO$_4$ addition. The test sample consisted of equal proportions of quartz, pyrite, chalcopyrite and sphalerite. The grains were agitated for 5 and 10 minutes after a sequential addition of reagents and analysed by XPS immediately after reaction. Three tests were performed: 1) in deionized water only; 2) with the addition of ZnSO$_4$; and 3) with the additions of ZnSO$_4$ followed by CuSO$_4$.

RESULTS

Mineralogy

Mean values for major components and PM in the reference material are presented in Table 1. The main sulphides identified were pyrite, sphalerite, chalcopyrite and galena. Gold and silver could be found as free particles and also as exposed grains in chalcopyrite. Gangue was mainly composed of silicates.

Impurities end up in a flotation concentrate due to 3 major factors: a hydrodynamic effect (entrainment of free particles); a mineralogical effect (particles not completely liberated); and inadvertent activation. After completing detailed mineralogical tests at the plant, it was found that hydrodynamic and mineralogical effects...
were not important problems for the Cu concentrate. Figure 1 presents the sphalerite associations found in the Cu concentrate of the rougher cells bank at LaRonde. In the contact cell labeled CCT06 more than 50% of ZnS was free. The other cells and the primary Cu concentrate indicate that ZnS was largely free (nearly 80%) confirming that inadvertent activation in the pulp was the dominant problem. Surface analyses with TOF-SIMS and XPS confirmed that this activation occurred mainly in the rougher flotation bank and was dominated by Cu$^{2+}$ and to a lesser extent by Pb$^{2+}$ (undisclosed data). Cu$^{2+}$ levels in solution were typically below 1 ppm.

**Flotation laboratory test**

In the lab, duplication of the grinding, conditioning and first kinetics of Cu flotation was achieved. Table 2 shows the cumulative distributions and grades of Cu, Pb, Zn and Fe for a 6-minute Cu rougher flotation test. This test represented the flotation “baseline”; it was repeated 13 times with a relative standard deviation of ±13% or better. Nearly 21% of the zinc was recovered as Zn impurities in the cumulative copper concentrate. In the plant, the subsequent cleaning and grinding steps to complete the Cu flotation circuit do reduce this percentage to around 6-7%, but still, a large proportion of Zn is lost to the Cu concentrate. In the second flotation test, an artificial Cu$^{2+}$ enrichment of 3 mg/L was done and a second baseline was generated. The two baselines, with and without Cu$^{2+}$ addition, are inserted in Figures 2 to 4.

All reagents used to control ZnS activation were tested against the two baseline tests to demonstrate their efficiency. The reagents were selected based on the following criteria: low impact on metal recoveries (PM, Pb and Cu) in the Cu flotation and following circuits; composition of reagent could only introduce common ions to the circuit or be easily destroyed during water treatment; ease and safe use at the plant; price and availability.

The first reagent selected for this study was zinc sulfate. It was tested at different dosages, with and without addition of Cu$^{2+}$. As seen in Figure 2, flotation tests with 25 g/t and 200 g/t of ZnSO$_4$ demonstrated that Zn recovery was reduced from 21% (baseline without Cu$^{2+}$ addition) to 17.5% and 18.6% respectively. With Cu$^{2+}$, and using 50 or 100g/t of ZnSO$_4$, inadvertent zinc recovery was reduced from 32.2% (baseline with Cu$^{2+}$) to around 17.5%. Other tests (not presented here) when adding ZnSO$_4$ at the grinding step or at different flotation steps in the presence of Cu$^{2+}$ gave similar results; this confirmed that Cu$^{2+}$ activation occurs mainly during Cu flotation. In all tests, PM recoveries were unaffected by the reagent. However, because Zn can passivate gold with a Zn hydroxide deposit (Giménez-Romero 2006, Marsden 1993), proper optimization of ZnSO$_4$ addition at the plant would be required.

Sodium bisulfite was the second reagent tested. It is well established that sodium sulfite as well as sodium bisulfite, metabisulfite or sulfur dioxide can be used as depressants for pyrite, galena and sphalerite in copper circuits at neutral pHs (Yamamoto, 1980; Pattison, 1983; Grano, 1997). The depressing effect of these reagents is also related to pH (Bulatovic 2007). Dávila-Pulido et al. have demonstrated that sulfite or metabisulfite reduce the contact angle of copper-activated sphalerite. They confirmed that ZnS depression is
mainly due to oxidation of the elemental sulfur (or polysulfide) at the mineral surface and is related to dissolved oxygen. Figure 3 presents the results of the flotation tests with sodium bisulfite. Used alone, at 1000 g/t, NaHSO₃ decreased the Zn recovery from 21% (baseline) to 16% in the Cu rougher concentrate. In the presence of copper ions in the pulp, NaHSO₃, at 500 g/t and 1000 g/t, decreased the recovery of zinc from 32.2% (baseline) to 13.8% and 17.4% respectively.

TETA was the last reagent tested, chosen especially to complex dissolved copper in the pulp. This reagent was selected for its ability to form chelates with transition metals (Shackleton, 2003.). Figure 4 shows that TETA was effective in limiting ZnS activation. At only 25 mg/L, TETA was able to reduce Zn recovery to 18.8% (test without Cu²⁺ addition) and to 18.7% (with Cu²⁺ addition).

For all tests conducted with TETA and sodium bisulfite, an improvement in Cu grade in the Cu rougher flotation concentrate was observed. Table 2 shows the results. For TETA, Cu grade increased from 2.9% (baseline) to 4.3% while NaHSO₃ brought the Cu grade up to 3.9%. TETA is not only a chelating agent, it is also capable of dissolving some oxidation products at the surface of mineral phases (Chen, 2006); this could explain the higher Cu grades obtained in the flotation tests. It is important to optimize the dosage of TETA with respect to the level of dissolved Cu²⁺ in the pulp but also with respect to already dissolved metals and all other metals associated to surface oxidation products (hydroxides, sulfates and carbonates) which can be partially dissolved. In the plant, the injection points of TETA should take into account the different sources of water and be added before reaching the Cu flotation cells. Reused water can sometimes be rich in dissolved copper depending on 1) efficiency of the tailings pond water treatment and 2) variation of water quality in the Zn flotation circuit (especially when CuSO₄ is used to activate ZnS). As for sodium bisulfite, this reagent can modify the Eh of the pulp and play an important role in flotation; this issue would require further investigation.

Surface analysis

Industrial samples

TOF-SIMS analyses were performed on sphalerite grains from the mill discharge sample, the first concentrate and reject samples of 4 tests: baseline, ZnSO₄ (25g/t), TETA (25mg/l) and NaHSO₃ (500g/t), all with Cu²⁺ addition. The data revealed that copper transfer occurred under all test conditions (Figure 5). Higher Cu intensities were recorded for the concentrate samples relative to the paired rejects. The greatest paired differences were noted for the baseline and the NaHSO₃ addition tests, where loading of Cu on the sphalerite grains from both concentrates is very similar. The smallest difference was observed in the ZnSO₄ test. The lowest degrees of Cu loading were observed in the ZnSO₄ and TETA tests. The intensity distribution of Cu in the samples mirrored that of the collector (3418A; data not shown). This data indicates that flotation was in response to collector attachment and, given that all sphalerite grains in the concentrate samples had some degree of Cu on their surface, the attachment was facilitated by Cu adsorption.
Both the ZnSO₄ and TETA test samples indicate that Cu was partially inhibited from attaching to the surface of the sphalerite grains. The operational mechanisms however were probably different, the former likely related to the development of oxidative species on sphalerite grains (Khmeleva 2006), the latter to the chelating capacity of TETA (Chandra 2006, Tukel 2010). The data from the NaHSO₃ tests shows a surprising significant loading of Cu on the surface of the sphalerite grains in the concentrate. This appears to contradict the recovery data that shows a decrease in Zn reporting to the Cu concentrate. Possibly more significant however is the collector response that did not correspond to the surface Cu distribution. Collector intensity data (not shown) for the concentrates and rejects from the NaHSO₃ test were the same as that for the rejects in the ZnSO₄ and TETA tests. Collector attachment in this case was not facilitated by the presence of Cu, consequently a greater proportion of the sphalerite reports to the rejects.

The surface of the sphalerite grains were examined for potential species acting as Cu inhibitors. Sphalerite grain surfaces in both the ZnSO₄ and NaHSO₃ tests reported the highest proportion of species indicative of oxidation such as Zn(OH)₂ and SO₃⁻. It is possible that a greater development of sulfoxyl and hydroxide species on the surface of the sphalerites, as identified by TOF-SIMS, may inhibit collector attachment, produce hydrophylic surfaces, and, in combination, result in poor flotation (Khmeleva 2006, Chandra 2006).

Bench tests

Analyses of sphalerite grains from the bench test, while not definitive, reveal a number of similar results to that observed by the TOF-SIMS study of the reference material. The XPS analyses did not confirm the presence of Zn(OH)₂, as the Zn2p peak at 1021.5 eV is characteristic of both ZnS and Zn(OH)₂ (Prestidge 1997, Shen 2001). However, the calculated modified Zn Auger parameter (Wegner et al., 2003; Biesinger et al. 2010) at 2011.05 eV falls into the oxide category and the broad oxide peak at 531.8 eV likely represents sulphonyl species and possibly Zn(OH)₂ (Prestidge 1997, Grano 1997). All Cu 2p spectra lack a characteristic Cu²⁺ shake up peak at 942 eV (Figure 6A) indicating that the Cu is present as Cu¹⁺ and not as Cu(OH)₂(liquid). It is also not likely (CuOH)⁺ weakly held to the sphalerite surface since it was not identified in the TOF-SIMS analysis and is generally not stable in this pH range. Given that the Cu appears as Cu⁺, it likely represents that which substituted for Zn in the upper layers of the mineral lattice – a generally agreed upon conclusion (Ralston 1980; Gerson et al. 1999; Smart 2003).

The S 2p₃/₂ XPS spectra (Figures 6B and C) show the presence of a number of S species. Those that are likely relevant to the depression of sphalerite are the sulfoxyl species. While both sulfates and sulfites were identified, it may be the latter, identified in the Cu test+ ZnSO₄ test (Figure 6C), that is linked to the depression of sphalerite. The spectral resolution of the instrument allowed for the identification of thiosulfite in the 163.5 eV region. It should be pointed out that other interpretations are possible; however, it seems relevant given the strong presence of SO₃ in the TOF-SIMS spectra. These data indicate a process similar to that outlined by Khmeleva et al. (2006) who studied sphalerite depression in response to NaHSO₃ addition. The following proposed scenario is based on the results obtained here. Sulfite ions present in solution as a result of ZnSO₄ dissociation adsorb to hydrophobic Cu coordinated S (polysulphide) generated as a result of
Cu substitution for Zn. The sulfite ion decomposition of the polysulphides, generates thiosulfate, which is subsequently oxidised to sulfate. Zn(OH)$_2$, identified in the TOF-SIMS analysis, likely forms concurrently at the surface of sphalerite as a result of liberated Zn ions combining with hydroxyls. The XPS spectrum of a sphalerite surface in Figure 6C potentially represents a snapshot into this process. Detailed investigations to confirm this proposed mechanism are under way.

**Plant implementation**

An industrial validation of ZnSO$_4$ as a reagent to control ZnS activation in the Cu flotation circuit was performed at LaRonde Division of Agnico-Eagle Mines Limited over the course of more than one year. Figure 7 presents the monthly mean Zn recovery during 2009. First trials occurred in September and regular additions (~40 g/t) started in October. Before adding zinc sulfate, Zn recovery in the final Cu concentrate was around 6%; after, this value dropped to almost 3.5%. ZnSO$_4$ additions continued during 2010 resulting in an average Zn recovery reduction of 2%. Gold recovery (data not shown here) was not affected.

Subsequently, tracking dissolved copper in the Cu and Zn flotation circuits allowed identifying two sources of Cu$^{2+}$: reused process water (main source) and reclaim water from the tailings pond. It was found that copper sulfate addition in the downstream Zn flotation circuit was not optimal with respect to Zn grade variations. An automatic valve was thus installed to link the additions to the consumption model based on daily Zn feed. This resulted in abating excess Cu$^{2+}$ in reused process water. It was also observed that operational problems and evaporation during summer could lead to Cu$^{2+}$ enrichment in the tailings pond. Means to provide online monitoring of this water are under study. From the better understanding of the chemistry of flotation circuits and water quality gained in this study, the addition of ZnSO$_4$ is still applied in 2012 but only as required.

First tests with TETA in the plant are ongoing. It appears that TETA can indeed limit Zn activation. Further work though is necessary to investigate the potential effect on the following Zn flotation and cyanidation circuits.

**CONCLUSIONS**

Mineralogy and surface chemistry analyses confirmed that 1) ZnS impurities in Cu rougher concentrates are mainly free particles and 2) inadvertent ZnS activation by Cu$^{2+}$ is the dominant phenomena occurring in the Cu flotation circuit at LaRonde. To control ZnS activation, potential depressants (ZnSO$_4$, NaHSO$_3$ and TETA) were tested. Controlled grinding was applied to reproduce the electrochemical and surface conditions occurring in the plant. All three depressants reduced ZnS recovery in the Cu rougher concentrate. Surface chemistry data indicate that Cu is partially inhibited from attaching to the surface of sphalerite grains when ZnSO$_4$ and TETA are used, the first likely by inducing oxidation species on ZnS grains and the second by chelating soluble copper. Data also suggest that ZnSO$_4$ and NaHSO$_3$ could promote the development of
sulfoxyl and hydroxide species on ZnS surfaces that inhibit collector attachment. PM recovery was not affected by any of the depressants. Based on these tests, the LaRonde plant started adding 40 g/t ZnSO\textsubscript{4} at the conditioning or cleaning stages. This first industrial implementation led to a one third reduction of the Zn in the Cu concentrate. Subsequently, specific Cu\textsuperscript{2+} control measures could be devised industrially.

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REFERENCES


Fig 1 - Sphalerite associations found in the Cu rougher concentrate at LaRonde (Feb 2009)

Fig 2 - Effect of zinc sulfate on ZnS in Cu rougher flotation tests, with and without Cu$^{2+}$
Fig 3 - Effect of sodium sulfite on ZnS in Cu flotation tests, with and without Cu$^{2+}$

Fig 4 - Effect of TETA on ZnS in Cu rougher flotation tests, with and without Cu$^{2+}$
Fig 5 - TOF-SIMS normalized intensity of Cu, ZnOH and SO$_3$ measured on the surface of sphalerite grains from the feed (F), concentrate (C) and reject (R) samples in the baseline, ZnSO$_4$, TETA and NaHSO$_3$ flotation tests.

Fig 6 - Sphalerite XPS spectra A) and C) with the additions of ZnSO$_4$ followed by CuSO$_4$; B) in deionized water only.
Fig 7 - Monthly mean of Zn recovery in the Cu flotation circuit at LaRonde (2009)
Table 1
Major components and PM in LaRonde reference material

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<tr>
<th>Tests</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>MgO (%)</th>
<th>CaO (%)</th>
<th>K₂O (%)</th>
<th>TiO₂ (%)</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Pb (%)</th>
<th>S (%)</th>
<th>Zn (%)</th>
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Table 2
Cumulative recoveries and grades of Cu, Pb, Zn and Fe in Cu rougher flotation tests with LaRonde reference material for baseline and cumulative Cu grades for different depressants

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<tr>
<th>Tests</th>
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<th>NaHSO₃ 1000 g/t</th>
<th>TETA 25 mg/l</th>
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<td>Cu Dist. (%)</td>
<td>Cu Grade (%)</td>
<td>Pb Dist. (%)</td>
<td>Pb Grade (%)</td>
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