The role of depressant and pH in the selective flotation of copper and zinc ore and insights from mineralogy

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Abstract

The challenges of selective depression of sphalerite from chalcopyrite has proven to be a difficult and a challenging endeavor in the mineral industry. Typically, the ores containing sphalerite and copper are complex. This complexity may induce the unwanted activation and flotation of sphalerite during the concentration of copper minerals. Furthermore, the addition of reagents may enhance this undesirable outcome. Given this, the depression of sphalerite is important.

The depressant system and pH play an important role in the selective copper and zinc flotation process. The current study examines the role of different depressants such as zinc sulphate heptahydrate, sodium monohydrogensulfide, sodium sulfite and sodium disulfite on the depression of sphalerite at different pH. The dosage and combination of these reagents is examined in detail and a mechanism is proposed. Moreover, the mineralogical characterization of the ore is discussed. This study provides an important reference for the selective depression of sphalerite from copper-zinc ore.

1. Introduction

Sphalerite and chalcopyrite are widely ubiquitous as a source of zinc and copper metals respectively. The processing of ores containing copper and zinc is typically carried out by sequential flotation process. First, copper is floated by utilizing the superior floatability of copper and its ease for collector adsorption compared to zinc. However, past research has shown that despite the inferior floatability of zinc in copper-zinc ores, the presence of enough activating ions such copper ions derived from surface oxidation and dissolution of chalcopyrite can propel the ease in floatability of zinc minerals

(Liu and Cao 2006; Liu et al., 2018). Therefore, the use of collector as the only designated reagent for selectively adsorbing copper minerals in copper-zinc ores are in this case not possible without the use of depressants.

The depression of sphalerite is commonly achieved by use of two or more depressant such as zinc sulfate and cyanide. Cyanide, which has been widely used has become restricted as it poses huge environmental problems (Bulatovic and Wyslouzil, 1994; Laiu et al., 2018). Much research has been carried out on the different depressant schema with zinc sulfate, however most of the publication presented use high purity minerals which have the potential to not clearly represent the role of these depressants in an actual ore. This work focuses on the role of different depressant schema (zinc sulfate heptahydrate only, zinc sulfate heptahydrate combined with sodium monohydrogensulfide or sodium sulfite or sodium metabisulfite) using real copper-zinc ore. The pH environment has shown to be a significant factor in the adsorption and depression of sphalerite and therefore was included in the study. The mineralogical properties of the ore were fully investigated to aid in the choice of depressant and the pH environment to carry out flotation for the copper-zinc ore.

2. Experimental

2.1 Materials and reagents used.

The ore samples used in the experiment were obtained from a mining company in Japan. The reagents used were of analytical grade. Zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) and sodium monohydrogensulfide ($NaSH.nH_2O$), sodium sulfite (Na_2SO_3) and sodium metabisulfite ($Na_2S_2O_5$) were used as depressant, and the pH was regulated using sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4). Potassium isopropyl xanthate (PIPX)was used as the flotation collector. Methyl isobutyl carbinol (MIBC) was used as frother. Reverse osmosis (RO) water was used throughout all the experiments.

2.2 Ore preparation, conditioning and flotation experiments

A weighted sample of 250g was wet ground in a pot mill (2 litres, Itoh mill) to d_{80}75µm. The depressants were added to the slurry sample prior to grinding. The grinding was carried out for 62 minutes. After grinding the sample was immediately transferred to an agitator-type flotation machine equipped with a 1litre flotation cell. Flotation was carried out for 14 minutes, and the concentrates were obtained at 6 intervals (0.5, 1,2,4,8,14 min) and tailing. The other flotation conditions were set as follows: 900 rpm of impeller speed, room temperature 25ºC, air flow rate of 3.5 L/min and pH was adjusted between 9 and 12. All the experiments were duplicated to ascertain the statistical differences.

2.3 Ore characterization

Mineralogical analysis was performed with Mineral Liberation Analyzer (MLA, 650, FEI) using a combination of backscattered electron (BSE) and EDX-spectra. The elemental composition of the copper-zinc ore was analyzed using ICP-OES (5110, Agilent technology).

3. Results and Discussion

3.1 Ore Characterization

The elemental composition of flotation feed is presented in Table 1. As it can be seen the elemental concentrations of Cu and Zn were 1.20wt% and 0.14wt% respectively. In mineral processing, it is very common to find the occurrence of a mineral of interest to occur in different phases with other minerals, as such the elemental distribution of copper and zinc were inspected. The mineral content of the flotation feed is listed in Table 2. The mineralogical studies indicate that Zn element occurs mainly in sphalerite with moderate amount of Fe, and to a lesser extent is found in marmatite and carbonate mineral phase. Copper on the other hand is mainly found occurring in chalcopyrite.

Table 1. Chemical elemental composition of copper-zinc ore.

Element	Al	Ca	Cu	Fe	Mg	Zn
Content [wt%]	2.01	4.58	1.20	21.71	2.19	0.14

Table 2. Mineral abundance of the host minerals in wt% for zinc and copper.

	Mineral phase	Mineral Formula	Mineral abundance [wt%]
Zn	Sphalerite	(Zn, Fe) S	95.74
	Marmatite	(Zn, Fe) S	2.63
	Smithsonite (Carbonate)	Zn (CO_3)	1.59
Cu	Chalcopyrite	$CuFeS_2$	99.74
	Covellite	CuS	0.21

3.2 Flotation Results

3.1 Effect of Zinc Sulfate ($ZnSO_4.7H_2O$)

Zinc sulfate is a widely used depresssant in the mineral processing of copper/zinc ores. The amount of $ZnSO_4.7H_2O$ plays a critical role in the downstream processing of Zn, therefore, the amount of $ZnSO_4.7H_2O$ on sphalerite depression was investigated. The results for the recovery of copper and zinc to the concentrates is given in Figure 1. As can be seen, the recovery of copper increased to more than 80% for all the amounts of $ZnSO_4.7H_2O$ used. In Figure 1 a) and 1 b) the zinc reporting to the concentrates is 57.18% and 58.48% respectively. When $ZnSO_4.7H_2O$ was increased to 2kg/t the recovery of Zn decreased to 54.30%. A moderate amount of $ZnSO_4.7H_2O$, 1.5kg/t, was chosen for further investigations.

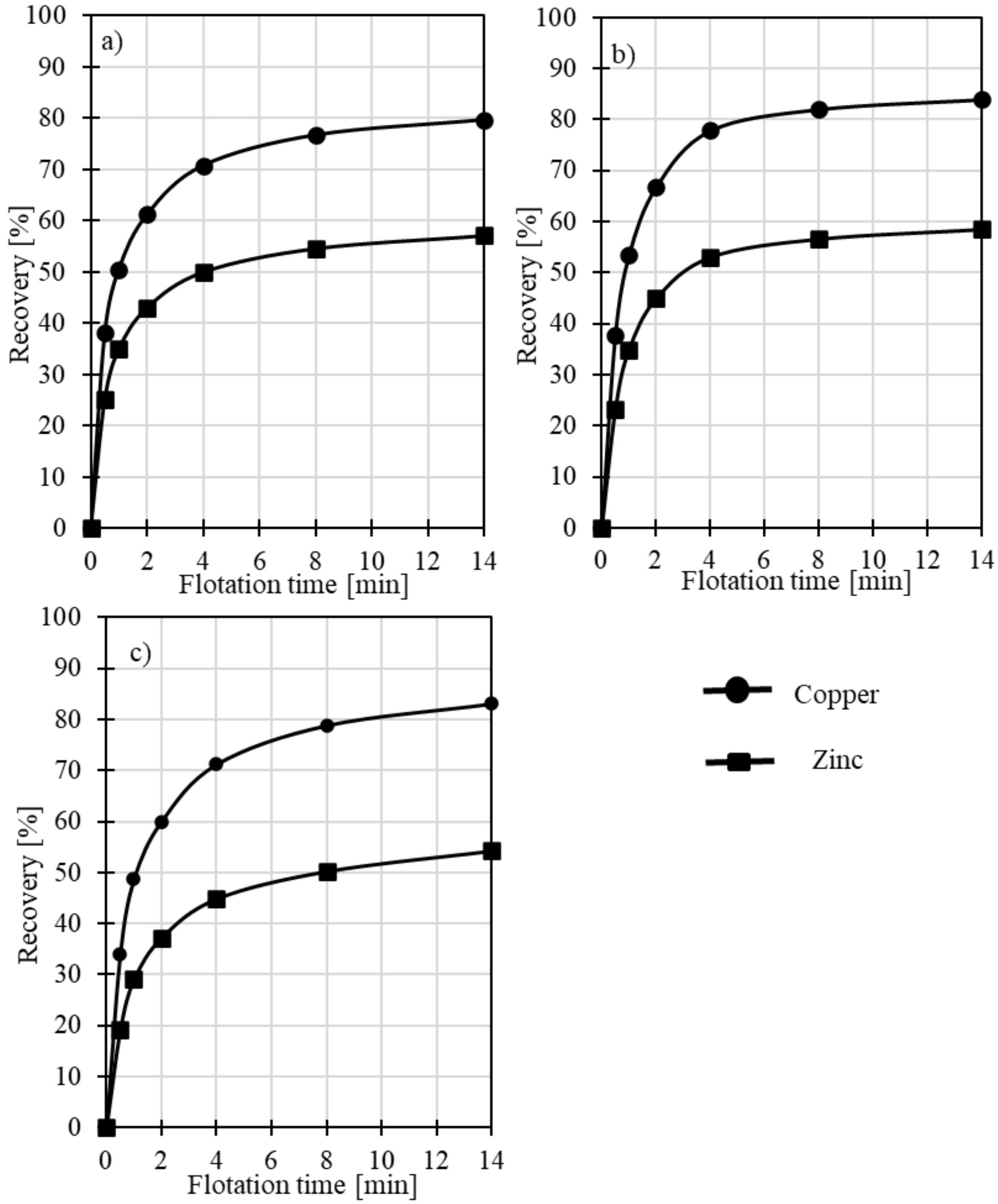

Figure 1. Recovery of chalcopyrite and sphalerite using zinc sulfate at different dosage a) 1kg/t, b) 1.5kg/t and c) 2kg/t

3.2 Effect of pH

The pH flotation of chalcopyrite and sphalerite has been well noted in literature (Liu and Cao 2006). The results for the influence of pH using zinc sulfate as the only depressant is presented in Figure 2. The recovery of copper reached approximately 80% under all pH conditions tested. Similarly, the recovery of Zn reached 59.80%, 53.21% and 58.49% at pH 9, pH 11 and pH 12 respectively. Given the range in which sphalerite was recovered with zinc sulfate, a combination of zinc with other depressants was investigated at different pH condition.

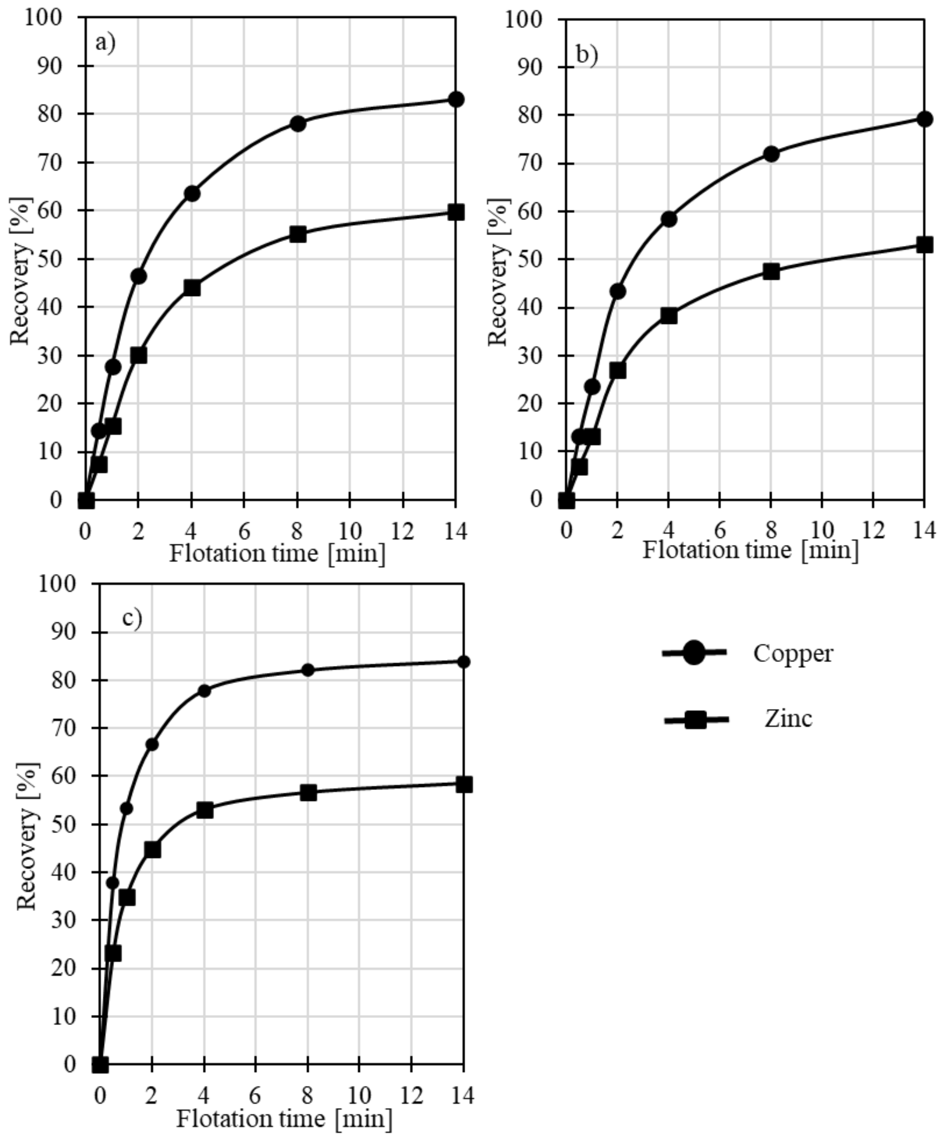

Figure 2. Recovery of chalcopyrite and sphalerite using zinc sulfate at different pH a) pH 9, b) pH 11 and c) pH12.

3.3 Effect of $ZnSO_4.7H_2O$ mixed with other depressants.

A combination of $ZnSO_4.7H_2O$ with other depressants namely, sodium monohydrogensulfide ($NaSH.nH_2O$), sodium sulfite (Na_2SO_3) and sodium metabisulfite ($Na_2S_2O_5$) were performed. The results are discussed below.

3.3.1. Effect of $ZnSO_4.7H_2O$ and sodium metabisulfite ($Na_2S_2O_5$)

The recovery of chalcopyrite and sphalerite using a combination of $ZnSO_4.7H_2O$ and $Na_2S_2O_5$ in the pH range 9,11 and 12 is shown in Figure 3. As shown in Figure 3 a) the recovery of zinc and copper at pH 9 reached 57.50% and 80.36% respectively. At pH 11, the recovery of zinc decreased to 56.13% while copper was 80.93% (Figure 3 b). Finally, in Figure 3 c) the recovery of zinc and copper at pH 12 were 56.29% and 81.61% respectively.

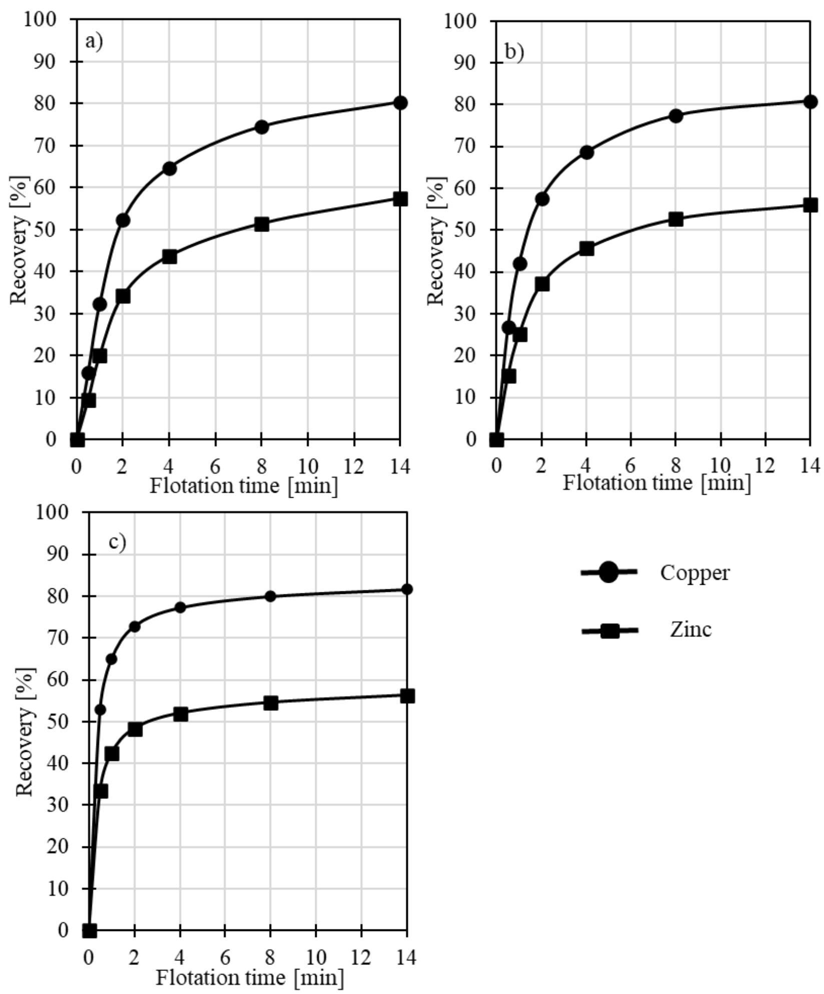

Figure 3. Recovery of chalcopyrite and sphalerite using zinc sulfate and sodium metabisulfite at different pH a) pH 9, b) pH 11 and c) pH12.

3.3.2. Effect of $ZnSO_4.7H_2O$ and sodium sulfite (Na_2SO_3)

The effect of a combination of zinc sulfate with sodium sulfite on the flotation of sphalerite and chalcopyrite is demonstrated in Figure 4. As shown in Figure 4, the use of $ZnSO_4.7H_2O$ and Na_2SO_3 exerts a somewhat similar copper and zinc recovery as the use of $ZnSO_4.7H_2O$ only. Figure 4a) shows the recovery of sphalerite at pH 9 to be a maximum of 47.37%. Zinc recovery increased from pH 11(4b) and pH 12(4c) to 54.78% and 54.23% respectively. The recovery of copper increases with an increase in pH from 74.60% to 80.15% and 82.41% at pH 9, 11 and 12 respectively.

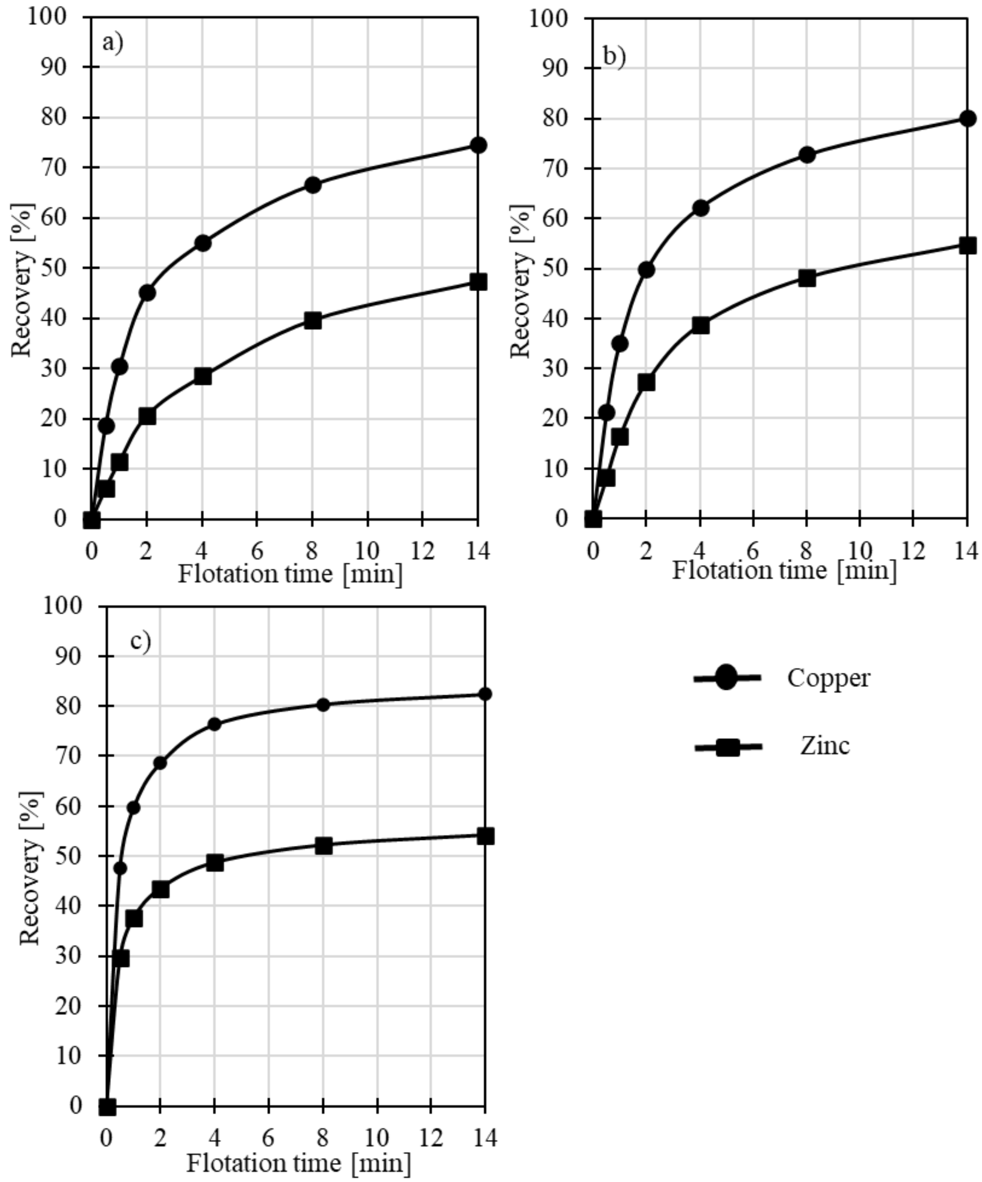

Figure 4. Recovery of chalcopyrite and sphalerite using zinc sulfate and sodium sulfite at different pH a) pH 9, b) pH 11 and c) pH12.

3.3.3 Effect of $ZnSO_4.7H_2O$ and sodium monohydrogensulfide ($NaSH.nH_2O$)

The flotation response of chalcopyrite and sphalerite with $ZnSO_4.7H_2O$ and $NaSH.nH_2O$ is the most pronounced of the depressant flotation schema investigated in this research. As shown in Figure 5, the addition of $NaSH.nH_2O$ had an obvious selective depression and separation of sphalerite from chalcopyrite from the Cu-Zn feed. Copper recovery showed a positive effect as it improved to 91.05%, 89.87% and 89.70% at pH 9(5a), pH 11(5b), and pH12(5c) respectively. The recovery of zinc in copper concentrate decreased significantly to 29.87%, 33.30% and 29.48% for pH 9, 11 and 12 respectively.

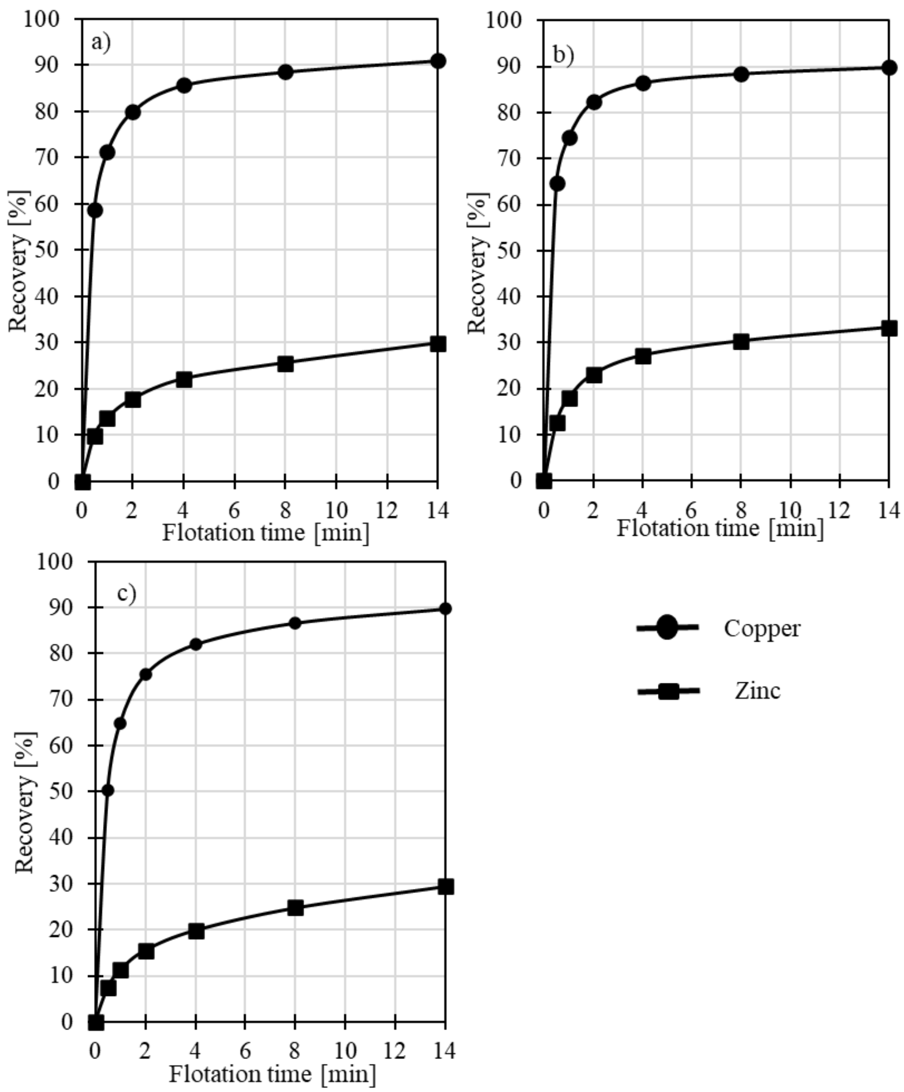

Figure 5. Recovery of chalcopyrite and sphalerite using zinc sulfate and sodium hydrosulfide hydrate at different pH a) pH 9, b) pH 11 and c) pH12.

3.4 Selective separation efficiency of chalcopyrite and sphalerite

The selectivity of chalcopyrite and sphalerite is important for the downstream pyrometallurgical treatment of the copper concentrates. The negative effect of copper concentrates containing a high level of sphalerite is well documented (Bulatovic and Wyslouzil, 1994; Feng et.al, 2019). In that case it is important to aim for higher selective separation of chalcopyrite and sphalerite. The results showing the Newton separation efficiency for chalcopyrite and sphalerite are presented in Figure 6. The use of $ZnSO_4.7H_2O$ as the only depressant showed that only 22.5%, 25.46% and 28.74% separation efficiency was obtained at pH 9, pH 11 and pH 12 respectively. Similarly, low separation efficiency between sphalerite and chalcopyrite is observed when $ZnSO_4.7H_2O$ is mixed with either sodium sulfite (Na_2SO_3) or sodium metabisulfite ($Na_2S_2O_5$). The floatability of sphalerite in the copper-zinc feed suggest that the presence of copper ions might have unintentionally activated sphalerite. The ease of collector adsorption on the copper activated sphalerite due to a weak inhibition of the depressants ($ZnSO_4.7H_2O$, $ZnSO_4.7H_2O$ with Na_2SO_3 or $Na_2S_2O_5$) resulted in increasing the hydrophobicity of zinc. A combination of $ZnSO_4.7H_2O$ and sodium monohydrogensulfide ($NaSH.nH_2O$) had the best separation performance at pH 9 with 61.18%, while pH 11 and 12 had 56.57% and 60.22% respectively.

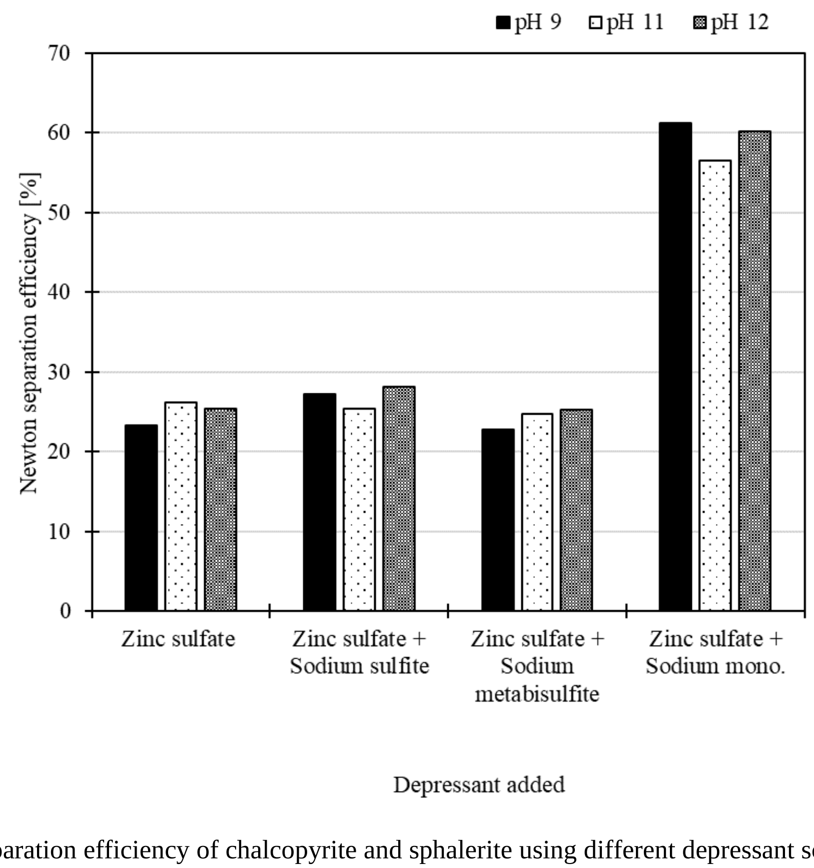

Figure 6. Separation efficiency of chalcopyrite and sphalerite using different depressant schema at different pH. (Sodium mono. => sodium monohydrogensulfide)

4 Conclusion

The copper-zinc ore used in this study was characterized by element and MLA analysis and the selective flotation performance was investigated by using different depressant schema at different pH. The following conclusions were drawn from the experiments:

- The sample feed used in this study had an "easy" mineralogical characteristic. That is, the elements of interest where mainly contained in two minerals, zinc was highly concentrated in sphalerite and copper in chalcopyrite.
- The undesirable recovery of sphalerite to the froth (copper concentrate) was observed in the reagent schema using zinc sulfate only, zinc sulfate with a combination of sodium sulfite or sodium metabisulfite.
- The recovery of sphalerite was approximately 50% or more when either zinc sulfate or a combination with sodium sulfite or sodium metabisulfite was used. Chalcopyrite had an average of 80% recovery under the same conditions.
- The combination of zinc sulfate with sodium monohydrogensulfide is noticeable for the selective separation sphalerite from chalcopyrite in the copper-zinc feed. Sphalerite recovery was reported to be an average of 30% across all the pH conditions tested. Chalcopyrite recovery improved to 90% when sodium monohydrogensulfide was used with zinc sulfate.

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