Comparative Cleaning Stages in Recovery of Copper and Cobalt from Tailings using Potassium Amyl xanthate as Collector

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Abstract — Copper and cobalt demand is projected to be increased from here to 2050 and the challenge is to find treat economically minerals which contains those metals. Several tailings from oxide ores throughout the world contain good grades of copper and cobalt that should be recovered by froth flotation. This paper investigates the recovery of copper and cobalt through reprocessing of spiral classifier tailings by determination of specific reagents dosage. The flotation behaviours of malachite and heterogenite were studied through many roughing and cleaning flotation tests in order to recovery most of copper and cobalt. The effect of specific reagents was be varied and others parameters were kept constant. The highest recoveries of both copper and cobalt in rougher concentrate were respectively 82.51% and 72.51% with grades of 12.52% and 0.99% respectively. However, the cleaner concentrate was 24.54 Cu% and 1.38% Co with recoveries of 69.26 % and 40.7% respectively. It was concluded that the reprocessing of spiral classifier tailings through froth flotation is benefit because it recovers most of desired metal and reduces the risk of their presence on environment through plant tailings. Recycling of cleaner tailings was also proposed.

Index Terms — Cobalt, Copper, Flotation, Spiral tailings, Xanthate.

I. INTRODUCTION

The Central African Copper Belt in the Democratic Republic of Congo and Zambia is one of oxide copper-cobalt ores container characterized by the size and quality, which are used in several domains [1]. The treatment by flotation of copper-cobalt oxide minerals has been studied by several authors [2]-[4]. Malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2 \cdot \text{H}_2\text{O}$), pseudo malachite ($\text{Cu}_5(\text{PO}_4)_2\text{OH}_4$), cuprite (Cu_2O), chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$), chrysocolla ($\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$), heterogenite ($\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) are among those minerals. Both malachite and heterogenite are most abundant copper and cobalt oxide minerals respectively. More than one author [3], [5] have studied several reagents and their combination for the recoveries of copper and cobalt. Among them, xanthates, dithiophosphates and dithiocarbamates as collectors; Dowfroth and Senfroth as frothers; acids and

bases as pH regulators; carbonates, silicates as depressants and dispersants; sodium sulphurs as sulfidisers agents. On another hand, [6] has studied the effect of lead nitrate as activator on sulfurizing flotation of a copper-cobalt oxide ore. It is known that bubbles into the froth may have good size to ensure a good recovery of valuable particles. [7] showed that larger bubble had high solid mass flow rate than small bubble. Xanthates are generally the most used of collectors due to the wide application and relatively cheap cost [8]. Potassium amyl xanthate (PAX) is one of them. Considering the structural viewpoint, they are product of carbonic acid, where the two oxygen atoms are replaced by sulfur and one alkyl group replaces a hydrogen atom. [2], [3], [8], [10] showed that for the treatment of oxide cobalt and copper ores, sulphidisation process is employed by using soluble sulphide salts into the pulp. [11] also investigated the uses of sodium sulfide (Na_2S) and NaCN (sodium cyanide) as depressants on the separation of copper and arsenic. Sodium hydrosulfide (NaHS) is one of the most commonly used reagents due to its low price and minimal impact on pH due to its hydrolysis in water. [12] showed that during sulphidisation phenomenon, NaHS addition converts an oxide mineral surface into a sulphide surface by making it more easily floatable by traditional sulphide collectors such as xanthate. Thereby, there is formation of sulfide surface onto oxide surface. On the other hand, [13] studied the use of acid activated as adsorbent for the adsorption of malachite. Besides, in Katanga, Democratic Republic of the Congo, about 77% of the copper and 75% of the cobalt were recovered by using sodium hydrosulphide with a concentration ratio of 3.0 [3]. [14] have shown that there is a correlation between malachite recovery and the content of sulfidization products, which are composed of cuprous monosulfide, cuprous disulfide, and cuprous polysulfide. The two last of the list were more important concerning activity of product.

Sodium silicate (Na_2SiO_3) is one of the most used modifiers for silicate gangue depression and dispersant but there is difficulty in understanding its action mechanism [9], [15]. The presence of generated ionic and colloidal species such as colloidal silicate, monomeric species and polymeric silica species, is the principal reason of those difficulty. According to [16], pH value and silica concentration in solution determine the prevalence of some of colloidal species.

Kamfundwa plant localized in DR Congo, treat copper-cobalt oxide minerals (malachite and heterogenite) in average 3% Cu. It has a spiral classifier, which produce concentrate in average 20-30% Cu and tailings in average 3% Cu. Those tailings contain more valuable metals such as

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copper and cobalt which can be recovered. Considering the adoption by several countries of environmental regulations about environment protection against heavy metals [17], [18] and the high grades of copper and cobalt into tailings, this paper aims at recovering those metals from spiral classifier tailings of Kamfundwa by froth flotation using optimal conditions. According to [19], spiral classifier has been used since the early 1940s and is known to be one of the most efficient and simple operation units. It can also be used to concentrate a variety of ores; however, they are cost effective [20]. [21], [22] showed that, heavy medium separation techniques were used since many years for riding gangue coarse (dolomite). Otherwise, malachite froth flotation using PAX and NaHS was very good in the presence of calcium, magnesium and bicarbonate ions [4].

The present research work is interested in the froth flotation of spiral classifier tailings to recover more valuable metals (copper and cobalt). For flotation tests, PAX ($C_5H_{11}OCS_2Na$) was used as primary collector, $NaSiO_3$ as gangue depressant and dispersant, Senfroth (G41) as frother, mixture (MIX: blend of gasoil and hydrolysed palm oil called rinkalore 10 in a ratio gasoil/rinkalore of 9/1) as secondary collector, sodium carbonate (Na_2CO_3) as emulsifier of MIX, NaHS as sulfidiser. Only PAX, NaHS, MIX and Na_2SiO_3 doses were varied and other parameters were kept constants such as particle size, pulp density, and impeller speed. pH was natural (about 8.5).

II. MATERIALS AND METHODS

A. Sample

Spiral classifier tailings were conveying to dam by conduct pumping. Sample was carried out from that conduct during 14 days. It has been dried and goodly conserved. The entire sample was homogenized in order to obtain a uniform composition for analysis and flotation tests. X-ray diffraction analysis has revealed malachite, pseudo malachite, chrysocolla, heterogenite and certain footprint copper sulfide minerals. Quartz and dolomite constitute gangue minerals. Table I shows sample contents after analysis by atomic-absorption ICP.

TABLE I: SAMPLE ANALYSIS BY AAS/ICP

Elements	Cu _{tot}	Cu _{ox}	Co	CaO _{tot}	CaO _{sol}	SiO ₂
Grade (%)	3,02	2,84	0,38	1,18	0,3	71,44

Sample sizing (Fig. 1) results have shown that -75 μ m solid particles represented 16% and coarse (+600 μ m) had high grade in both copper and cobalt. Comminution was very important in order to liberate valuables particles.

Fig. 1. Sample sizing.

B. Reagents

Na_2SiO_3 was prepared at 30%, PAX was prepared at 1.2%, MIX at 1.2% by mixing 1.08 g gasoil, 0.12 g rinkalore 10, 100 ml water (H_2O) and drops of Na_2CO_3 at 1.2%. NaHS and G41 were used as pure. Equation (1) was used to transform g/t to millilitre.

$$V = \frac{\text{mass of ore sample (kg)} \times \text{reagent dose (g/t)}}{\text{reagent concentration (g/l)}} \quad (1)$$

C. Equipment

The following equipment was used: flotation machine DENVER, laboratory mill, wash bottle of 1 liter, flotation cell of 2.5 L and 1.5 L, VIBRA electronic balance, panels, graduated vessels for reagents, pH meter, propipette, pallet.

D. Grinding

The comminution of sample has consisted to grinding 1 kg of sample in 1 L of water during 5, 10, 15, 20 and 25 minutes respectively. Sieving on 75 μ m has revealed results showed in Fig. 2 and according to that, 18 minutes of grinding are required to achieve the wanted liberation (30% of refusing particles on 75 μ m sieve).

Fig. 2. Grinding curve's ore of Kalukuluku.

E. Flotation test

According to [23] and [24], flotation efficiency depends on a number of parameters which include particle size, pulp density, water quality, pH and reagent dosage. These parameters are used in their optimal values to achieve the max recovery with high grades [25]. In order to realize a good floatability of studied tailings, several flotation tests were made. After sample grinding of 1 kg in 1 L of water during 18 minutes, pulp was placed into a 2.5 L flotation

cell and pulp density was fixed at 30% solid, followed by activation of machine with an impeller speed of 1200 trs/min.

As shown in Fig. 3 Na_2SiO_3 and MIX were added for a conditioning time of 3 minutes and 1 minute respectively, followed by NaHS and PAX addition for a conditioning time of 5 minutes. 30 seconds were sufficient for conditioning of G41 (50 g/t). Natural pH was about 8.5 and temperature was ambient. After air admission, 5 concentrates during 2 minutes per each were collected in simple roughing. Concentrates and tailings were sent in lab for analysis in order to determine copper and cobalt grades. Note that 60% of PAX and NaHS were added in the head concentration and the 40% remaining were fractionally added in the other concentrations.

Fig. 3: Simple roughing flotation tests scheme.

C₁: head concentrate.
C₂, C₃, C₄ and C₅: concentrates.
Rougher concentrate (RC): C₁+C₂+C₃+C₄+C₅.
T: tailings.

III. RESULTS AND DISCUSSION

Scheme of Fig. 3 were used for flotation tests in simple roughing and doses of NaHS, PAX, Na_2SiO_3 and MIX were varied. Other parameters have been used: $d_{80}=75\ \mu\text{m}$, pulp density 30% solid, G41 (50 g/t) and impeller speed 1200 trs/min.

A. Effects of NaSH and PAX

PAX dose was taken in a ratio of PAX/NaHS=1/10, thereby NaHS doses were varied from 2000 g/t to 5000 g/t. Na_2SiO_3 and MIX doses were kept constants: 400 g/t and 300 g/t respectively. Fig. 4 and 5 show variations of grade vs recovery of both copper and cobalt.

According to Fig. 4 and Fig. 5, at 3000 g/t of NaHS and 300 g/t of PAX, rougher concentrate (RC) was produced at 7.53 % Cu and 0.68 % Co with yields of 82.36% and 73.47% respectively. At optimal collector dosage, as studied by [8] and [26], the liberation of xanthate ions (X⁻) is sufficient to create adsorption on the activated minerals surfaces in the form of hydrophobic species, followed by attachment between mineral particles and air bubbles, thereby good collection is observed.

It can also be observed that under-sulphidising prevents

the mechanism of collection and high quantity of sulfidiser depresses flotation, confirming [3] and [27] studies.

Fig. 4. Effects of NaSH and PAX (10/1) on copper recovery.

Fig. 5. Effects of NaSH and PAX (10/1) on cobalt recovery.

B. Effect of Na_2SiO_3

Na_2SiO_3 doses were varied from 200 to 500 g/t and PAX, NaHS, MIX doses were kept at 300 g/t, 3000 g/t, 300 g/t respectively. Flotation results are shown in Figs 6 and 7.

Na_2SiO_3 doses were varied from 200 to 500 g/t and PAX, NaHS, MIX doses were kept at 300 g/t, 3000 g/t, 300 g/t respectively. Flotation results are shown in Fig. 6 and 7. Copper and Cobalt flotations are best at 200 g/t Na_2SiO_3 . Beyond those doses, there is production of poor concentrates with lower yields.

Fig. 6. Effect of sodium silicate on copper recovery.

Fig. 7. Effect of sodium silicate on cobalt recovery.

This confirms [2], who said that in excess of Na_2SiO_3 there is production of fragile air bubbles leading to an unfavourable collection. At optimal dose, it was observed the maximum efficiency of Na_2SiO_3 as gangue depressant in the pulp and at natural pH, as studied by [28]. In these conditions, rougher concentrate was at 12.52 % Cu and 0.99 % Co with yields of 82.51 and 72.51% respectively.

C. Effect of MIX

By maintaining NaHS, PAX, MIX doses at 3000 /t, 300 g/t and 200 g/t respectively, 100, 200, 300 and 400 g/t of MIX were used. Results are illustrated in Fig. 8 and Fig. 9.

According to results, situations at 200 g/t and 300 g/t are almost similar for both copper and cobalt recoveries but the optimal dose is 300 g/t with obtainment of 7.53% Cu and 0.68% Co in rougher concentrate with yields of 82.36 and 73.47% respectively.

Fig. 8. Effect of MIX on copper recovery.

Fig. 9. Effect of MIX on cobalt recovery.

D. Cleaning stages

[2] has developed cleaning stages in order to simulate a flow sheet and have given goods results. In this paper, four different cleaning stages have been tested as shown in Fig. 10, Fig. 11, Fig. 12, Fig. 13 and Fig. 14. In each case, 300 g/t PAX, 3000 g/t, 200 g/t Na_2SiO_3 and 300 g/t MIX were used.

For Fig. 10-13, RC: rougher concentrate; SC: scavenger concentrate; CC₁: cleaner 1-concentrate; CC₂: cleaner 2-concentrate; CT₁: cleaner 1-tailings; CT₂: cleaner 1-tailings.

Fig. 10. Cleaning flotation/ Scheme 1.

Fig. 11. Cleaning flotation/ Scheme 2.

Fig. 12. Cleaning flotation/ Scheme 3.

Fig. 13. Cleaning flotation/ Scheme 4.

According to Fig. 10, there are two stages cleaning of the rougher concentrate. Note that last three Figs. are different in roughing, scavenging and cleaning flotation times. FC concerning scheme 1 was directly considered as CC₂. For scheme 2, 3 and 4, FC was obtained by mixing RC and CC₂. It can also be seen that FC of scheme 1 has a better grade in both copper and cobalt but with a weak recovery, followed by FC of schemes 2 and 3. FC of scheme 4 is slightly graded in both copper and cobalt comparing to other schemes; but is better concerning the recovery.

On the other side, Fig. 11, Fig. 12 and Fig. 13 are characterized by separation of rougher concentrate and scavenger concentrate that pass by two-stage cleaning. However, scheme 4 gave good results producing a FC at 24.54% Cu and 1.38% Co with recoveries of 69.26% and 40.7% respectively.

Another fact is that CT_{2s} of schemes 1, 2 and 3 contained high copper grade comparing to scheme 4. [2] have proposed recycling of CT to diminish valuable metal grade. Thereby, in the case of this study, it can be envisaged recycling of CT₂ to the feed of scavenger flotation, and of CT₁ to the feed of rougher flotation; in order to recover metals that are more valuable.

IV. CONCLUSION

This paper aimed to find optimal conditions for the froth flotation of spiral classifier tailings mainly constituted of oxide copper-cobalt minerals. It was also intended to compare cleaning stages and simulate a flow sheet after cleaning flotation tests. Flotation test using 300 g/t PAX, 3000 g/t NaHS, 2000 g/t Na₂SiO₃, 300 g/t MIX, natural pH (about 8.5), 10 minutes of flotation time; and keeping constant other parameters. In those conditions, it was obtained a RC in average 12.52% Cu and 0.99% Co with yields 82.51 % Cu and 72.51 % Co. Considering cleaning flotation tests, the scheme 4 has given good results producing a FC in average 24.54% Cu and 1.38% Co with yields of 69.26% and 40.70% respectively.

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