Recovery of copper and cobalt in the comparative flotation of a sulfide ore using xanthate and dithiophosphate as collectors

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Abstract — Copper and cobalt are two major metals used in industry. They play a role in widely many domains like that electricity, chemistry and electrochemistry. They are contained into several minerals like chalcopyrite, carrolite, chalcocite, etc. associated to pyrite. The froth flotation and behaviors of chalcopyrite and carrolite were investigated through many flotation tests in order to recovery copper and cobalt. This paper investigates the effect of potassium amyl xanthate (PAX) and sodium dithiophosphate (DANA) performance on both copper and cobalt recovery in single roughing flotation. The effect of pH on the flotation is proposed. Some parameters were kept constant such as particle size d80=75 μm, pulp density 10% solids, impeller speed 1300 rpm, and PAX doses of DANA (105 g/t per each) as collectors, dose of DF250 (5 drops) as frother, dose of Na2SiO3 (200 g/t) as dispersant and depressant. Only the pulp pH was varied from the natural pH to 11, using Ca(OH)2 as regulator. According to results, PAX (105 g/t) was found as the best collector for recovery of copper both at natural pH and pH=11. At natural pH, the concentrate was found at 16.1% copper recovery with a yield of 99.63%. At pH=11, the concentrate was found at 16.1% copper recovery with a yield of 99.05%. For the recovery of cobalt, DANA (105 g/t) was found better as the collector at natural pH producing a concentrate at 0.51% cobalt recovery yield of 76.48%. At pH=11, PAX (105 g/t) was found better as the collector. The concentrate was found at 0.91% cobalt with a recovery yield of 85.13%.

Index Terms — cobalt, copper, dithiophosphate, flotation, xanthate.

I. INTRODUCTION

The evolution of technology has led the development of several mining techniques for base metals that are most used. Copper and cobalt are part and are contained in the oxidized minerals, sulphide or mixed. They are used in several disciplines: electricity, robotics, battery manufacturing, metal alloys, machine building, and the list is not exhaustive [5], [9], [11], [19]. Copper is a strategic metal and its demand is growing rapidly [15]. Cobalt has also a great role for the growth of humans, animals and plants. However, it cannot be taken to avoid excessively toxic effects. [17]. Copper-cobalt ore from copper and cobalt come from the Central African Copper Belt in the Democratic Republic of Congo and Zambia. Copper sulphide minerals are chalcopyrite CuFeS2, chalcocite CuS2, bornite Cu9FeS8. Cobalt sulphide minerals are cobaltine (CoAsS), carrollite (Cu (Co,Ni)2S4) and linneite (Co,S2).

Several studies on the treatment of copper-cobalt minerals were conducted and have shown that at pH (about 4), the flotation of cobalt from sulfide already is best using xanthate collector. When using nitrosonaphthol chelating reagents, the flotation of cobalt oxides from already is best at the pH of about 7.5 [4].

The flotation foam of a mineral sulphide Cu-Co produce a Cu-Co bulk concentrate. During the flotation, Cu-Co float at natural pH or pH 11 using xanthate or dithiophosphate. This occurs when the copper mineralization as chalcocite. Thereafter separating copper and cobalt in the bulk concentrate is done by raising the pH to at least 11, which depresses the cobalt minerals. It has been shown that xanthates float better the cobalt minerals at pH=11 and dithiophosphates do at natural pH [4].

In this study, we collected samples in the mine of Kalukuluku in Lubumbashi in the Democratic Republic of Congo. Chalcocite is abundant copper mineral and carrolite is abundant mineral cobalt. For flotation tests, potassium amylxanthate (PAX: C6H11OCS2Na) family of xanthates and sodium amyl diithiophosphate (DANA:C6H4O3PS2Na) family diithiophosphates were used as collectors. Polypropylene glycol methyl ether (Dowfroth 250: DF250) was used as foaming and sodium silicate (Na2SiO3) as depressing and dispersant. Slaked lime (Ca(OH)2) was used as a pH regulator. The latter was varied keeping all other parameters constant: particle size, pulp density, impeller speed, reagents doses (PAX, DF250).

Flotation kinetics was treated for study the variation of the cumulative recovery of a component (copper and cobalt) proportionally to flotation time [18], as a time-rate recovery process.

II. MATERIALS AND METHODS

A. Sample

The ore sample on which we worked was from mine of Kalukuluku in Lubumbashi in the Democratic Republic of Congo. It has been crushed in a laboratory jaw crusher (primary) and then in a cylindrical laboratory crusher (secondary) to have a size <1.7 mm. We collected 25 kg for the result of our tests. The X-ray diffraction analysis revealed the presence of chalcopyrite CuFeS2, of chalcocite Cu2S and Carrolite CuCo2S4 as sulphides. The matrix was made of quartz SiO2, Dolomite CaMg(CO3)2, Feldspar AlSiO3 and talc Mg3Si2O10(OH)2. After analysis by atomic-absorption ICP, the contents of Table 1 have been revealed.
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Table 1: Chemical analysis of the sample by AAS/ICP

| Elements | Contents (%) |
|---------|-------------|
| CuT     | 3.57        |
| CuOx    | 0.4         |
| CoT     | 0.39        |
| CoOx    | 0.01        |
| Fe      | 2.94        |
| Mn      | 0.13        |
| Ca      | 9.765       |

B. Reagents

PAX and DANA were used as collectors and have been prepared at 1% by dissolving 1 g in 100 ml of water. Na<sub>2</sub>SiO<sub>3</sub> was used as depressing and dispersant and was prepared at 30% by dissolving 30 g in 100 ml of water. Ca(OH)<sub>2</sub> as a pH regulator was prepared at 20% by dissolving 20 g of CaO in 100 ml water. DF250 has been used as frother. Tap water was used for the flotation tests. Equation (1) was used for the passage of g/t to ml for each reagent.

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

C. Equipment

The following equipment was used: a laboratory mill (length: 260 mm, diameter: 180 mm, rotation speed: 100 rpm), a flotation machine DENVER, flotation cell of 2.5 L, panels, an VIBRA electronic balance, graduated vessels for reagents, a pH meter, a propipette, a wash bottle of 1 liter, a pallet.

D. Grinding

1 kg of sample was mixed with 1 l of water in the mill with 50% solids into the mill. This grinding was carried out at different times 15, 20 and 25 minutes respectively. The pulp from the mill was placed on a sieve of 75 μm and then the refusing was oven dried and weighed. According to Fig. 1, grinding curve was plotted by varying the refusing 75-μm size vs time.

For our flotation tests, we had considered 20% of refusing on the sieve of 75 μm. And in view of Fig. 1, 18 minutes of grinding has been required.

E. Flotation test

Before the flotation tests in single roughing, pH meter has been calibrated. The ore was ground for 18 minutes. The pulp was placed into the flotation cell of 2.5 L. Having lowered the rotor into the pulp, we operated the operation at 1300 rpm. We added Na<sub>2</sub>SiO<sub>3</sub> conditioned for 3 minutes and Ca(OH)<sub>2</sub> for pH regulation. Note that have worked at natural pH and pH 11. Then collector (45 g/t) and frother (5 drops) were added conditioned for 2 minutes. After that, we opened the air valve at 5 L per min and collected concentrates in fractions of 0.5; 0.5; 1; 2; 2 and 2 minutes respectively. The first 4 fractions were made the head concentrate. All concentrates and tailings were sent to the laboratory for chemical analysis by AAS-ICP to determine the amounts of copper and cobalt.

The 60 g/t corresponding to the remaining collector were added after the recollection fractions coming after the first, during a conditioning time of one minute. The flotation kinetics was also evaluated for comparison between PAX and DANA in recovery of copper and cobalt, using the variation of constant rate vs time. The flotation scheme in simple roughing is shown by the Fig. 2.

III. RESULTS AND DISCUSSION

A. Variations recovery vs time and grade vs time

Fig. 2 was used to study concerned variations by changing every time the pH using Ca(OH)<sub>2</sub>. We worked in at natural pH and pH=11. The other parameters were kept constant: d<sub>80</sub>=75 μm, PAX (105 g/t), DF250 (5 drops), pulp density 10% solids and impeller speed of 1300 rpm. The pulp produced by milling for 18 minutes was placed in 2.5 L. Ca(OH)<sub>2</sub> was added (only to adjust pH to 11), PAX and DF250 was added conditioned for 5 minutes. Then the air intake was introduced at 5 L per min. Finally, concentrates and tailings were collected, sent to laboratory for analysis by ICP-AAS to determine grades of copper and cobalt, as well as recovery yields.

1) Variations for copper

Figs. 3 and 4 show results of recovery and grade of copper vs time at different pH values. By comparison with the results of Fig. 3 and 4, we note that at natural pH, copper recovery is fast with DANA until the fifth minute. After the fifth minute, recovery of copper with PAX is better and gives a concentrate at 16.1% with a yield of 99.63%. At pH=11, the curve of the PAX is better than DANA, giving a concentrate at 16.1% copper with a yield of 99.05%.

Thus, the copper recovery is quick at natural pH with the DANA until the fifth minute. After the fifth minute of flotation, the PAX is better. At pH=11, PAX have a good selectivity.
Fig. 3: Variation of copper’s grade vs time at different pH values

Fig. 4: Variation of copper’s recovery vs time at different pH values

These results confirmed that the flotation by PAX is steady in an alkaline medium condition [16].

2) Variations for cobalt

Figs. 5 and 6 show results of recovery and grade of cobalt vs time at different pH values.

Fig. 5: Variation of cobalt’s grade vs time at different pH values

According to Fig. 5 and 6, we observe that at natural pH, selectivity of DANA is higher than selectivity of PAX. Cobalt recoveries for both collectors are almost the same to the third minute and beyond the third minute, the growth recovery is more pronounced for DANA than for PAX.

Thus, with DANA, we obtain a concentrate at 0.51% cobalt at a yield of 76.48%. With PAX, 1.13% cobalt concentrate is obtained with a yield of 47.37%.

At pH=11, PAX is largely better from the beginning to the end of cobalt recovery. It gives a concentrate at 0.91% cobalt with a yield of 85.18%, it is most selective. This confirms the study [14] who said that the alkaline pH depresses pyrite in the presence of xanthates, increasing the selectivity of the used collector.

B. Determination of flotation rate constant

Several authors have investigated the first order flotation kinetics models [1], [6], [8], [10], [12]-[13]. Among those models, the classic model is investigated for our study and according to this model; we have calculated the first order rate constant k from equation (2).

[2] and [7] have shown that the flotation kinetics studies the quantitative variation of the recovery R of the floatable mineral in concentrate vs time t.

\[ R = R_\infty (1 - e^{-kt}) \]

where \( R_\infty \) is the maximum recovery achievable or the cumulative recovery at time infinite (%), \( R \) is the recovery at time t (%), k is the first order rate constant (s\(^{-1}\)), t is the flotation time (s). After developing the formula (2), we obtain equation (3).

\[ kt = -\ln\left(1 - \frac{R}{R_\infty}\right) \]

In the case of our study, we evaluate the variation of the factor \( -\ln\left(1 - \frac{R}{R_\infty}\right) \) vs flotation time to find the rate constant k, both for copper and cobalt.

1) For copper

According to Fig. 7, at natural pH, the flotation rate constant is better by DANA till the 5\(^{th}\) minute and after that, the flotation rate by PAX increased till the end of flotation. At pH=11, the flotation rate is largely best by PAX than by DANA. In copper recovery, the rate flotation constant is higher by PAX at natural pH (0.634 s\(^{-1}\)) and pH=11 (0.443 s\(^{-1}\)). Another very important observation concerning PAX is that its faster kinetics in the recovery of copper both at natural pH and at pH=11.

Fig. 7: Determination of rate constant in flotation of copper at different pH values

In both the values of pH, the first order rate constant for copper recovery by PAX was found to be higher than that by DANA.

2) For cobalt

Fig. 8 shows that the rate flotation constant is better by DANA at natural pH and by PAX at pH=11 from the
beginning to the end of flotation. Another confirmation is that the rate flotation constant increases rapidly after the third minute by DANA at natural pH.

Fig. 8: Determination of rate constant in flotation of cobalt at different pH values

In cobalt recovery, the rate flotation constant is higher by DANA at natural pH (0.172 s⁻¹) and by PAX at pH=11 (0.203 s⁻¹).

IV. CONCLUSION

This study was intended to compare the selectivity and kinetics of PAX and DANA in recovery of copper and cobalt from a sulfide Copper-Cobalt ore. Keeping the particle size, pulp density, impeller speed, and reagents doses as constant parameters, only the pH was varied from the natural and pH=11. At natural pH, PAX was given the good results for the recovery of copper obtaining a concentrate of 16.1% with a yield of 99.63% and a flotation rate constant of 0.634 s⁻¹. For the recovery of cobalt, DANA was found as better collector obtaining a concentrate of 16.1% Cu and 0.91% Co respectively. The flotation yields were 99.05% and 85.18% respectively. Flotation rate constants were 0.443 s⁻¹ and 0.203 s⁻¹ respectively. According to these results, it is clearly shown that at both natural pH and pH=11, the kinetic of copper recovery is better by PAX than by DANA. However, for the kinetic of cobalt, DANA is better than PAX at natural pH. It is therefore recommended that a kinetic study be further undertaken in acidic conditions.

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REFERENCES

[1] A. Agar, G. E. Chia, and C. L. Requis. (1988). Flotation rate measurements to optimize an operating circuit. Minerals Engineering, 11(4), 347–360.
[2] I. Bobin and N. Petrovskaya. (2008). Usage of inertial model of 1st order with delay for analysis of kinetics of flotation.
[3] S. M. Bulatovic, C. J. Ferron, and W. T. Yen. (1992, August 2–6). Development and Plant Application of New Collector for Oxide Copper/Cobalt Ore Flotation for Gecamines, Zaïre Flotation Plants, Copper '92, Ottawa.
[4] S. M. Bulatovic. “Handbook of Flotation Reagents, Chemistry, Theory and Practice: Flotation of Sulfide Ores”, Elsevier Science & Technology Books, Vol.1, 2007, pp. 5-31, 105–109, 177–178, 235-239.
[5] W. L. Cornell and D. C. Hultgrefe. (1989). Continuous Flotation Testing to Recover a Bulk Sulfide Concentrate from Missouri Lead Ore Tailings, U.S. Bur. Mines, RI 9265.
[6] E. C. Dowling, R. R. Klimpel and F. F. Aplan. (1985). Model discrimination in the flotation of a porphyry copper ore. Minerals and Metallurgical Processing, 2(2), 87–101.
[7] M. Gharaei and R. Venugopal. (2016). Modeling of flotation process: An overview of different approaches. Mineral Processing and Extractive Metallurgy Review, Vol. 37, N°2, pp. 120–133.
[8] C. J. Jameson, S. Nam and M. M. Young. (1977). Physical factors affecting recovery rates in flotation. Miner. Sci. Eng., Vol. 9, N°3, 103–118.
[9] H. Kazutoshi, T. William and S. Atsushi. (2012). Investigation of Flotation Parameters for Copper Recovery from Enargite and Chalcopyrite Mixed Ore Materials Transactions, The Japan Institute of Metals, Vol. 53, N°4, pp. 707 to 715.
[10] A. Kestev, B. Kestev, Z. Zdravev, S. Ferat, J. Zivanovik and Z. Gocev. (2013, June 12–16). The kinetic flotation modelling of chalcopyrite from domestic ores using software tool. Proceedings of the XV Balkan Mineral Processing Congress, Sozopol, Bulgaria.
[11] R. Z. Liu, W. Q. Qin, F. Jiao, X. J. Wang, P. Bin, Y. J. Yang and C. H. Lai. (2016). Flotation separation of chalcopyrite from galena by sodium humate and ammonium persulfate. Trans. Nonferrous Met. Soc. China, Vol. 26, pp. 265–271.
[12] R. Natarajan and I. Nirdosh. (2006). A Comparative Study of Kinetics of Flotation of a Copper-Nickel Ore by N-Hydrocinnamoyl-N-Phenylhydroxylamine (HCNPHA) Vis-A-Vis Potassium Amyl Xanthate (PAX), Proceedings of the International Seminar on Mineral Processing Technology, Chennai, India. pp. 236–242.
[13] M. Polat and S. Chandler. (2000). First-order flotation kinetics models and methods for estimation of the true distribution of flotation rate constants. International Journal of Mineral Processing, Vol. 58, pp. 145–166.
[14] W. Trahar, G. Senior and L. Shannon. (1994). Interactions between sulphide minerals–the collectorless flotation of pyrite. International Journal of Mineral Processing, Vol. 40, N°3–4, pp. 287–321.
[15] M. Villena and G. Fernando. (2018). On Resource Depletion and Productivity: The Case of the Chilean Copper Industry. Resource Policy, Vol. 59, p. 553.
[16] B. A. Wills. Mineral processing Technology. New York: Pergamon Express, 1988.
[17] Y. Xinrong, T. Changqing and Z. Yujun. (2019). IOP Conf. Series: Earth and Environmental Science 237 032104.
[18] X. M. Yuan, B. J. Palsson and K. S. E. Forssberg. (1996). Statistical interpretation of flotation kinetics for a complex sulphide ore. Minerals Engineering, Vol. 9, N°4, pp. 429–442.
[19] C. Zhang, N. Song, G. M. Zeng, M. Jiang, J. C. Zhang, X. J. Hu and J. M. Zhen. (2014). Bioaccumulation of zinc, lead, copper, and cadmium from contaminated sediments by native plant species and Acrida cinerea in South China. Environ. Monit. Assess., Vol 186, pp. 1735–1745.
[20] M. Gharai and R. Venugopal. (2016). Modeling of flotation process: An overview of different approaches. Mineral Processing and Extractive Metallurgy Review, Vol. 37, N°2, pp. 120–133.