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Influence of Lead Nitrate on Sulfurizing Flotation of a Copper-Cobalt Oxide Ore

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Abstract

Copper-cobalt oxide ores contain several minerals that are economically treatable by concentration techniques. The most used technique is froth flotation in which selective reagents are used to recover more valuables. It is, therefore, important to examine the optimal doses of those reagents while investigating the behaviors of minerals at the same time. This study explored the influence of lead nitrate $Pb(NO_3)_2$ on the froth flotation of oxide ore to increase valuable metals recoveries. Four factors were investigated including $Pb(NO_3)_2$ dosage, its conditioning, its addition dose in the 2nd fraction, and sulfidiser dosage. Other parameters were kept constant. The optimum was found at 25 g/t of $Pb(NO_3)_2$, conditioning together with sodium silicate (Na_2SiO_3) for 5 min, the addition of 5 g/t of $Pb(NO_3)_2$ in the 2nd fraction, and 3,000 g/t of sulfidiser. Recoveries in concentrates were 79.51 % Copper (Cu) and 60.27 % Cobalt (Co), with grades of 9.49 and 0.67 %, respectively. The conclusion was that the use of $Pb(NO_3)_2$ can considerably improve copper and cobalt recoveries.

Keywords: Cobalt, Copper, Lead nitrate, Oxide ore, Xanthate, Sulfurizing flotation

Introduction

In the Democratic Republic of the Congo, most of the concentration plants treat oxide minerals in ranges 1.5 - 3 % Copper grade and 0.2 - 1 % Cobalt grade [1,2]. The principal used method of concentration is sulfurizing flotation, producing final concentrate with grades of 10 - 16 % Copper and 0.6 - 1.2 % Cobalt, and yields of 50 - 70 and 30 - 60 %, respectively. However, tailings contain a considerable amount of valuable metals.

According to Shengo [2], the mineralogy of the Kamfundwa mine (located in Haut-Katanga Province, the Democratic Republic of the Congo) is constituted by oxide minerals containing mainly Copper and Cobalt. Malachite ($Cu_2CO_3(OH)_2.H_2O$), cuprite (Cu_2O), pseudomalachite, chrysocolla ($CuO.SiO_2.2H_2O$), and heterogenite ($CoO.2Co_2O_3.6H_2O$) are among those minerals. Silica constitutes the gangue mineral (about 95 %). However, malachite and heterogenite are abundant. The following reagents are frequently used: sodium hydrosulfide (NaHS) as sulfidiser, potassium amylxanthate (PAX: $C_5H_{11}OCS_2Na$) as a collector, sodium silicate (Na_2SiO_3) as depressant and dispersant [3], senfroth (G41) as frother, and dolomitic mixture (MIX) as a mineralizing agent. It has been shown by Bulatovic [4], Blazy [5], and Wills [6] that lead, zinc, and copper oxide ores are hardly floatable because they are more soluble in comparison to correspondent sulfide ore. On another side, cobalt oxide ores are easily floatable by palm oil but the process is not selective and produces poor rougher concentrate [7]. On the other hand, the use of certain metal ions can largely improve the recovery of some minerals in froth flotation [8].

Several authors [9-12] have studied the effect of the lead ion as an activator of many minerals. According to their results, the addition of $Pb(NO_3)_2$ enhanced recoveries of valuable metals by a mechanism of adsorption of lead on mineral surfaces and coordination of collector with lead ions. Miller *et al.* [13] have also studied PAX and $Pb(NO_3)_2$ effects on the pyrite surface. It has been shown that the addition of those reagents created the establishment of a hydrophobic pyrite surface. Liuyin *et al.* [14] also demonstrated that $Pb(NO_3)_2$ was a good activator for rare earth flotation.

In contrast to Du Plessis *et al.* [15], the hydrophobic pyrite surface state was beneficial when a significant concentration of cyanide was added into pulp by using $Pb(NO_3)_2$ and PAX as activator and collector, respectively. Leppinen *et al.* [16]; Zohir and Djamel [17] investigated Fourier-transform infrared spectroscopy (FTIR) and scanning electron micrograph (SEM) techniques. In their study, they observed the adsorption of xanthate on galena surfaces consisting of exchange between xanthate and hydroxide. The mechanism was followed by the formation of dixanthogen (X_2) and its diffusion across the surface. On the other hand, 2 mechanisms occurred during the absorption of xanthate on the sulfide mineral [18,19]. In the 1st one, called chemisorption, there was the formation of a bond with lead atoms at the sulfide surface from adsorbed xanthate molecule. In the 2nd one, called electrochemical, there was the production of oxidation product species rending the sulfide mineral hydrophobic [20,21].

According to Gang [11] and Poling *et al.* [19], activation of galena by copper took place at pH 9.5 and Copper Amylxanthate (CuAX) was formed after the addition of PAX, rending galena surface strongly hydrophobic. On another side, the formation of Lead Xanthate (PbX_2) species also contributes to the hydrophobicity of the surface Eq. (1).

$$PbS + 2X^- \rightarrow PbX_2 + S^0 + 2e^- \tag{1}$$

It is known that flotation efficiency depends on several of parameters such as particle size, pulp density, water quality, pH, and reagent dosage [22,23]. In this paper, flotation tests in simple roughing were performed by using PAX (300 g/t) as primary collector, $NaSiO_3$ (300 g/t) as gangue depressant and dispersant, G41 (90 g/t) as a frother, MIX (300 g/t) as a secondary collector, NaHS (3,000 g/t) as sulfidiser. Only $Pb(NO_3)_2$ dose was varied and pH was natural.

Material and methods

Sampling

The Sample was collected from the Kamfundwa deposit and prepared for analysis. Atomic absorption spectroscopy has revealed the results presented in **Table 1**.

Table 1 Sample AAS/ICP analysis of raw ore.

Component	Content (%)
Total Copper (Cu_{tot})	2, 55
Copper oxide (Cu_{ox})	2, 10
Total Cobalt (Co_{tot})	0, 20
Cobalt oxide (Co_{ox})	0, 12
Total Calcium oxide (CaO_{tot})	0, 38
Soluble Calcium oxide (CaO_{sol})	0, 11

Reagents

MIX 1.2 % was prepared by mixing 1.08 g gasoil (90 %) and 0.12 g of synthetic acids (10 %) named rinkalore 10. A small amount of sodium carbonate 1.2 % (Na_2CO_3) was added to emulsify the mixture. Note that rinkalore 10 is a mixture of fatty synthetic acids.

PAX 1.2 %, NaHS 12 % and Na_2SiO_3 30 % were prepared and G41 was used pure. Finally, $Pb(NO_3)_2$ 1.2 % was prepared. Eq. (2) below was used to transform g/t to milliliter.

$$V = \frac{\text{mass of ore sample (kg)} \times \text{reagent dose(g/t)}}{\text{reagent concentration(g/l)}} \tag{2}$$

where V = volume of reactant

Equipment

The following equipment was used for flotation tests: flotation machine DENVER, graduated vessels for reagents, laboratory mill, wash-bottle of 1 L, flotation cell of 2.5 L, Erlenmeyer, SARTORIUS electronic balance, panels, pH meter, propipette, pallet, and drier.

Grinding

Grinding of the sample for 5, 10, 15, 20, and 25 min, respectively, drying, and sieving enabled researchers to determine the optimal time to achieve the liberation of valuable particles (**Figure 1**). After 22 min of grinding, 70 % of solid particles passed on a 75 µm sieve. According to **Figure 2**, about 20.135 % of Copper particles and 18.561 % of Cobalt particles were above the size of 75 µm.

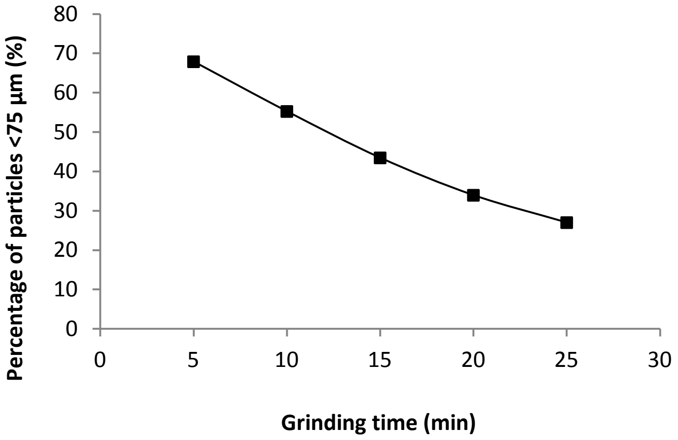

Figure 1 Sample grinding curve.

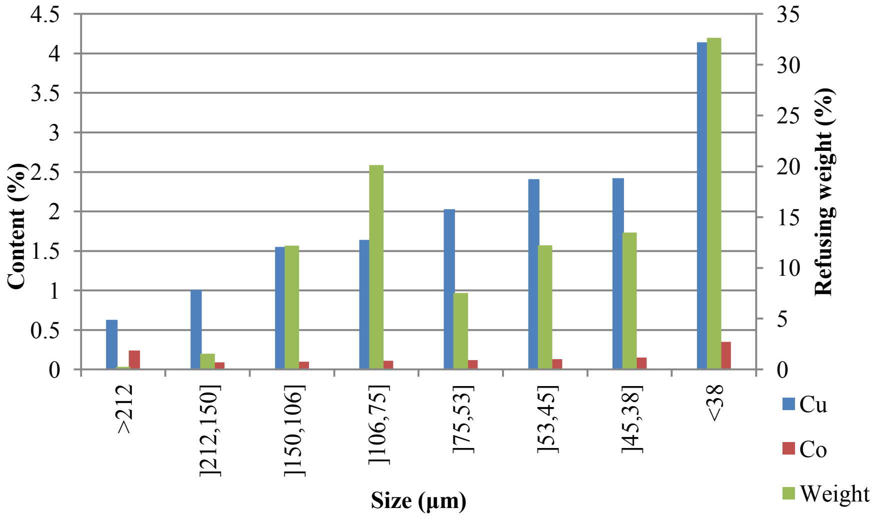

Figure 2 Sample sizing.

Flotation test

Before flotation tests with $Pb(NO_3)_2$, the flotation test in simple rougher was done under reference conditions (**Figure 3**). One kg of sample was mixed with 1 L of water for grinding for 22 min. Pulp with a specific weight of 1,340 g/L was transferred into a flotation cell of 2.5 L under a speed impeller of 1,200 trs/min. Na_2SiO_3, MIX, NaHS, PAX, and G41 were added fractionally for conditioning before open-air admission. The conditioning times of Na_2SiO_3, MIX, NaHS, PAX, and G41 were 5, 2, 3, 2, and 1 min, respectively. Sixty percent of PAX, and NaHS, were added in the head concentration and the 40 % remaining were fractionally added in the other concentrations. After the collection of 6 concentrates of 2 min and tailings, they were sent to the lab for analysis to determine copper and cobalt contents.

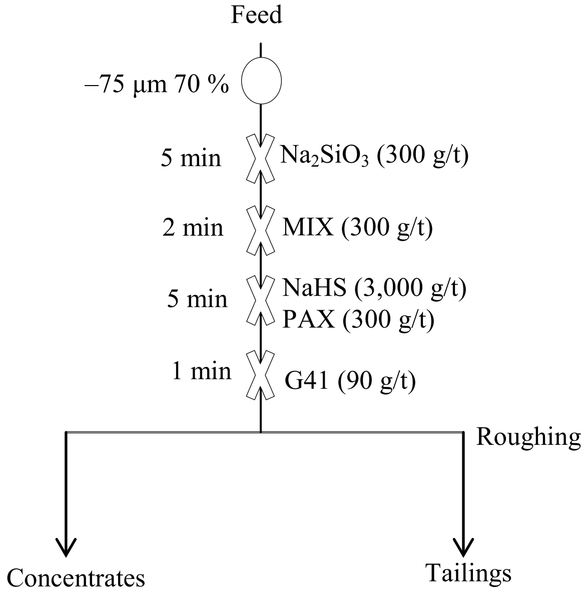

Figure 3 Flotation scheme under reference conditions.

Results and discussion

By maintaining constant parameters as seen in **Figure 3**, 4 factors were investigated to find out the effects of $Pb(N0_3)_2$. **Table 2** and **Figure 4** show the results of the flotation test under reference conditions. The final concentrate had a content of 8.31 % copper with a recovery of 75.52 % while the content of cobalt was 0.54 % with a recovery of 61 %.

Table 2 Contents and yields of Copper and Cobalt after flotation under reference conditions.

Fractions (concentrates)	Copper		Cobalt	
	Content (%)	Yield (%)	Content (%)	Yield (%)
A	22.55	28.81	0.81	12.87
A + B	21.37	54.55	1	31.66
A + B + C	16.67	64.59	0.86	41.4
A + B + C + D	12.21	69.16	0.69	48.7
A + B + C + D + E	9.72	72.75	0.6	55.3
A + B + C + D + E + F	8.31	75.52	0.54	61
Tailings	0.77	24.48	0.1	39
Feed	2.45	100	0.2	100

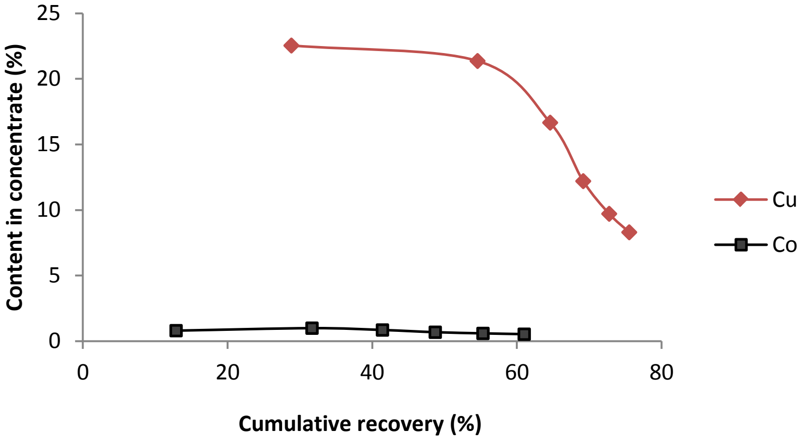

Figure 4 Reference flotation test without $Pb(NO_3)_2$.

Influence of $Pb(NO_3)_2$

To determine the optimal dose of $Pb(N0_3)_2$, 5, 25, 50, 75, and 100 g/t were used, and results were obtained (**Figures 5** and **6**). It could be overserved that for copper recovery, the difference was viewed in head concentrates and there was a similarity for rougher concentrates; for cobalt recovery, 25 g/t was directly considered as the optimal dose.

Table 3 Influence dose of $Pb(NO_3)_2$ on copper and cobalt recoveries.

Dose of $Pb(NO_3)_2$ (g/t)	Copper analysis (%)			Cobalt analysis (%)		
	Feed	Concentrate	Final recovery	Feed	Concentrate	Final recovery
5	26.24	8.09	81.44	0.84	0.56	77.7
25	27.68	11.24	76.83	1.16	0.66	73.89
50	20.92	6.62	83.47	0.89	0.43	70.65
75	20.2	8.16	79.99	0.68	0.51	56.47
100	16.81	7.68	79.74	0.64	0.46	61.89

It is observed in **Table 3** that the maximum recoveries of both copper and cobalt were observed at 25 g/t of Pb(N0$_3$)$_2$, producing a concentrate at 11.24 % Copper and 0.66 % Cobalt with yields of 76.83 and 73.89 %, respectively. That dose was considered and used for the following flotation tests.

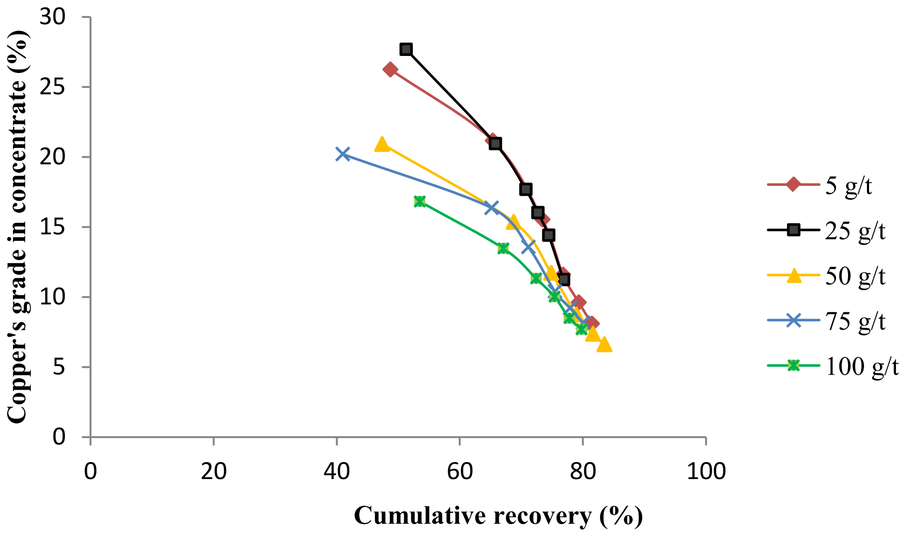

Figure 5 Influence of Pb(NO$_3$)$_2$ on copper recovery.

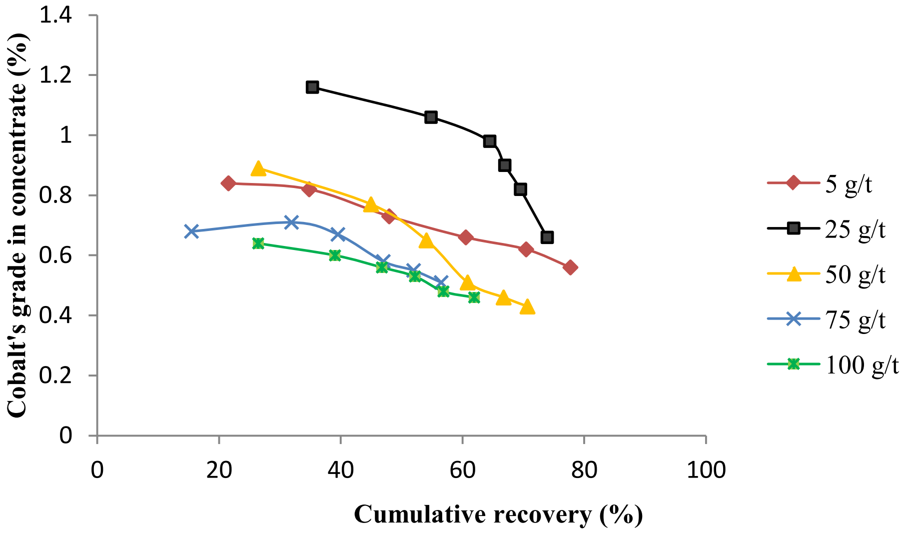

Figure 6 Influence of Pb(NO$_3$)$_2$ on cobalt recovery.

The increase in the dose of $Pb(NO_3)_2$ leads to the excessive production of lead hydroxide ($Pb(OH)_2$) which is soluble in solution and thereby prevents the selectivity of the frother and the collection. Eqs. (3) and (4).

$$\mathrm{NaSH} + \mathrm{H_2O} \rightarrow \mathrm{Na^+} + \mathrm{OH^-} + \mathrm{H_2S} \tag{3}$$

$$\mathrm{Pb(NO_3)_2} + \mathrm{OH^-} \rightarrow \mathrm{Pb^{2+}} + \mathrm{OH^-} + 2\mathrm{NO_3^-} \tag{4}$$

Influence of conditioning of $Pb(NO_3)_2$

Four flotation tests have been done to study the effect of conditioning of $Pb(NO_3)_2$:

- The conditioning for 5 min before the addition of Na_2SiO_3
- The addition without conditioning
- The co-conditioning with Na_2SiO_3 for 5 min

Table 4 $Pb(NO_3)_2$ conditioning influences on recoveries of both Copper and Cobalt.

Conditioning	**Copper analysis (%)**			**Cobalt analysis (%)**		
	Feed	**Concentrate**	**Final recovery**	**Feed**	**Concentrate**	**Final recovery**
5 min before Na_2SiO_3	32.81	7.72	82.88	1.2	0.47	72.68
Without conditioning with Na_2SiO_3	32.34	5.81	86.65	1.15	0.36	80.66
With Na_2SiO_3	30.9	6.43	87.27	1.15	0.35	82.58

Na_2SiO_3 was conditioned for 5 min in all cases.

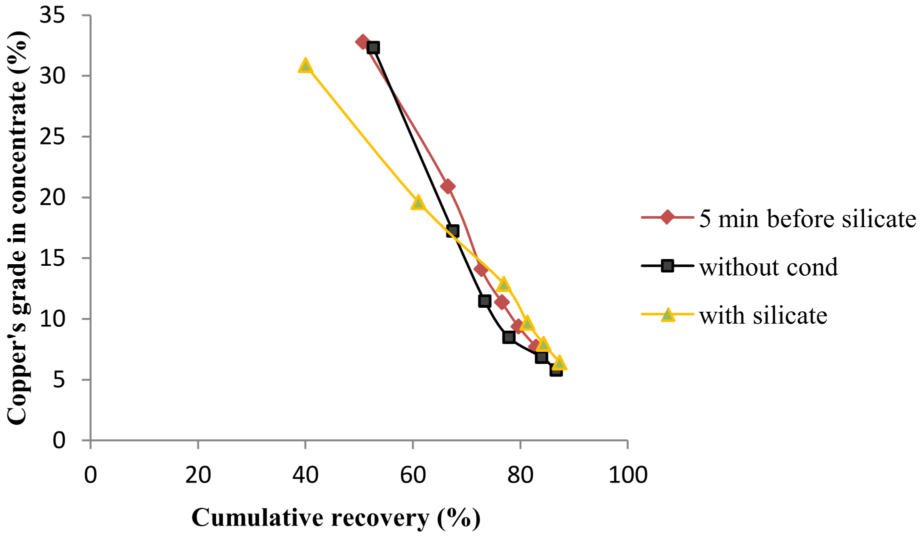

Figure 7 Effect of $Pb(NO_3)_2$ conditioning on copper recovery.

In contrast to **Figures 7** and **8**, and **Table 4**; Copper and Cobalt recoveries are little sensitive to the variation of conditioning time of $Pb(NO_3)_2$ and rougher concentrates are nearly the same. It can also be said that $Pb(NO_3)_2$ is rapidly soluble in solution reason why there is a similarity for all the cases. Recoveries of both copper and cobalt are high when $Pb(NO_3)_2$ is added together with Na_2SiO_3 for a conditioning time of 5 min. The rougher concentrate is produced with 6.43 % Copper grade and 0.36 % Cobalt grade, and yields of 87.27 and 82.58 %, respectively.

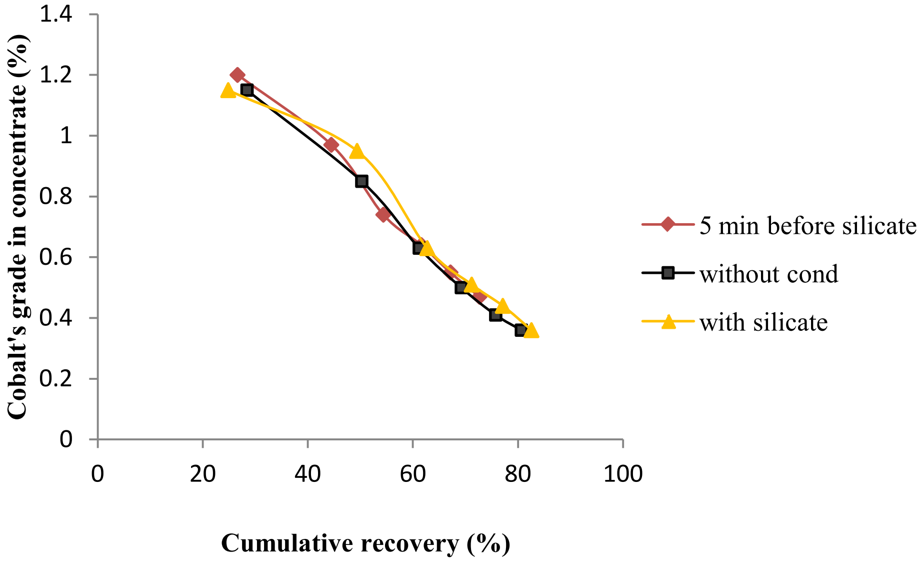

Figure 8 Effect of $Pb(NO_3)_2$ conditioning on cobalt recovery.

Influence of $Pb(NO_3)_2$ addition

The addition of $Pb(NO_3)_2$ was investigated to extend its effect on selectivity. However, 5, 10, 15, and 20 g/t of $Pb(NO_3)_2$ respectively were added in the 2nd fraction, after prior addition of 25 g/t for 5 min of conditioning time with Na_2SiO_3. The following table shows the influence of the $Pb(NO_3)_2$ addition on recoveries.

Table 5 Influence of $Pb(NO_3)_2$ addition on recoveries of both Copper and Cobalt.

Dose of $Pb(NO_3)_2$ (g/t)	Copper analysis (%)			Cobalt analysis (%)		
	Feed	Concentrate	Final recovery	Feed	Concentrate	Final recovery
5	29.23	9.49	79.51	1.26	0.67	60.27
10	35.8	9.35	76.65	1.14	0.64	61.91
15	27.91	7.04	83.44	1.12	0.44	74.42
20	23.47	8.93	79.01	0.94	0.53	64.24

According to results shown in **Figures 9** and **10**, the addition of Na_2SiO_3 has a low influence on recovery and there is a demarcation at 15 g/t on the recoveries of both copper and cobalt. The optimal dose addition was 5 g/t and with yields of 79.51 % Copper and 60.27 % Cobalt with grades of 9.49 and 0.67 %, respectively.

As shown in Eqs. (3) and (4), increasing the dose of $Pb(NO_3)_2$ increases the $Pb(OH)_2$ concentration. This situation disadvantages the collection of valuable particles and prevents the action of the collector.

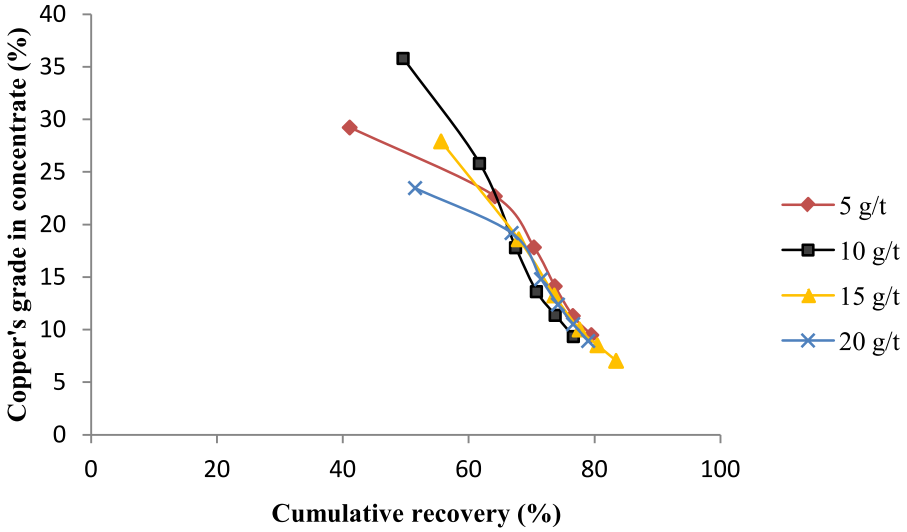

Figure 9 Effect of $Pb(NO_3)_2$ addition on copper recovery.

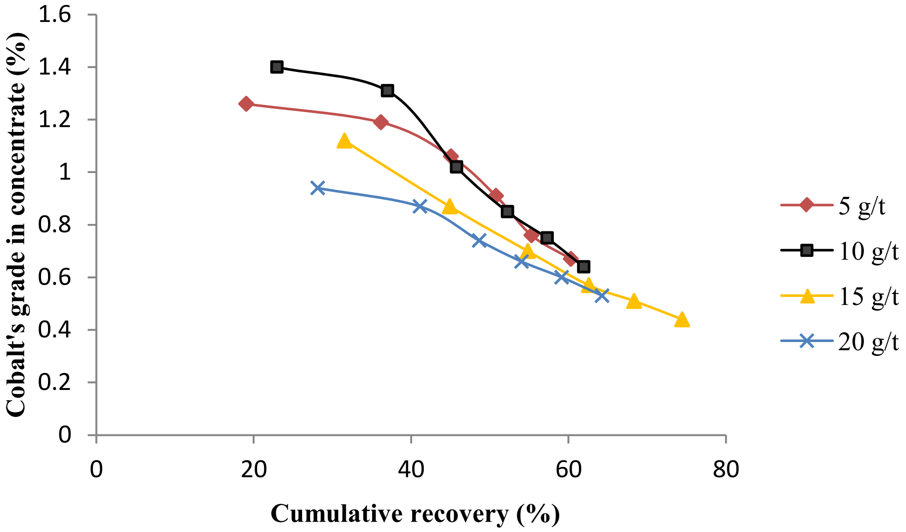

Figure 10 Effect of $Pb(NO_3)_2$ conditioning on cobalt recovery.

Influence of sulfidiser's diminution

Improvement of selectivity produced by the addition of $Pb(NO_3)_2$ has suggested the possibility of reduction of sulfidiser consumption. Thus, 1,500, 2,000, 2,500, and 3,000 g/t were used to envisage the diminution of NaHS. **Table 5**, **Figures 11** and **12** show the results for copper and cobalt, respectively.

According to the obtained results, the diminution of NaHS decreases flotation performances due to the depreciation of sulfurizing activity.

Table 6 Diminution of NaSH dose on recoveries of both Copper and Cobalt.

Dose of NaSH (g/t)	Copper analysis (%)			Cobalt analysis (%)		
	Feed	Concentrate	Final recovery	Feed	Concentrate	Final recovery
1,500	5.75	3.52	71.39	1.63	1.28	47.58
2,000	19.41	6.76	84.1	0.69	0.43	68.28
2,500	21.27	7.89	81.87	0.69	0.43	62.26
3,000	29.23	9.49	79.51	1.26	0.67	60.27

Another fact is that the diminution of sulfur ions leads to the diminution of created hydrophobic surfaces which rending the flotation non-selective and poor. However, the dose of 3,000 g/t was retained as optimal producing 9.49 % Copper and 0.67 % Cobalt with yields of 79.51 and 60.27 %, respectively.

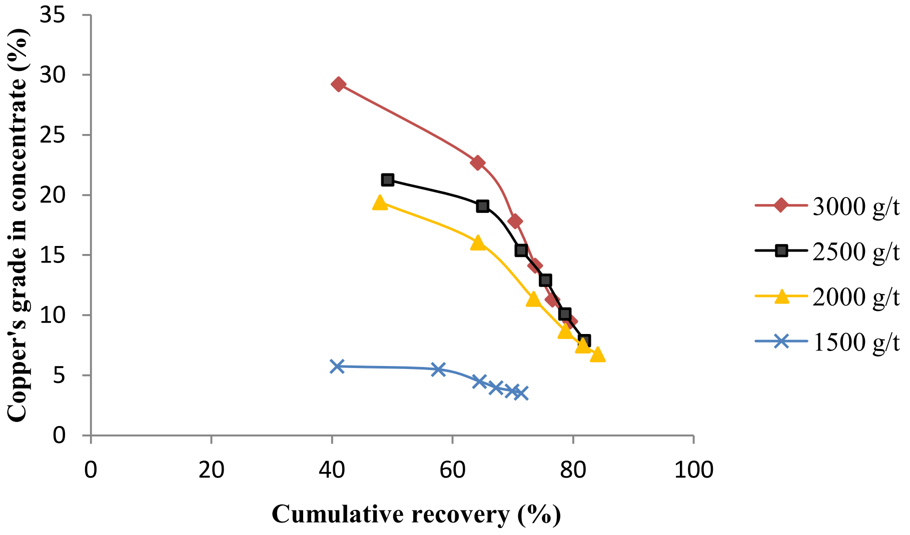

Figure 11 Influence of NaHS diminution on copper recovery.

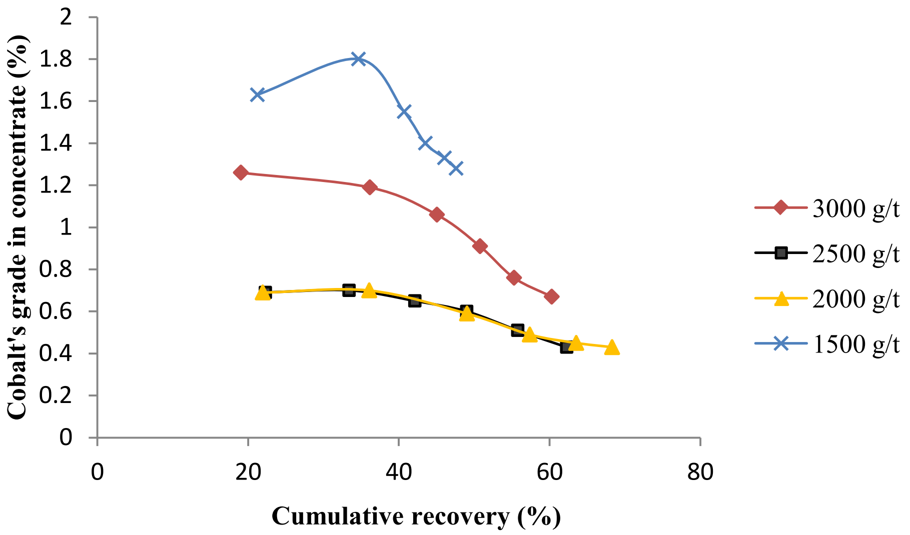

Figure 12 Influence of NaHS diminution on cobalt recovery.

Comparison between the use of $Pb(NO_3)_2$ results and reference results

The reference results (**Figures 3** and **4**) were obtained by using reference conditions shown above: PAX (300 g/t), $NaSiO_3$ (300 g/t), G41 (90 g/t), MIX (300 g/t), and NaHS (3,000 g/t). The result by using $Pb(NO_3)_2$ was obtained at 25 g/t conditioned with Na_2SiO_3 for 5 min followed by the addition of 5 g/t in the 2nd fraction and 3,000 g/t of NaHS (**Figures 11** and **12**).

As shown in **Figure 13**, $Pb(NO_3)_2$ increases metals recoveries with a notable improvement in the quality of concentrates and yields.

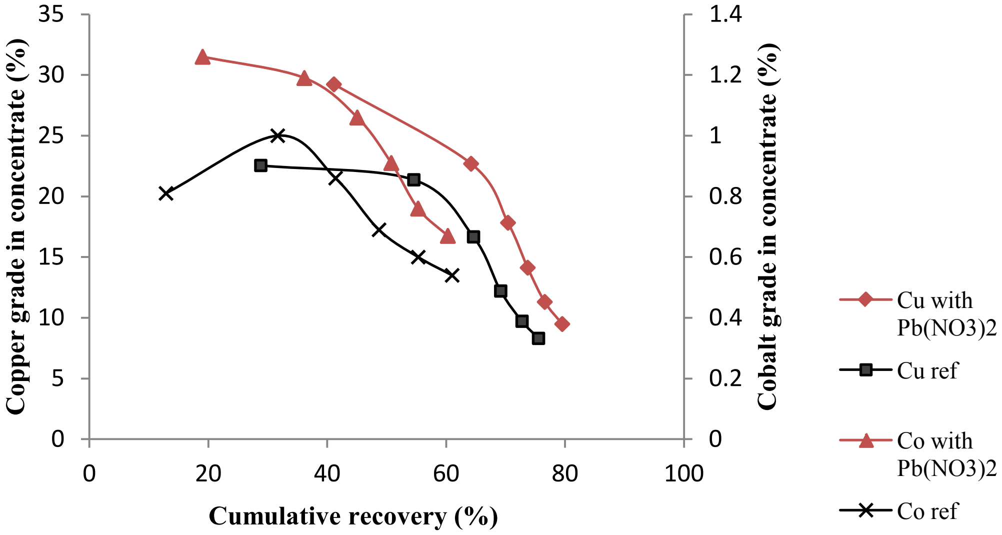

Figure 13 Comparative flotation with and without $Pb(NO_3)_2$.

The effects of $Pb(NO_3)_2$ can be resumed on the following:

1) After the addition of NaHS, there are formations of both copper sulfide (CuS) and lead sulfide (PbS)
2) After the addition of PAX, xanthate ions react with CuS and PbS, Eqs. (5) and (1);

$$CuS + 2X^- \rightarrow CuX_2 + S^0 + 2e^- \tag{5}$$

3) View the liberation of OH^- ions from malachite, there are transfers of $Cu(OH)^+$ into CuS and of $Pb(OH)^+$ into PbS, Eq. (6)

$$PbS + Cu(OH)^+ \rightleftarrows CuS + Pb(OH)^+ \tag{6}$$

4) It can be supposed a double activation: the 1st concerns PbS on CuS surface and the 2nd concerns CuS on PbS surface (**Figures 14A** and **14B**).

Figure 14 Double activation during flotation using $Pb(NO_3)_2$ as an activator; (A) PbS on CuS surface; (B) CuS on PbS surface.

Those 4 points should be confirmed by further studies including the adsorption mechanism of xanthate by FTIR and SEM techniques.

Conclusions

In contrast to this study, the following conclusions can be made regarding $Pb(NO_3)_2$ during a copper-cobalt oxide ore.

- The use of $Pb(NO_3)_2$ as an activator has favored the improvement of copper and cobalt flotation obtaining high-grade concentrates in comparison with reference flotation.
- The optimal dose was at 25 g/t, conditioned with 300 g/t of Na_2SiO_3 during 5 min, followed by the addition of 5 g/t of $Pb(NO_3)_2$ in the 2nd fraction.
- At optimal conditions, concentrates have been obtained at 9.49 % Copper and 0.67 % Cobalt with yields of 79.51 and 60.27 %, respectively.
- As a hypothesis, after the addition of lead ions, it could be observed the adsorption of generated product PbS on the mineral surfaces increasing the number of active sites. On another hand, CuAX generated played the role of activator towards PbS, which increased the selectivity.

It is suggested that the interaction between copper and lead cations be studied with variable potential values.

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