

## Study of process water effect on the activation of sphalerite during differential flotation of Pb-Cu-Zn

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**Abstract:** This work was aimed to analyze the effect of concentration of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions in flotation process water with sphalerite activation, the analysis was performed at Cozamin Mining flotation circuit. This analysis demonstrated that (i) it was possible to determine the relationship between Sodium Cyanide and Ammonium Bisulfite used as depressants and Cu<sup>2+</sup> and Pb<sup>2+</sup> contents in the process water. (ii) It also proved the relationship between lead and iron content in the head with the Pb<sup>2+</sup> ions in process water. According to the data gathered and analysis performed, (iii) it was also determined that it was possible to reuse process water as long as the use of Ammonium Bisulfite was reduced and recommended replacing the use of Sodium Cyanide with Zinc Sulfate (ZnSO<sub>4</sub>) as a depressant of Sphalerite. Additionally, the concentration of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions in the water should be controlled in a range of 10 to 20 ppm and 0.10 to 0.20 ppm, respectively.

**Keywords:** sphalerite activation, process water, differential flotation, copper ions, lead ions

### 1. Introduction

Flotation is known as an effective unit operation in mineral processing. In recent decades, new horizons have been opened for this physical-chemical process, particularly in the selective separation of polymetallic minerals.

For years, polymetallic sulfide minerals of copper, lead, and zinc have played an important role in everyday life (Haga et al., 2012). The most significant copper and zinc minerals are chalcopyrite and sphalerite, respectively, which always coexist with each other and with other copper and zinc mineralogical species. The processing of these copper-lead-zinc complex sulfides is carried out through a differential flotation process, which demands large amounts of water. Therefore, recently, the mining industry has been characterized for recycling water, which is achieved by recovering water from the tails, filters, thickeners, etc. However, the use of such water (called process water) has significant effects on minerals flotation, since it has a variable chemical composition that can include many ions and metallic complexes.

During the differential flotation of the Pb-Cu-Zn minerals, chalcopyrite and galena are first floated and then sphalerite (Liu et al., 2018) because sphalerite has lower buoyancy by nature, also, the absorption of xanthate on its surface is weak (Liu et al., 2014) because it requires metal ion activation for flotation. However, the oxidation of minerals and the presence of oxidized minerals during the

beneficiation process introduces various impurities into the water used in flotation which interacts with the species of interest, affecting the process efficiency.

During the flotation of Pb-Cu-Zn sulfides ores, there are  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  ions present. The  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions frequently cause inadvertent Sphalerite activation, promoting a reduction in the Cu concentrate grade (Rashchi et al., 2002; Jin et al., 2015; Aikawa et al., 2020). For example, this phenomenon occurs at Cozamin mine, located in Zacatecas, México, where after the grinding process, the pulp is fed into the flotation process: It begins with bulk copper-lead concentrate flotation with depressed zinc, and continues with the copper-lead separation and later with a subsequent flotation in a zinc circuit. However, undesirably the hydrophobicity of sphalerite can increase significantly by the presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in the process water, resulting in the loss of a large amount of Zn and a decrease in Cu concentrate.

Since the activation of sphalerite causes a reduction in the Cu concentrate grade, and also it represents a product penalty when the sphalerite concentration exceeds 5%, for these reasons, it is necessary to control and decrease the concentration of sphalerite in the Cu concentrate. Therefore, this work focused on the effects of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions present in process water and the activation of the sphalerite in the operation of the processing plant at the Cozamin Mining Unit.

## 2. Materials and methods

To analyze the effect of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in the flotation process, different data was collected, such as chemical analysis of Cu concentrates, process water, raw ore, and the reagents used in the flotation of approximately one year. With such a data set, the Spearman's rank correlation coefficient was calculated by considering the database the zinc in copper concentrates, to determine the relationship between them and to establish the relevance of the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in the activation of sphalerite.

The mineralogical characterization of the raw ore was carried out using a Scanning Electron Microscopy (SEM) Jeol 6300 and with the energy dispersive spectra analysis and X-Ray Diffraction with a Bruker D8 Focus with monochromatic Cu  $\text{K}\alpha$  radiation working in  $\theta/2\theta$  configuration. X-Ray Diffraction, and chemical analysis aimed to know the species that are present in the differential flotation process as well as in the Cozamin Mine process water.

## 3. Results and discussion

Currently, Cozamin Mine treats an average of 3,700 Mgp/d which goes through a differential flotation process represented in Fig. 1.

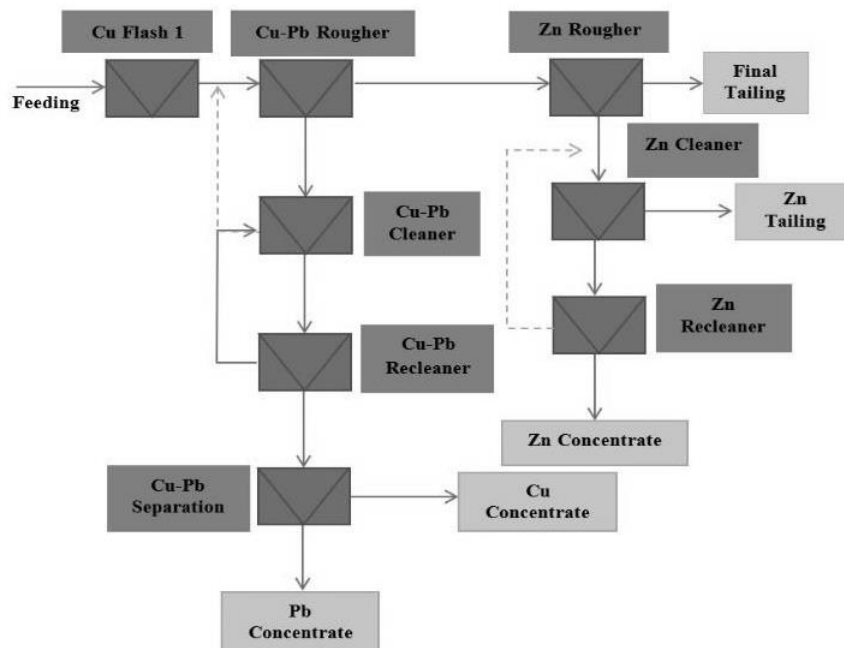


Fig. 1. Diagram of the differential flotation process at Cozamin Mine

Fig. 1 shows the process flow diagram for the differential flotation of Cu-Pb-Zn polymetallic sulfides where zinc is depressed first to perform a bulk Cu-Pb concentrate flotation with sodium isopropyl xanthate, ammonium bisulfite in the grinding, sodium Cyanide like depressor, followed by the separation of copper-lead with sodium Cyanide. Thereafter, zinc is activated again for its flotation with copper sulfate; however, the Cu-Pb separation presents several complications, including sphalerite activation. In recent times, zinc percentage has increased in copper concentrates.

The pH of the process water was measured before being fed into the beneficiation plant, which is in a range of 7.5 to 8.5, and is ruled out as a possible cause of sphalerite activation since it does not present any trend. The effect of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions within the process water, in the operation of the Cozamin Mine beneficiation plant, is analyzed, since it has already been reported in the literature that the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions cause unnoticed activation of sphalerite (Bıçak et al., 2012; Aikawa et al., 2020). For this study, the freshwater average quality that analyzed is: 167.1 Ca, 0.02 As, 0.02 Ba,  $0.43 < \text{Cd}$ , 0.05 Co,  $0.01 < \text{Cr}$ , 0.08 Cu, 0.29 Fe,  $0.03 < \text{Pb}$  and 0.12 Se (all in mg/dm<sup>3</sup>).

A characteristic of the differential flotation process is that feeding back water recovered from the same process may cause the concentration of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions to increase. However, the use of recovered water is not the only source of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions which can come from the same mineral that is oxidized during the process and from carbonates or oxides contained in the charge (Bıçak et al., 2012; Liu et al., 2013).

Fig. 2 shows the trend of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in process water of the three-word shifts in the analyzed period. It is observed that  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions present in the process water have high variability, so it is important to determine the relationship between  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions and the Zn content in copper concentrate.

The Spearman's rank correlation coefficient was calculated by considering the database from the graph (Fig. 2) and the zinc in copper concentrates (Walpole et al., 2012). The results are presented in Table 1. The data of the Spearman's rank correlation coefficient has a 95% reliability, with a critical value of 0.3 and a Spearman value different from zero and greater than 0.3, which indicates the existence of a strong relationship between the two variables. The Spearman's rank correlation coefficient demonstrates that the content of Zinc in the Copper concentrate and the  $\text{Cu}^{2+}$  ions and  $\text{Pb}^{2+}$  present in the process water are interrelated. Therefore, determining its origin is critical to controlling the process.

As mentioned,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions can come from different sources, one of them is the nature of the mineral itself which can be known through a mineralogical characterization. Table 2 presents the

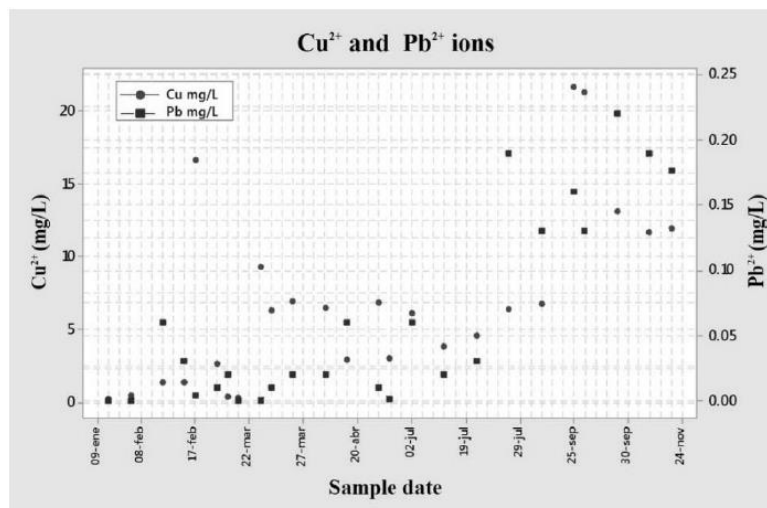


Fig. 2. The average concentration of three shifts by day of the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in the process water

Table 1. Spearman's rank correlation coefficient

Variables	Spearman
$\text{Cu}^{2+}$ vs. Zn content in Cu concentrate	0.582
$\text{Pb}^{2+}$ vs. Zn content in Cu concentrate	0.666

percentage of each mineralogical species and the calculated grades. It is observed that the elements of interest such as copper, zinc, and lead are present in chalcopyrite, sphalerite, and galena, respectively. The mineralogical study shows that the main species presented in the mineral are sphalerite, chalcopyrite, galena, arsenopyrite, and pyrite.

Table 2. Relative abundance in percent and distribution of metals

Mineral	% Weight	Ag (g/Mg)	Pb %	Cu %	Zn %	Fe %	As %
Min Ag	0.006	46					
Galena	0.08		0.07				
Chalcopyrite	4.33			1.50		1.32	
Sphalerite	1.18				0.67	0.12	
Pyrite	12.89					6.00	
Arsenopyrite	0.16					0.06	0.07
Mineral tails	81.34						
	100	46	0.07	1.50	0.67	7.5	0.07
Recalculated Feed							

Mineralogy does not clearly show the presence of oxidized copper and lead, which could be soluble in water, and justify the presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions. However, the hypothesis points out that only a small region of the surface oxidizes (Liu et al., 2013; Bahrami et al., 2019), and dissolve cannot be ruled out. This can also be caused by some reagents, such as sodium cyanide, which tends to dissolve the surface of copper particles and form soluble copper cyanide complexes as explained by Rao et al. (Rao et al., 2011) in Reactions (1) and (2):

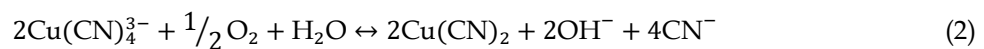


Fig. 3 shows the micrographs taken by SEM, and it is observed that sphalerite has inclusions of the order of 2 to 10  $\mu\text{m}$  of jarosite, chalcopyrite, and even galena, which represents unnecessary ore milling to those particle sizes, and it is considered acceptable to work at a  $d_{80}$  at 150  $\mu\text{m}$ , as the Cozamin mine usually does.

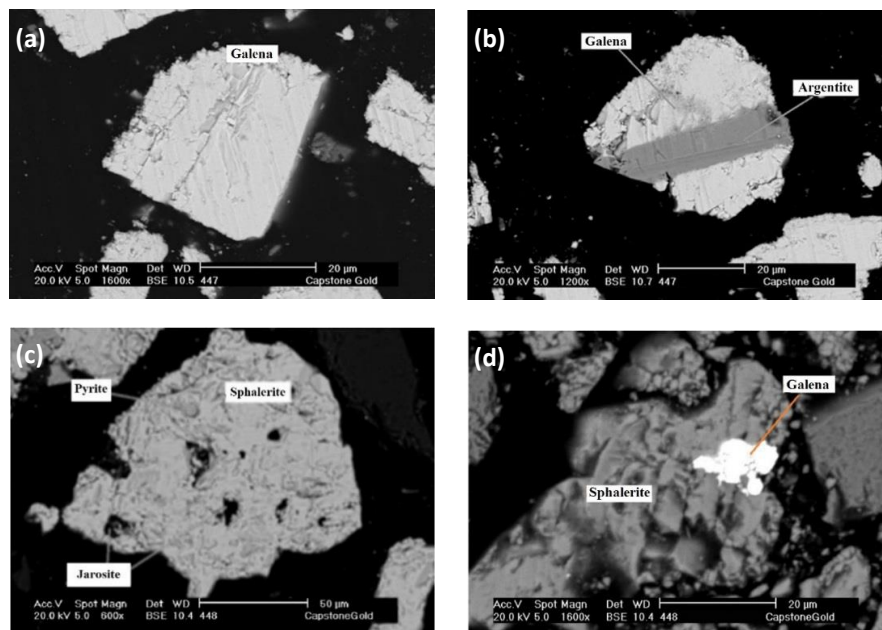


Fig. 3. Micrograph A) shows a particle liberated of galena at 40  $\mu\text{m}$ , B) shows a particle liberated at 50  $\mu\text{m}$  with inclusions of argentite, C) shows a particle liberated of 150  $\mu\text{m}$  with jarosite and pyrite inclusions, and D) shows a particle of sphalerite mixed with lead ore

Fig. 4 shows the sodium cyanide consumption during the studied period. When comparing Fig. 4 and the zinc in copper concentrates, the Spearman rank correlation coefficient was calculated at 0.644, which indicates a relationship between  $\text{Cu}^{2+}$  ions and sodium cyanide consumption. However, the oscillation of  $\text{Cu}^{2+}$  ions observed in Fig. 2 is attributed as a result of its accumulation due to the recovery of water and its reincorporation into the process. This behavior shows that some  $\text{Cu}^{2+}$  ions present in process water come from the partial dissolution of chalcopyrite and the formation of copper cyanide complexes.

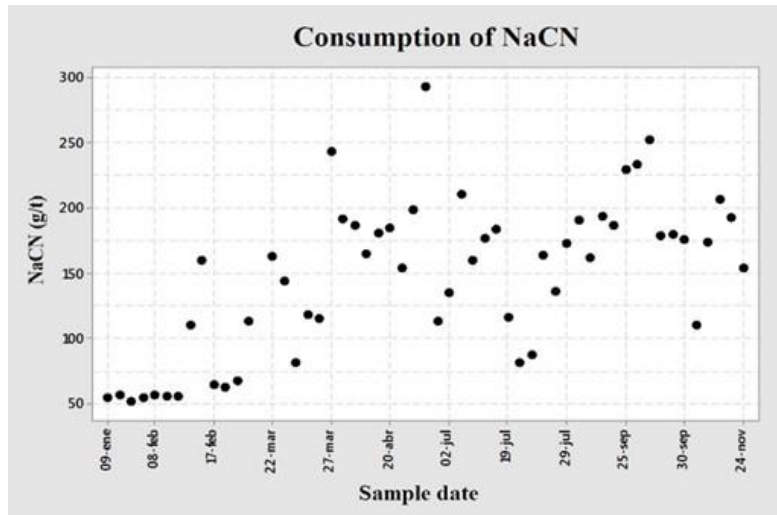


Fig. 4. Consumption of NaCN in the process

Dávila (Dávila-Pulido et al., 2011) reported that the use of excess ammonium bisulfite promotes the decomposition of elemental sulfur by bisulfite, resulting in the formation of thiosulfate, and consequently the inadvertent activation of sphalerite and pyrite by  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions. Such a process is due to the oxidation reaction of sulfur, which generates copper sulfate or lead sulfate, promoting the activation of these minerals. The mechanism of formation of these ions and their interaction is represented in Reactions (3) and (4):

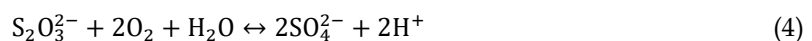
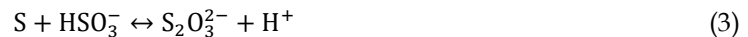


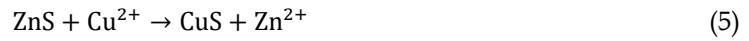
Fig. 5 shows the consumption of ammonium bisulfite and the presence of  $\text{Pb}^{2+}$  ions in the studied period, the graph shows that when high bisulfite additions (above 600 g/Mg) promote galena oxidation, increasing  $\text{Pb}^{2+}$  ions concentration in the system. Therefore, activating the sphalerite. As the trend is only observed in part of the increase in the consumption of ammonium bisulfite, there are few data to calculate the Spearman's rank correlation coefficient. However, some data show some discrepancies between  $\text{Pb}^{2+}$  ions and the consumption of ammonium bisulfite, which is indicative that the increased use of ammonium bisulfite is not the only cause of  $\text{Pb}^{2+}$  ions.

Wenqing (Qin et al., 2015; Aikawa et al., 2020; Wang et al., 2020) reported that  $\text{Pb}^{2+}$  ions are caused by the galvanic interaction that exists between galena and pyrite, which can produce  $\text{Pb}^{2+}$  ions in the form of hydroxides by the electrochemical interaction as shown in Fig. 6. Because galena is electrochemically more active than pyrite and hence serves as an anode in galvanic combination with pyrite.

Therefore, another source of the  $\text{Pb}^{2+}$  ions present in process water comes from the electrochemical reaction of galena and pyrite. This is supported by the increase in Fe and Pb content in raw ore, which can be seen in Fig. 7, how pyrite/galena ratio as the higher the ratio the higher the galena oxidation and the  $\text{Pb}^{2+}$  ion activation of the sphalerite.

Given the above, the presence of the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in process water within the differential flotation of Cu-Pb-Zn becomes relevant, and the fact of monitoring its variation to avoid inadvertently activating the Sphalerite is of utmost importance. The activation of Sphalerite by  $\text{Cu}^{2+}$  ions has been previously

studied (Gerson et al., 1999; Rao et al., 2011; Jin et al., 2015; Chen and Yoon, 2000) and it has been shown that  $\text{Cu}^{2+}$  ions activate Sphalerite according to the following mechanism:



In the case of  $\text{Pb}^{2+}$  ions the mechanism is similar (Basilio et al., 1996; Rashchi et al., 2002):

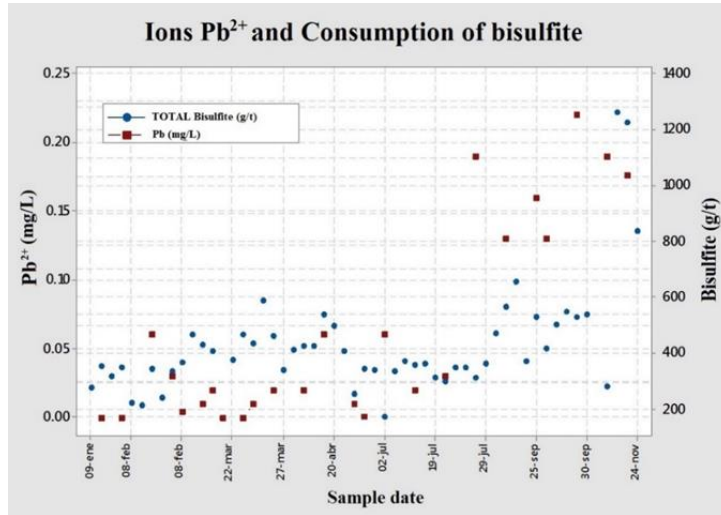


Fig. 5. Relationship between the consumption of ammonium bisulfite and  $\text{Pb}^{2+}$  ions

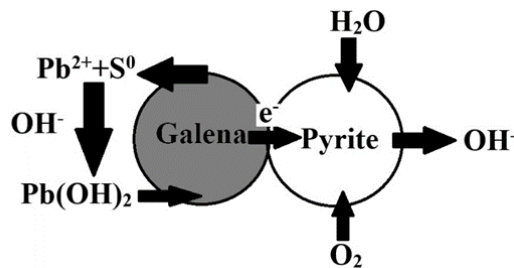


Fig. 6. Interaction galvanic between galena and pyrite (Qin et al., 2015)

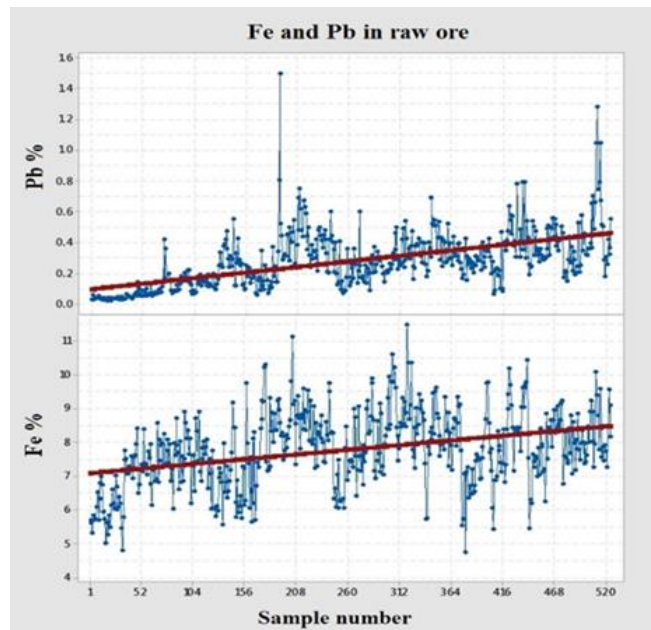


Fig. 7. Pb and Fe content in raw ore in the study period

Copper or lead sulfide reacts with the collector (Xanthate) and forms a stable copper or lead Xanthate to modify the surface of sphalerite and turn it into a hydrophobic surface (Chen and Yoon, 2000; Rashchi et al., 2002).

Fig. 8 shows a graph of how zinc content in copper concentrate is increasing and a common practice in the Cozamin plant is the use of sodium cyanide and ammonium bisulfite as depressants in the copper flotation. It is observed in Fig. 8 that the percentage of zinc in the copper concentrate increases, that is, if sphalerite and pyrite are activated, the most logical action in the plant is to increase the dosage of sodium cyanide and ammonium bisulfite to depress iron and zinc (pyrite and sphalerite), and in turns, it can cause the generation of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions (which activate sphalerite). This leads to a vicious circle that increases the consumption of reagents and does not solve the problem.

Considering the difficulty to have ion-free process water and aiming to solve such a problem, the first step was to determine a range in which it is possible to control the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in process water and the activation of the Sphalerite. Fig. 8 shows the relationship between activation and the presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions.

In the case of Cozamin Mine, when correlating between the  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  ions in process water and the Zn content in the copper concentrate, it is observed that the Zn content is related to the activation of sphalerite during the Pb-Cu flotation process, and it can be seen that to avoid excess Zn in the Cu concentrate, the  $\text{Cu}^{2+}$  ions must be kept to the minimum or work in a range of 20 to 10 ppm and the  $\text{Pb}^{2+}$  ions to the minimum possible or work in a range of 0.10 at 0.20 ppm.

Process water is treated with ammonium bisulfite to break the cyanide and hydrated lime complexes to form hydroxides and precipitate them, and to keep the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in process water within the established ranges. The following was to reduce the use of Sodium Cyanide and replace it with the Zinc Sulfate depressant. The effects of these controls are observed in Fig. 9, where the behavior can be seen before applying the controls, and in the shaded part after applying the controls, the percentage of Zn in the copper concentrate was reduced, and the use of sodium cyanide.

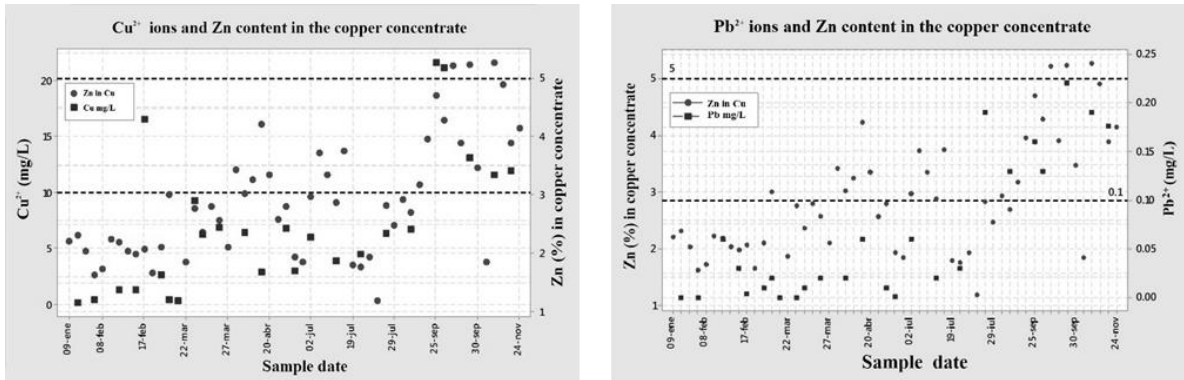


Fig. 8. The Zn% in the Cu concentrate and the Pb<sup>2+</sup> and Cu<sup>2+</sup> ions

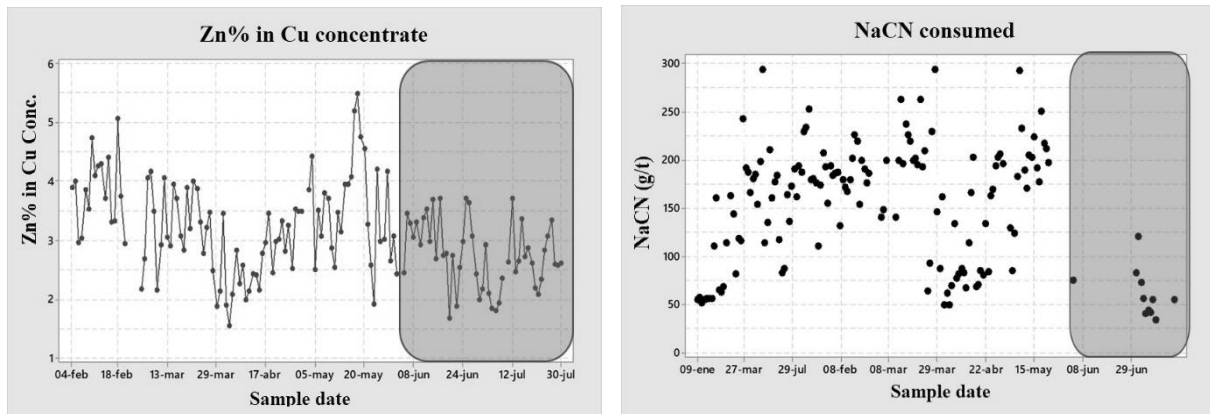


Fig. 9. Zn% graphs in Cu concentrate and NaCN consumption



#### 4. Conclusions

The results show that the presence of the  $\text{Cu}^{2+}$  ions in process water has its main origin in the superficial leaching of Chalcopyrite, due to sodium cyanide. The content of the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions in process water in the Cozamin plant causes activation of sphalerite that causes a drop in the copper concentrate grade.

Controlling the activation of Sphalerite by  $\text{Cu}^{2+}$  ions is feasible if it is kept to a minimum possible of  $\text{Cu}^{2+}$  ions or in a range of 20 to 10 ppm in process water, reducing the use of sodium cyanide as a depressant and replacing it with Zinc Sulfate ( $\text{ZnSO}_4$ ) along with ammonium bisulfite.

The results show that the presence of  $\text{Pb}^{2+}$  ions in process water has two main sources: the galena-pyrite interaction and the excess of ammonium bisulfite.

Controlling the activation of Sphalerite by  $\text{Pb}^{2+}$  ions is feasible, keeping a minimum of  $\text{Pb}^{2+}$  ions or in a range of 0.10 to 0.20 ppm in process water and reducing the use of ammonium bisulfite as a depressant.

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