

Article

Reducing Negative Effects of Oxidation on Flotation of Complex Cu–Zn Sulfide Ores

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Abstract: Surface oxidation of the sulfide minerals negatively affects the flotation performance, i.e., the selectivity and even the recoveries at heavy oxidation conditions. Oxidation may take place during the formation of the ore, during mining and stockpiling, and during the flotation process. Stockpiling of large amounts of ore is a common practice in mine sites for blending the process–plant feed. However, a long stockpiling time may cause severe surface oxidation of the complex sulfide ores, particularly the complex Cu–Zn sulfide ores containing secondary copper minerals, which resulted in loss of Cu–Zn selectivity and copper recovery. A complex Cu–Zn sulfide ore was used to investigate effects of stockpile time on flotation performance and to determine the most efficient mitigation method to restore the flotation performance. Batch-scale flotation tests were performed on a heavily oxidized sample using sulfidization, high intensity conditioning, and their combination. The results showed that sulfidization desliming and stage addition of depressants during flotation was the most effective method for producing a copper concentrate from oxidized ores.

Keywords: oxidation; flotation; depressants



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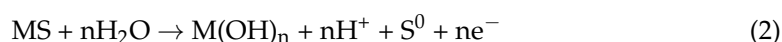
1. Introduction

Sulfide minerals are thermodynamically unstable in the presence of aerated, aqueous conditions and open-atmosphere, moist conditions because of the electrochemical interactions that occur between sulfide minerals and the solution species. This phenomenon leads to surface oxidation which plays a very important role in the flotation process, since sulfide flotation depends on the proportion of hydrophobic and hydrophilic species covering the surfaces. Mild oxidation results in a surface that is rich in polysulfides, with some metal hydroxides present at the surface, due to the dissolution of metal ions from the surface and near-surface layers as shown in *Reactions* [1,2].

In acidic conditions:

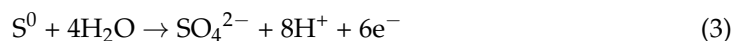


In alkaline conditions:

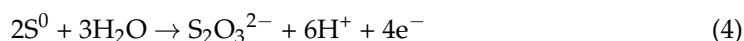


where M is the metal ion [1,2].

Slight surface oxidation may enhance the flotation performance of the sulfide mineral but extensive oxidation results in high quantities of metal hydroxides on the mineral surface [3–6]. Sulphate or thiosulphate would form (*Reactions* [3,4]), cause a lack of hydrophobicity, which reduces the floatability of sulfide minerals and their selectivity [1,7–10].



and/or



Surface oxidation may occur during in situ weathering of an ore body, or during the different extraction and processing stages (mining operations, stockpiling, crushing, milling, and flotation). The oxidation reactions arise from the presence of oxidants, as well as galvanic interactions between sulfide minerals, milling media, and solution species [11]. Various techniques—Eh, dissolved oxygen demand test, EDTA extraction technique, XPS and Auger surface analysis, optical mineralogy, infrared spectroscopy, flotation, contact angle, and zeta potential—have been reported to determine the degree of oxidation in the literature [4,8,12–14]. Auger and electron microscopies have shown the extent of surface mineral oxidation to be a thin layer (5–80 nm) of adsorbed oxidation products (e.g., metal hydroxides), precipitated colloidal particles of metal hydroxides (1–5 microns), and fine mineral particles of a few microns in size [15]. The interaction between the oxidation products and the mineral surface is generally weak, as sonication/decantation may remove most of these oxidation products [15]. However, in some cases, severe oxidation may cause alteration of mineral surfaces and formation of a thin layer of metal oxy/hydroxides. In these circumstances, chemical treatment, such as sulfidization, is required to clean the mineral surfaces and restore the flotation performance. The adsorption or precipitation of these oxidation products on mineral surfaces has been described as indiscriminate, preventing reagents such as collectors to reach their targeted minerals [16].

In the literature, there have been several methods used to reduce the negative effect of oxidation, such as ultrasonication [17,18], EDTA extraction [19], sulfidization [20,21], and high intensity conditioning [22–24]. Efficiency of these methods depends on the ore type, the conditions that lead to surface oxidation, and the type of surface oxidation species.

Each ore type has a different tolerance to surface oxidation depending on the mineralogy and ore genesis. The rapid oxidation of complex sulfide ores, particularly the ores containing high amounts of electrochemically active pyrite and secondary copper minerals, is observed during the mining phase and in the stockpiles. Effects of the stockpile time on flotation performance have been investigated using a complex Cu–Zn ore from the northwest of Turkey [25]. The results of aging tests showed that the flotation performance (i.e., copper recovery and Cu–Zn selectivity) was negatively affected after a two-week stockpile period.

For this type of ore, the mine schedule/ore production should be optimized to minimize the stockpile period and, hence, surface oxidation of the sulfide minerals. However, it may not be possible to manage the ore stockpiling through mine scheduling, and a large portion of valuable ore would stay in a stockpile for a long period. Significant problems may occur in these circumstances because the blending of the oxidized ore may deteriorate the flotation performance of the unoxidized ore. Therefore, the oxidized ores should be treated in a campaign mode of operation under different flotation conditions than that applied on the unoxidized ore.

In this paper, different methods were tested for mitigation of the negative effects of surface oxidation on a Cu–Zn complex sulfide ore. Sulfidization, high-intensity conditioning, combination of sulfidisation desliming, and stage addition of depressants were tested on a highly oxidized ore sample to restore the flotation performance. These methods were compared and the optimum surface-cleaning/flotation conditions were recommended based on the test results.

2. Materials and Methods

2.1. Ore Samples

A Cu–Zn complex sulfide ore from Turkey was used in the test work. Head assays of the ore samples are given in Table 1. The fresh ore sample was prepared from fresh drill cores and tested immediately after drilling. The oxidized ore sample was prepared using drill cores from twin drill holes, approximately one year old. The oxidized drill cores were selected from the unprotected drill core boxes. The fresh ore sample was used as a benchmark to illustrate the differences in the degree of oxidation between the fresh ore and the oxidized ore samples, and the effects of surface oxidation on the flotation performance.

Table 1. Head assay of the ore samples used in the tests.

	Cu (%)	Fe (%)	Zn (%)	Pb (%)	S (%)
Fresh Ore	0.70	35.60	1.78	0.16	40.11
Oxidized Ore	0.78	29.7	1.95	0.27	32.7

Both ore samples were from the same lithology/alteration and represent the sulfide ore zone in the deposit. Therefore, mineral distribution and liberation characteristics of the ore were discussed based on the mineralogical analysis of the fresh ore sample performed by the QEM-SCAN technique. Table 2 shows that 77% of the sample was pyrite. The major copper mineral was chalcopyrite, with a minor amount of secondary copper minerals, i.e., chalcocite/covellite. Sphalerite and galena were the zinc and lead minerals. There was approx. 1% talc as the naturally floatable gangue mineral in the ore, given that a pre-flotation stage is included in the flowsheet to remove the talc particles before the copper flotation stage.

Table 2. Mineralogical characterization of the ore sample.

	% Mass in the Sample
Pyrite	76.6
Sphalerite	2.70
Galena	0.56
Arsenopyrite	0.02
Chalcopyrite and Cu-sulfide intergrowths	2.06
Covellite/chalcocite	0.50
Tennantite-tetrahedrite	0.03
Talc and similar	1.02
All other silicates	7.48
Fe-(Ti)-oxides/oxyhydroxides/carbonates	4.26
Ankerite-dolomite/calcite	2.12
Barite	2.55
All other minerals/steel	0.26
Total	100

Grain size distribution and liberation analysis of the ore samples show that the ore requires fine grinding to achieve the required degree of liberation for flotation. A comprehensive flotation test program had been conducted on the sulfide ore sample to determine the optimum flotation flowsheet and conditions to produce saleable copper and zinc concentrates. The optimum primary grind size was determined to be $p_{80} = 38 \mu\text{m}$ based on the liberation analysis and flotation tests. The rougher copper and zinc concentrates were reground to $p_{80} = 15 \mu\text{m}$ and $p_{80} = 20 \mu\text{m}$, respectively [25].

2.2. EDTA Tests

EDTA (Ethylenediaminetetraacetic acid) is a colorless, water-soluble, solid acetate. EDTA has the ability to dissolve the oxidation products of the sulfide minerals and form metal complexes but does not react with metal sulfides [8,26,27]. Hence, EDTA extraction is used as a practical method for assessment of the surface oxidation of the sulfide minerals both in laboratory- and plant-scale applications.

A representative 10 g ore sample ground to $p_{80} = 38 \mu\text{m}$ (the grind size in the flotation tests) was used in the EDTA tests. The sample was stirred for 30 min in 3% *w/w* EDTA solution adjusted to a pH of 7.5 using NaOH. The sample was then filtered and passed

through a 0.45 µm Millipore membrane. The pregnant solution was analyzed for Cu, Fe, Pb, and Zn using AAS. Analytical-grade chemicals were used in this section.

Percentage of an oxidized element was calculated using the following equation:

$$\text{EDTA extractable M} = \frac{\text{Mass of M in EDTA solution}}{\text{Mass of M in solids}} \times 100 \quad (5)$$

where M is the metal [8]. The EDTA values of Cu, Pb, Zn and Fe were used for assessment of surface oxidation of the copper minerals, galena, sphalerite, and pyrite, respectively.

2.3. Batch Flotation Tests

A comprehensive flotation test program had been conducted on this ore in previous phases [25]. The ore contains highly activated sphalerite particles which make selective Cu–Zn flotation impossible without using a strong depressant scheme. A depressant scheme using a combination of Na₂S, ZnSO₄, and MBS (Na₂S₂O₅) was used to depress sphalerite particles in the copper flotation stage. Pyrite was also depressed effectively under this condition. The optimum flotation conditions applied on the unoxidized ore are called Standard Conditions, the details of which are given below.

The standard flotation reagent scheme includes:

1. Pre-Flotation: 25 µL MIBC.
2. Copper Flotation: 3 kg/t MBS, 1 kg/t ZnSO₄, 500 g/t Na₂S added in the mill pH 6–7 90 g/t Sodium Aerofloat (NaAF, a dithiophosphate-type collector) + 30 g/t Aero8761 (modified thionocarbamate).
3. Zinc Flotation: pH 11.5 600 g/t CuSO₄ 40 g/t SIPX (Sodium Isopropyl Xanthate).

The batch-scale flotation tests were conducted to investigate the effects of sulfidization, desliming, Na₂S dosage, and sequence of depressant addition. Figure 1 shows the flowsheet options applied for different test conditions. In the standard flowsheet, a 1.7 kg ore sample was ground at 60% w/w solids content in the presence of the depressants in a ball mill with high-chrome balls. The flotation was performed at 30% w/w using a Denver flotation machine and 4.5 L volume cell as sequential pre-flotation, copper flotation and zinc flotation.

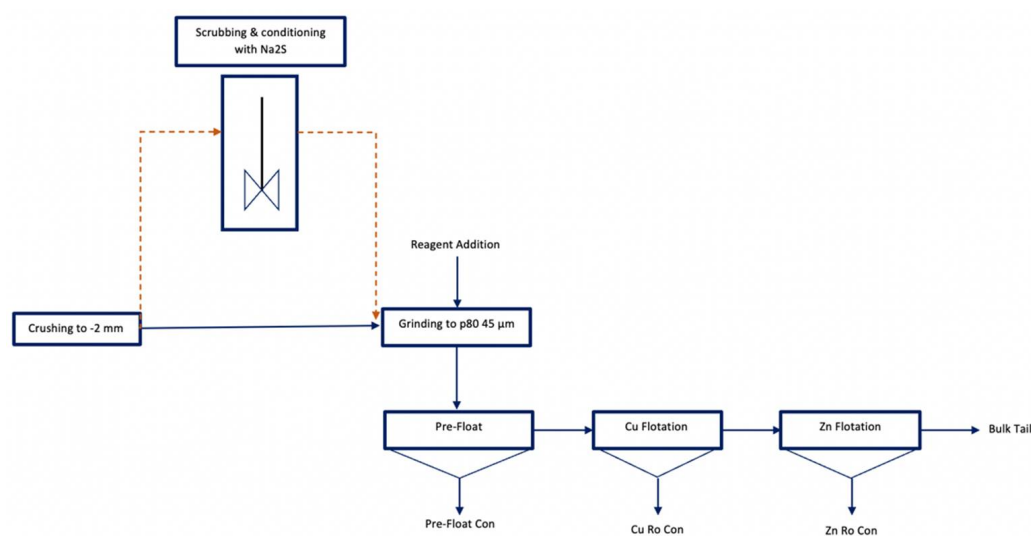


Figure 1. Flowsheet options of the batch scale flotation tests.

A sulfidization-desliming test was performed using a –2 mm ore sample. After desliming, the ore was ground under the standard flotation conditions. The same procedure was applied to the HIC (High Intensity Conditioning) test.

Open-cleaner flotation tests were performed to determine the grade and recovery of the final copper concentrate. The rougher copper concentrate was ground to p80 = 15 µm using a laboratory-scale rod mill with stainless-steel rods. Three stages of cleaner flotation

were applied with stage addition of depressants and collector addition in the Cleaner 1 and Cleaner Scavenger flotation stages.

Simulation studies were performed using the results of open-cleaner tests to estimate flotation performance of a closed-circuit operation, as in a locked-cycle test. JKSimFloat v6.1 was used for the mass balance and simulation studies. In the literature, the details of the simulation methodology and comparison of the simulation results with locked-cycle results are given for a complex sulfide ore [28]. It was clearly shown that the simulation studies could be used with confidence to estimate the closed-circuit flotation performance.

3. Results and Discussion

3.1. Effects of Surface Oxidation

The EDTA tests were performed on the fresh and oxidized samples to measure the quantity of the oxidation products present on the mineral surfaces. The EDTA results are given in Table 3.

Table 3. EDTA test results of fresh ore and oxidized samples.

	EDTA Extractable Metal/Total Metal (%)			
	Cu	Fe	Pb	Zn
Fresh Ore Sample	3.48	0.07	31.81	0.24
Oxidized Ore	15.87	0.21	40.52	2.67

The EDTA extractable copper increased from 3.48% in the fresh sample to 15.87% in the oxidized sample. EDTA values of the other elements also increased in the oxidized sample. These values indicated that surface oxidation of all the sulfide minerals increased considerably. The oxidation species, particularly the copper compounds, may dissolve during grinding and flotation and activate the other minerals present in the ore samples, such as sphalerite and pyrite. It is likely that both the recovery and selectivity of the separation would be negatively affected [29].

Rougher kinetic flotation tests with stage collector addition were conducted using the fresh and oxidized ore samples under standard conditions. Figure 2 shows that lower copper recovery was obtained per unit of mass pull with the oxidized sample. The total copper recovery of the two samples was close, but at much higher mass pull of the oxidized ore. The Cu–Zn selectivity was completely different between the two samples. The zinc recovery was even higher than the copper recovery with the oxidized sample.

Oxidation of chalcopyrite and the secondary copper minerals causes the dissolution of Cu ions from the mineral surface, the release of some metal hydroxide in alkali conditions, and a layer rich in sulfur-rich metal on the surface [30–33]. That being said, the flotation rate of the copper minerals decreased to some extent; however, the Cu Zn selectivity was strongly affected. The presence of dissolved Cu ions promoted sphalerite flotation by Cu adsorption on their surface, and adversely affected the selectivity of copper flotation [32,34,35]. In further oxidation, the amount of hydrophilic metal hydroxides increases, the hydrophobicity of the mineral decreases, and the collector selectivity deteriorates, making it less selective to various sulfur minerals [7,19]. However, in this case, the sulfide minerals were not heavily oxidized as their total recoveries were still high and close to the fresh ore sample, but at significantly higher mass pull.

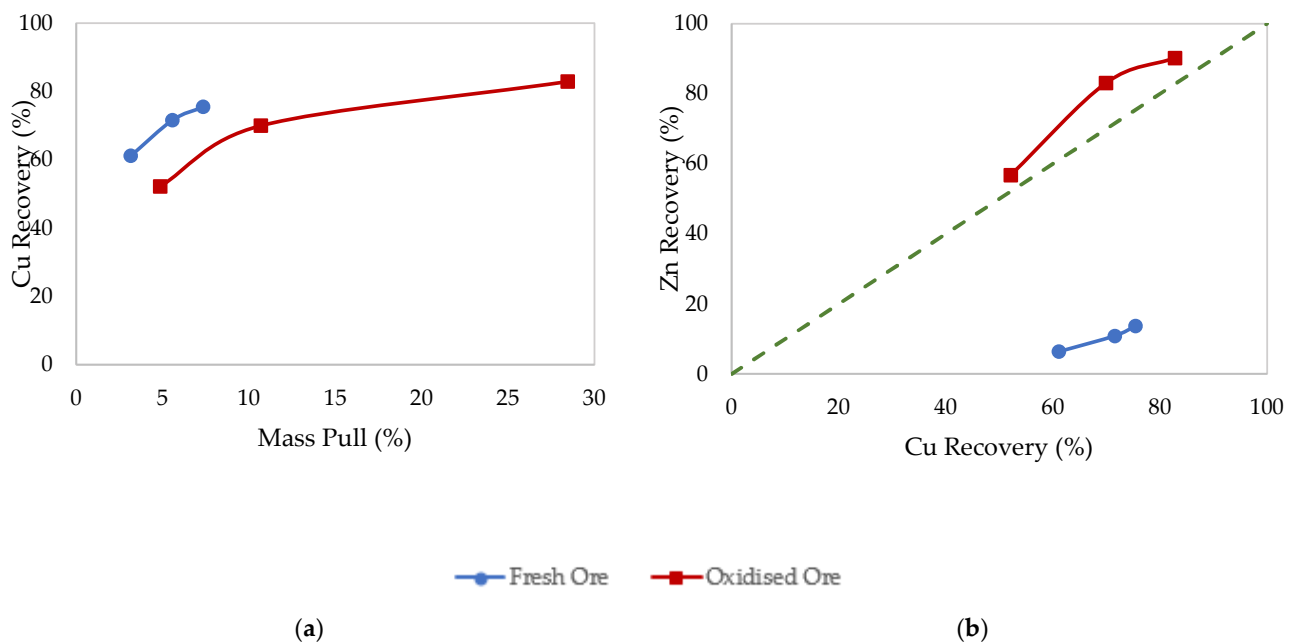


Figure 2. Relationship between Mass Pull and Cu Recovery (a) and Zn Recovery and Cu Recovery (b) in Cu Ro Stages.

3.2. Effects of Sulfidization

Na_2S is generally used for chemical surface cleaning, particularly for in situ pre-activated sphalerite by heavy metal cations. Na_2S is part of the standard depressant scheme and is used at a 0.5 kg/t dosage for the fresh ore sample to improve the Cu–Zn selectivity. In this section of the tests, effects of Na_2S were tested on the oxidized ore sample at five different dosages. The other parameters, such as the addition of MBS, ZnSO_4 , and collector dosages were kept the same as in the standard flotation conditions. Figure 3 shows the rougher copper recovery as a function of flotation time and mass pull obtained at different Na_2S dosages.

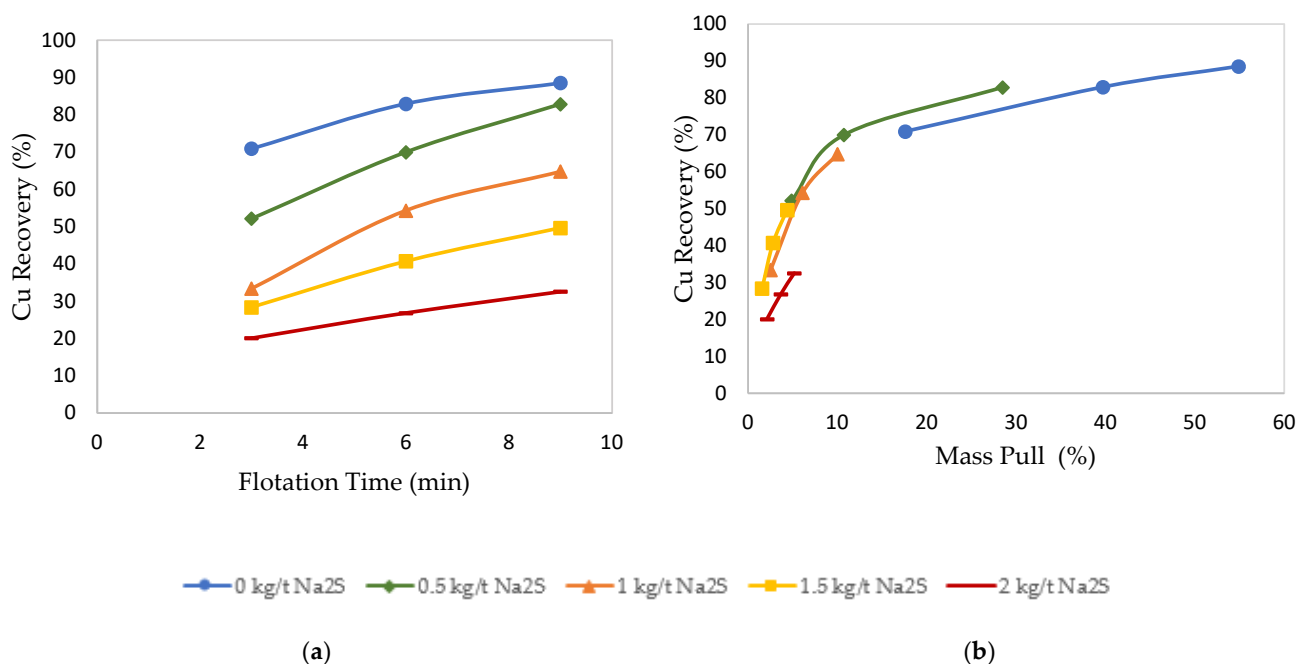
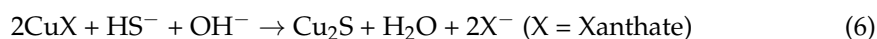


Figure 3. Effects of Na_2S on (a) Cu Recovery and (b) mass pull on copper flotation performance.

The copper recovery decreased significantly with increasing Na₂S dosage, particularly at 1 kg/t and higher dosages. The highest copper recovery was 88% and obtained in the absence of Na₂S. The mass pull also decreased from about 55% down to 5%, which in turn affected the copper recovery. The lower mass pull and copper recovery was attributed to the depressing effect of Na₂S at high dosages. The generally accepted depression mechanism of Na₂S on sulfide minerals is the removal of collectors from the surface (Reaction 6).



The hydrosulfide ion (HS[−]), a result of the dissociation and hydrolysis of Na₂S, removes the collector from the surface of the chalcopyrite and renders it hydrophilic [36,37].

Na₂S is also a strong reducing reagent. The excess amount of Na₂S reduces the redox potential of the flotation pulp and hinders adsorption of collectors on the mineral surfaces. Figure 4 shows the redox potential of the flotation pulp after the pre-flotation stage. The pre-flotation stage acted as a pre-aeration and increased the pulp potential from about −200 mV after grinding to higher values. The Eh was −40 mV even after 5 min of pre-flotation at 1 kg/t Na₂S and decreased gradually down to about −70 mV at higher dosages.

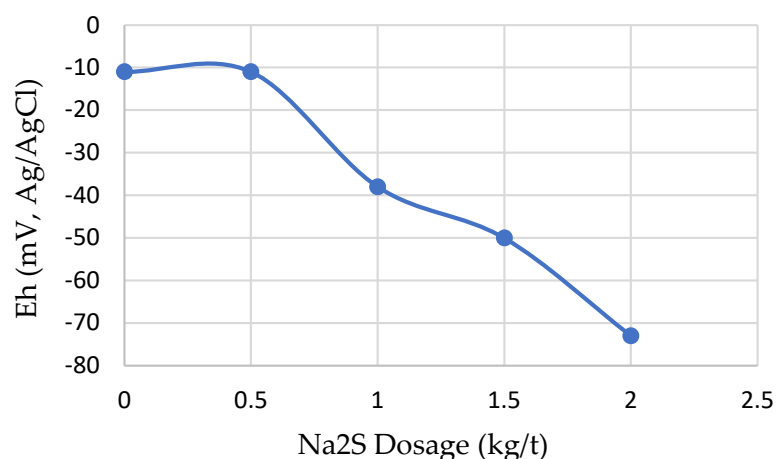


Figure 4. Redox potential of the pulp after pre-flotation as a function of Na₂S dosage.

The effects of Na₂S dosage on Cu–Zn and Cu–Pyrite selectivity was evaluated using the selectivity curves given in Figure 5 and the Gaudin Selectivity Index (SI) (Figure 6), because the Selectivity Index takes into account both the recovery and grade of the copper and zinc. SI are calculated by Equation (2), where R_m and R_g are the recoveries of valuable and gangue minerals [38].

Pyrite was depressed effectively even with small dosages of Na₂S due to the lower mass pull values in the presence of Na₂S. Pyrite was hydrophilic under the standard flotation conditions and its recovery was controlled by mass pull. However, the situation with the Cu–Zn selectivity and recovery of sphalerite was completely different.

The trend of the Cu–Zn selectivity curves was similar at 0 kg/t and 0.5 kg/t dosages, and above the reference line. The zinc recovery was higher than the copper recovery during the entire flotation test. Better Cu–Zn selectivity was obtained in the initial stages of flotation at 1 kg/t Na₂S, but it could not be maintained in the final stage of the flotation. The best selectivity was obtained at 1.5 kg/t Na₂S but the copper recovery decreased to 50%. This was confirmed by the Selectivity Index values, as shown in Figure 6.

$$\text{SI}^2 = \frac{R_m \times R_g}{(100 - R_m) \times (100 - R_g)} \quad (7)$$

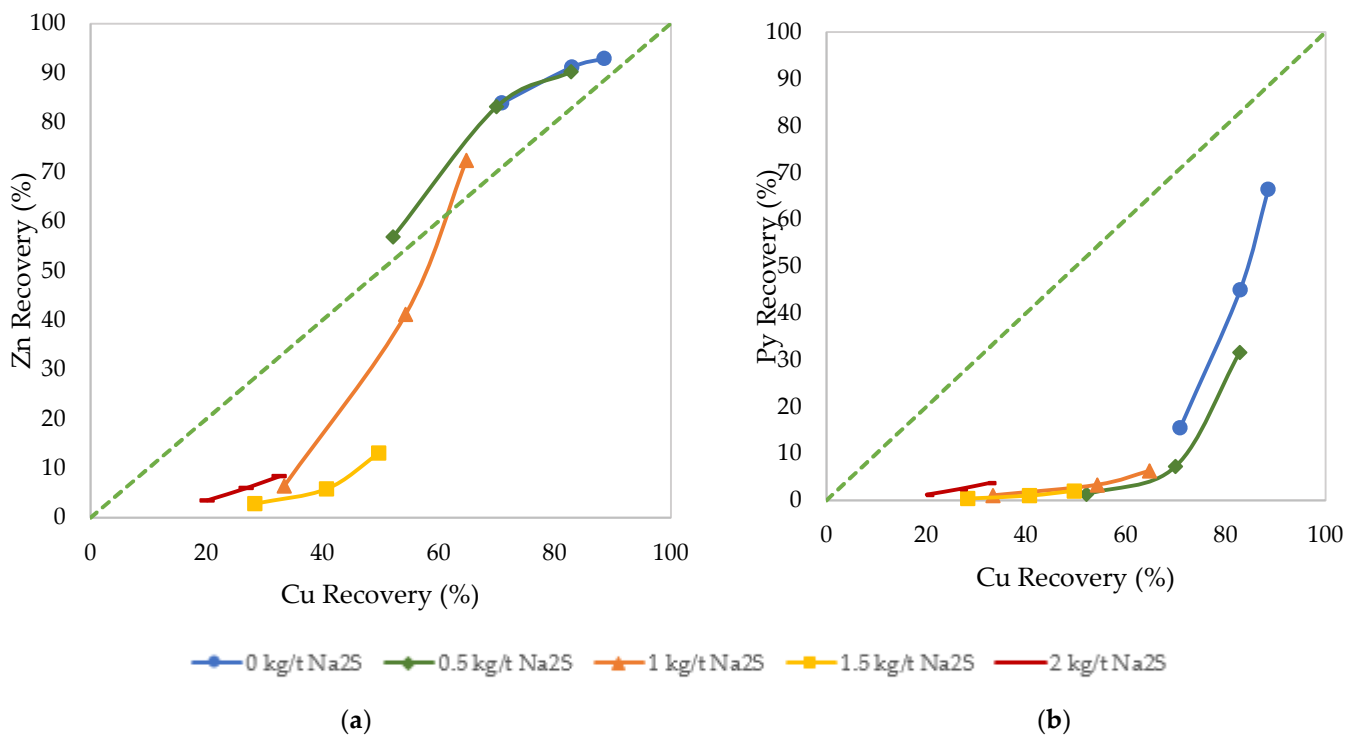


Figure 5. Effects of Na_2S dosages on Cu-Zn (a) and Cu-Pyrite (b) selectivity in the Cu flotation section.

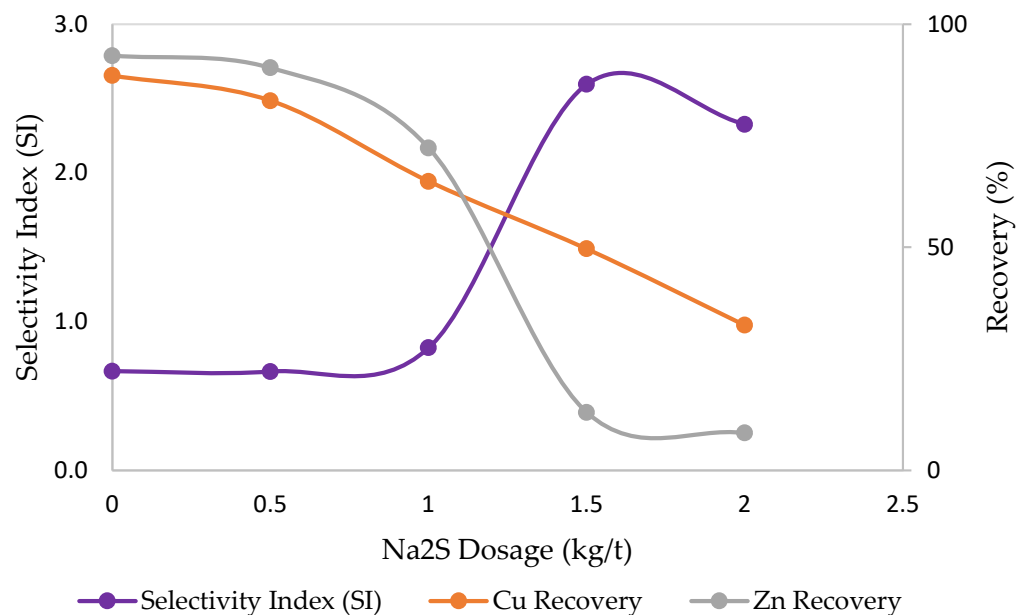


Figure 6. Gaudin Selectivity Index as a function of Na_2S dosage.

3.3. Effects of Desliming

The addition of Na_2S dosages higher than 1 kg/t increased the Cu-Zn selectivity by the surface cleaning effect; however, the presence of high dosage of Na_2S in the flotation pulp had a negative effect on Cu recovery due to low redox potential. The surface cleaning step was therefore separated from the flotation and a dewatering step was included to remove the excess sulfide ions from the pulp before the flotation step. The ore sample of -2 mm particle size was conditioned at high intensity with and without 1 kg/t Na_2S . After the high intensity conditioning, desliming was performed by decantation and the pulp was

washed with fresh water. The standard grinding-flotation conditions were then applied to the washed ore sample.

The Cu–Zn selectivity curves of these tests are given Figure 7. The selectivity curves of the standard conditions and sulfidization at 1 kg/t tests are also given for comparison of the flotation performance. High intensity conditioning and desliming without addition of Na_2S showed an acceptable Cu–Zn selectivity in the beginning of the flotation, but the selectivity disappeared as the flotation continued with stage addition of collector. The final copper and zinc recoveries were very close to the test performed under standard flotation conditions.

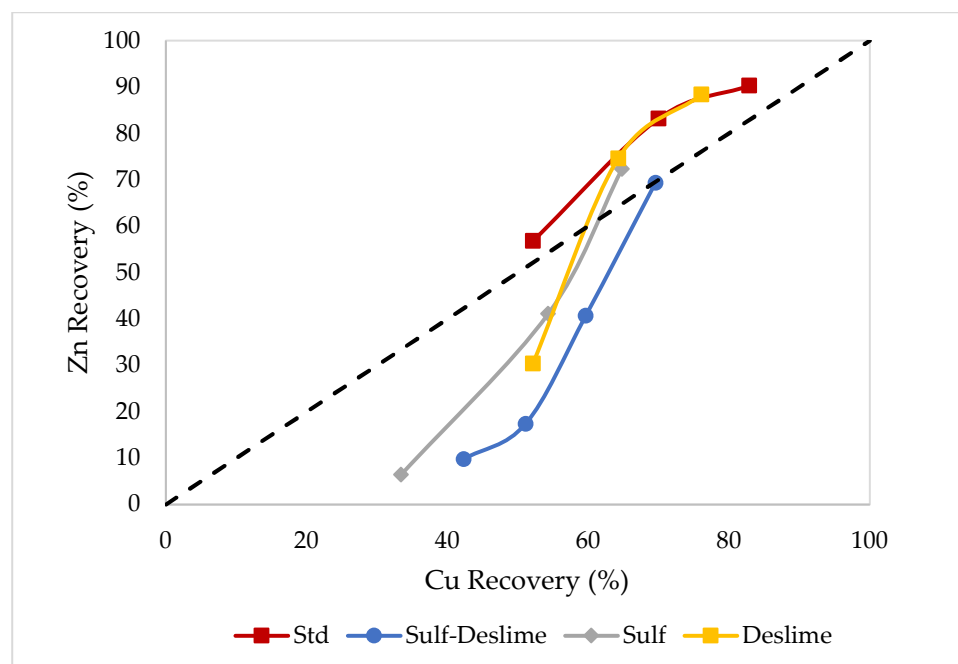


Figure 7. Effects of desliming with and without sulfidization on the Cu–Zn selectivity.

The test performed with high intensity conditioning in the presence of 1 kg/t Na_2S -desliming produced the highest Cu–Zn selectivity. However, the same trend was observed as the flotation continued with extra collector additions to increase the copper recovery. It appeared that the high Cu–Zn selectivity disappeared as the flotation continued. The depressing effect of Na_2S and MBS diminished with increasing collector dosage.

3.4. Effects of Stage of Depressants

In order to increase the copper recovery without negatively affecting the Cu–Zn selectivity, stage addition of depressants was applied together with extra collector addition. Additional 160 g/t Na_2S and 1 kg/t MBS was introduced in the Cu Ro 3 and Cu Ro 4 stages; therefore, the redox potential of the pulp was maintained at about -40 mV, which was the optimum value to achieve the highest Cu–Zn selectivity (Figure 6).

Figure 8 shows the Cu–Zn selectivity curves of the standard condition, sulfidization-desliming and sulfidization desliming stage addition of depressants. The copper recovery could be increased to 71% at the highest Cu–Zn selectivity with the stage addition of depressants.

Open cleaner flotation tests were conducted under the standard condition and the stage addition of depressants to determine the final copper concentrate quality and copper recovery after regrinding and three stages of cleaner flotation. In order to estimate the influence of recirculation of the cleaner flotation tailings, grade and recoveries of the final concentrate in closed circuit operation were calculated by simulation using JKSimFloat v6.1. The flowsheet and simulation results of the stage addition of depressants test are given in

Figure 9. A final copper concentrate could be produced assaying 22.14% Cu, 14.71% Zn, and 3.22% Pb at recoveries of 62.36%, 17.72%, and 33.61%, respectively.

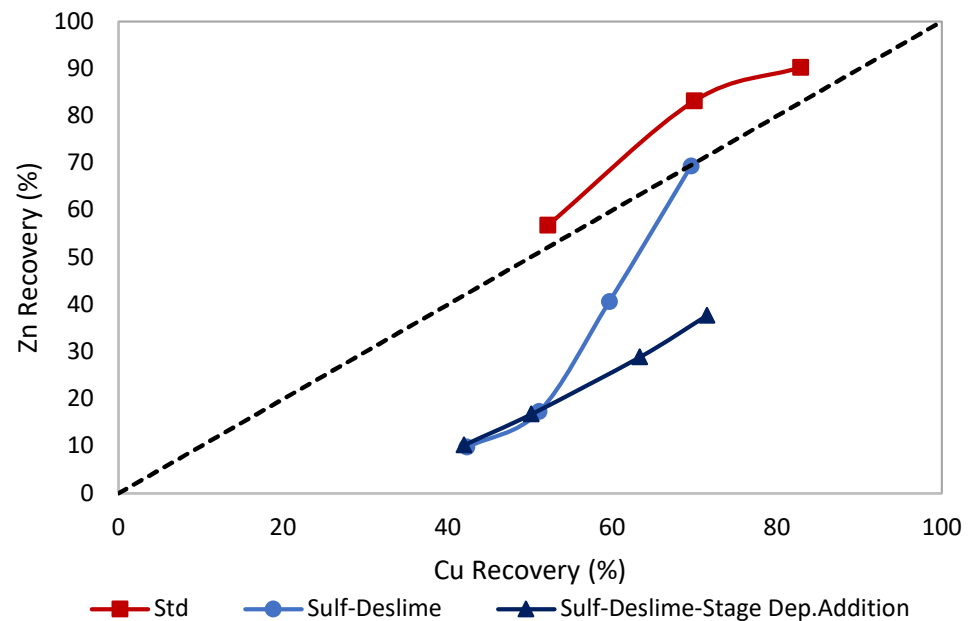


Figure 8. Effects of stage addition depressants on the Cu–Zn selectivity in the Cu section.

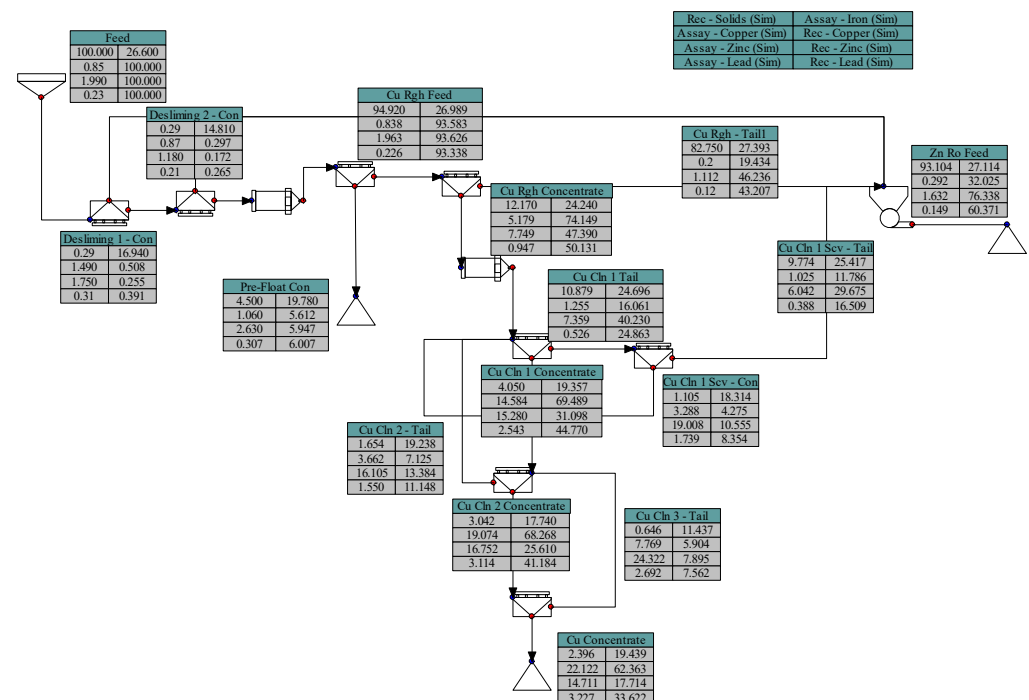


Figure 9. Simulation of the closed-circuit flotation for the test with sulfidization desliming stage addition of depressants.

Comparison of the flotation performances of the standard and stage addition of depressants conditions is given in Table 4. It is clearly shown that stage addition of depressant improves considerably the quality of the copper concentrate at 62% copper recovery, which was approx. 8% lower than the fresh ore sample. The copper concentrate was still highly contaminated, but it could be blended with the high-quality concentrate produced from the fresh ore, and additional revenue could be obtained from the copper metal.

Table 4. Comparison of the copper final concentrates produces from the standard flotation and stage addition of depressants conditions.

	Grade (%)			Recovery (%)		
	Cu	Pb	Zn	Cu	Pb	Zn
Standard Condition	11.74	1.47	38.1	41.13	20.61	61.07
Stage Add. of Dep.	22.13	3.22	14.71	62.36	33.61	17.72

4. Conclusions

A complex Cu–Zn sulfide ore was used to investigate effects of stockpile time on flotation performance and to determine the most efficient mitigation method to restore the flotation performance. A heavily oxidized ore sample was used in the tests. Various methods, such as sulfidation, high intensity conditioning, desliming, and their combinations were tested.

Oxidation did not decrease the copper recovery, but the Cu–Zn selectivity was completely lost. The zinc recovery was higher than the copper recovery even in the presence of high dosages of depressants.

The use of a high dosage of Na₂S during the grinding stage improved the Cu–Zn selectivity; however, the copper recovery decreased considerably due to low redox potential. Sulfidization, desliming and dewatering improve the copper recovery, but it was still low. The results showed that the Cu–Zn selectivity was high in the beginning of the flotation, but it was lost as the flotation continued. Given that stage addition of depressants was applied in the third and fourth stages of rougher flotation. The copper recovery increased to over 70% with acceptable Cu–Zn selectivity.

An open-cleaner flotation test with three stages of copper cleaner flotation was applied using the sulfidization-desliming-stage addition of the depressant method. Simulation studies were performed to estimate the flotation performance of a closed-circuit operation. The results showed that a final copper concentrate could be produced assaying 22.14% Cu, 14.71% Zn and 3.22% Pb at recoveries of 62.36%, 17.72% and 33.61%, respectively.

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