OPTIMIZING OF LIxivIANT AND REDUCTANT ON THE LEACHING OF
OXIDIZED COPPER-COBALT ORES

Barriga, A.*, Frenay, J., Patiño, E.

1 - Metallurgie et Traitement des Minerais (Geomac). Chemins des Chevreuils 1, B 52, University of Liege, 4000 Liege-Belgium

2 - Engineering Department. Av Arturo Prat 2120, Casilla 121. University Arturo Prat, Iquique-Chile

epatino@unap.cl

The Luiswishi deposit is operated by a joint venture between EGMF (Enterprise Générales Malta Forrest) and Geacamines (Générale des Carrières et des Mines). The copper-cobalt ore is beneficiated by the sulphidization process at the NCK (New concentrator of Kipushi) at Kipushi. Sulphidization followed by flotation with sulphydryl collectors is a common practice for the treatment of oxidized base metals ores. A new laboratory research program was carry out to find an alternative route of treatment using hydrometallurgical approach. Consumption of sulphuric acid and ferrous iron as lixiviant of copper and reductant of cobalt, respectively, are the critical parameter for design of the process. However optimisation of reactives consumption has not been focussed on the fundamental basis. were optimizated. The study was focussed in leaching technique using sulphuric acid and ferrous iron as reductant of cobalt by finding the range of acid concentration where the leaching rate is depending of acid concentration. The specific influence of acid and ferrous iron concentration on the copper and cobalt leaching kinetic, are reported in this paper.

Key words: leaching, reductant, copper, cobalt

Area tematica: Hydrometallurgy
INTRODUCTION

The copper-cobalt Luiswishi deposit of the Southern Group at Katangan Copper Belt are operated by a joint venture between EGMF (Enterprises Générales Malta Forrest) and Gecamines (Générales des Carrières et des Mines). The copper-cobalt ore is beneficiated by the sulphidization process at the NCK (New Concentrator of Kipushi). Sulphidization followed by flotation with sulphydryl collectors is a common practice for the treatment of oxidized base metals ores (Shungu et al, 1988, 163, Zhang, 1993, 619). This process is complex and its application at the industrial scale is quite sensitive. In central Africa it is also a cost intensive as the sulphidizing agent has to be imported. In order to improve the metallurgical performances and to optimise the economy of the process, a laboratory research program was carried out by the laboratory of Metallurgy and Mineral Processing (MTM) of the University of Liège- Belgium. This program includes two branches:

- Study of various flotation reagents as dispersing, depresssing and activating agents (Bastin, 2003, 180)
- Study of new alternatives of copper-cobalt ores treatment

The application of leaching methods in sulphuric acid-ferrous sulphate medium of copper-cobalt ores offers many potential advantages from environmental and operational point of view. It is relatively easy to implement, so is very attractive for its application because is not necessary large investment. One the most operational advantage is the treatment of finest fragmentation by the agglomeration technique, so the operative cost of milling is reduced specially when the gangue is closed inside hard minerals like quartz.

Few or not investigations have been carried out in support the leaching process of copper-cobalt oxidized ores, being last one devoted to stirred tank leaching in sulphuric acid-ferrous sulphate medium demonstrating the technical feasibility of this application (Naweje, 2002). On the basis of this preliminary results indicating the feasibility of this hydrometallurgical process, the leaching in column and the optimisation of reagents applied have been studied.

MATERIALS AND METHODS

The copper-cobalt ores employed in this program was obtained from Luiswishi deposit (Democratic Republic of Congo), and it consisted of major malachite and heterogenite the main copper and cobalt bearing minerals. The grade of ore was essayed to be Cu 1.98 % and Co 1.51 %.

For the liberation of cobalt from heterogenite, ferrous iron was used as reductant. In the present study, ferrous iron in medium sulphate and sulphuric acid were used to solubilization of cobalt and copper from ore, respectively. The general reaction of solubilization of cobalt and copper are as follow:

\[ 2\text{CoO(OH)} + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{CoSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \quad (1) \]

\[ 2\text{CuCO}_3\cdot\text{Cu(OH)}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{CuSO}_4 + 4\text{H}_2\text{O} + \text{CO}_2 \quad (2) \]
From both reactions, it is possible calculate the theoretical consumption of ferrous sulphate for Co (III) reduction and sulphuric acid necessary for the dissolution of both metals Cu (II) and Co (II).

The screen analysis of the ore used for the leaching work was as show in the Figure 1. It presents a great amount of fine size.

![Figure 1. Grain size analyses of oxidized Cu-Co ore from Luiswishi deposit (Democratic Republic of Congo)](image)

**CONSUMPTION REAGENTS TESTS**

A sample of 20 grams of mineral (-100m +150m Tyler) in 200 ml. of deionised water (for obtain pulp of 20% solids) was prepared. This pulp was agitated in all cases at 300 rpm during 3 hours using a solution containing ferrous iron sulphate and sulphuric acid. The amount of reagents used were calculated from the stoichiometric requirement considering heterogenite and malachite as a major source of copper and cobalt (reactions 1 and 2): for 20 grams of mineral, 0.286 grams of Fe (II) and 1.364 grams of H$_2$SO$_4$, were required. The Fe (II) was added as FeSO$_4$•7H$_2$O and sulphuric acid as technical reagent. Tests of reagents consumption were carry out, adding sulphuric to maintain constant the pH of medium. Pregnant solution was analized by copper, cobalt and total iron content by absorption spectrophotometry and for ferrous iron by titration with dichromate. Table I shows the sulphuric acid and ferrous iron consumed in these tests.

<table>
<thead>
<tr>
<th>pH</th>
<th>H$_2$SO$_4$ added (g)</th>
<th>Fe$^{II}$ added (g)</th>
<th>Fe$^{II}$ in PLS (g)</th>
<th>Fe$^{II}$ consumed (g)</th>
<th>Recovery %Cu</th>
<th>Recovery %Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>3.37</td>
<td>0.376</td>
<td>0.086</td>
<td>0.290</td>
<td>94.56</td>
<td>94.83</td>
</tr>
<tr>
<td>1.5</td>
<td>1.98</td>
<td>0.434</td>
<td>0.217</td>
<td>0.217</td>
<td>94.76</td>
<td>83.48</td>
</tr>
<tr>
<td>2.0</td>
<td>1.26</td>
<td>0.376</td>
<td>0.173</td>
<td>0.203</td>
<td>83.89</td>
<td>73.93</td>
</tr>
</tbody>
</table>
From results presented in Table 1, it is possible to see that maintaining high pH, the recovery of copper and cobalt are not the highest. The best value for copper extraction is pH = 1, however for cobalt extraction, the best condition is representing for pH=1.5. The consumption of sulphuric acid is near 3 times the theoretical requirement which is a practical common in the industry. For ferrous iron, the consumption is nearly to the theoretical requirement, confirming that there is not another mineral consuming this reagent.

COLUMN LEACHING TEST

The apparatus used for leaching it consisted of 9 cm-ID PVC columns, 50 cm height, resting on 25-L PET reservoirs. The columns were generally filled with 1-Kg of ore to height of about 15 cm. The tests were carry-on at room temperature. The leaching solutions were pumped to the top of the column and kept at 5 L.m⁻².Hr⁻¹ and they percolated through the ore at the rate of approximately 15 cm/hr. Periodically the solutions in the reservoir was analysed for copper, cobalt and total iron by atomic absorption spectroscopy and for ferrous iron by titration with potassium dichromate. In the present study it was used fractions sized less than 15mm which were attacked with ferrous iron sulphate-sulphuric acid solution during manual agglomeration. In Figure 2 it can see the ore after curing agglomeration step. The red colour in the surface ore explains the presence of cobalt salts.

![Cobalt's Salts](image)

Figure 2 Curing-agglomeration products of copper-cobalt oxidized ores showing cobalt salts

To evaluate the effect of particle size on the copper-cobalt extraction, experiments of leaching using particles between 9 to 15 mm and irrigation with ferrous sulphate-sulphuric acid solution were carried out. The monosize percolation leach was carried out with 1kg. of coarse mineral between 9 and 15 mm, in a column of PVC and was pumped and irrigated at 5 L/m².H in the top of the column. The pregnant leach solution was recolected in the base and it was analysed by copper, cobalt and total iron by atomic absorption and the ferrous iron by titration with dichromate. The ore was irrigated with sulphuric acid - ferrous sulphate medium; the solution was prepared for 20 g/L H₂SO₄ and 3.8 g/L Fe⁺⁺. Figure 3 shows the copper and cobalt recovery of 60 and 65 respectively in 28 days of leaching. From the same Figure 3 it is possible to see that cobalt extraction is arising still; but the time of leaching is so large.
The Thin layer leaching method was carried out with 1 kg. mineral minus 15 mm in size, in a column of PVC and was pumped and irrigated at 5 L/m²H in the top of the column, the pregnant leach solution obtained was analysed by copper, cobalt and total iron by atomic absorption and the ferrous iron by titration with dichromate. Agglomeration of fines to coarser particles were made in manual way, using a solution of sulphuric acid – ferrous sulphate in strong concentration. The amounts of ferrous sulphate and sulphuric acid employed for this essay were the 50% of the theoretical consumption (in this case for 1 Kg of the employed ore, the theoretical consumption is 14.3 grams of Fe⁺⁺ and 68.3 grams of H₂SO₄). The volume of solution used for agglomeration was 100 mL (10% of mineral weight). The material was irrigated with sulphuric acid – ferrous sulphate medium; the solution was prepared for 10 g/L H₂SO₄ and 2.2 g/L Fe⁺⁺ (determined by titration with dichromate). Figure 4 shows the kinetic of copper and cobalt recovery (74% in both cases copper and cobalt at 28 days of percolation).
Grains sized minus 15 mm were agglomerate with sulphuric acid-ferrous sulphate (20% of the theoretical consumption for both reagents) and irrigated with a solution of 10 g/l of sulphuric acid and 2.2 g/l of ferrous iron. Figure 5 shows the results of copper and cobalt solubilization.

From this Figure, clearly, the effect of diminishing the amount of ferrous iron and sulphuric acid used in the agglomeration step have an positive effect on the global recovery of copper and cobalt. This is a result which have an explanation on the kinetic of gangue dissolution.

![Figure 5](image)

**Figure 5.** Cu-Co recuperation for thin layer leaching with grain size less than 15 mm using 20% of required reagents in the agglomeration

**CONCLUSIONS**

- Percolation leaching of copper-cobalt oxidized ores has been demonstrated, as an alternative to actual sulphidization-flotation process at Luiswishi deposit – New concentrator of Kipushi (Republic Democratic of Congo).
- Leaching test in column have demonstrated better recovery compared with leaching in stirred tank, which presents comparative advantages
- The effect of reagents dosification between agglomeration and leaching steps have been demonstrated as an important technique of management to improves the recovery of copper and cobalt
- Further studies will be carried out to determine the kinetic models; studies to regenerated the ferrous iron will be carried out using bacteria ferric reducer in anoxic environment.

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