Laboratory Column Leaching of Cobalt using Raffinate and Sodium Metabisulfite

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Minerals containing trivalent cobalt (Co_2O_3) are known to have poor leaching characteristics in sulfuric acid medium, without the use of reducing agents such as sodium metabisulfite ($Na_2S_2O_5$), sulfur dioxide (SO_2), ferrous sulfate ($FeSO_4$) or copper powder (Cu°). This study was carried out with the purpose of testing the use of sodium metabisulfite as a reducing agent to increase the laboratory column leaching efficiency of cobalt from low-grade copper ore. In an agitation leach plant producing copper cathodes and cobalt salts and operating using the BASF Split Circuit™, low-grade raffinate is sent to impurities removal followed by cobalt precipitation. The high-grade raffinate is recycled to leaching. The low-grade raffinate, with its acid content to be neutralised in the cobalt plant, was used to leach the ore considered as being too low grade for agitation leaching. The advantages of this are reduction of neutralisation chemicals costs in the cobalt plant, while increasing the production of copper and cobalt. This paper presents the results of the laboratory tests together with discussions for plant implementation.

INTRODUCTION

In the oxide ores of the Democratic Republic of the Congo (DRC), cobalt oxide occurs mostly in the Co^{3+} form. While cobalt carbonate (Co^{2+}) is highly soluble in sulfuric acid medium, cobalt(III) oxide requires the use of a reducing agent to leach it by lowering its state from Co^{3+} to Co^{2+} (Mwema *et a*l., 2011; Kafumbila, 2018).

In most agitation leaching plants in the DRC, the copper–cobalt ore with less than 1.5% Cu is, in general, considered as mining waste. Many of the operations have started considering treating these big volumes of mined and stockpiled low-grade copper ore by heap leaching.

This paper considers the benefit of using low-grade (LG) raffinate as heap leaching solution, to reduce the acid contained in it (which would otherwise need to be neutralized in the cobalt salt production plant), while increasing the production of both copper and cobalt. The most commonly used process for cobalt salt production consists of impurity removal followed by cobalt precipitation (Ilunga *et al*., 2015).

Reducing Agent: Sodium Metabisulfite

Sodium metabisulfite (SMBS) is one of the most commonly used reducing agents for trivalent cobalt, although its consumption can go as high as 0.8 ton/ton solubilized Co and represents, in some cases, up to 47% of the operating cost per ton of the produced metallic cobalt (Mwema *et al*., 2011; Ntakamutshi *et al*., 2017).

The dissolution of SMBS and the mechanism of Co^{3+} reduction into aqueous solution are illustrated by the following reactions:

$$Na_2S_2O_5 + H_2O \longrightarrow 2NaHSO_3 \quad [1]$$

$$2NaHSO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2SO_2 + 2H_2O \quad [2]$$

$$SO_2 + Fe_2(SO_4)_3 + H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad [3]$$

$$2FeSO_4 + Co_2O_3 + 3H_2SO_4 \rightarrow 2CoSO_4 + Fe_2(SO_4)_3 + 3H_2O \quad [4]$$

When leaching is performed at pH < 1, SO_2 undergoes parasitic reactions with Cu^{2+}, which precipitates in the form of Chevreul's salt (CuO.FeO or $CuO.FeO_2$) (Seo *et al.*, 2012; Stuurman *et al.*, 2014). In addition to the reduction of the amount of copper leached, these parasitic reactions increase the overall consumption of SO_2 and thus of SMBS (Tshipeng *et al.*, 2017).

Split Circuit™ Conceptual Flowsheet

In hydrometallurgical plants using the BASF Split Circuit™ (see Figure 1), the copper solution fed to SX is split into high-grade (HG) and low-grade (LG) pregnant leach solution (PLS). The HG raffinate is recycled to leaching as the main source of acid, while the LG raffinate is sent to the cobalt plant with the benefit of lowering the acid neutralization costs, resulting in the reduction of the overall plant operating costs (Nisbett *et al.*, 2007).

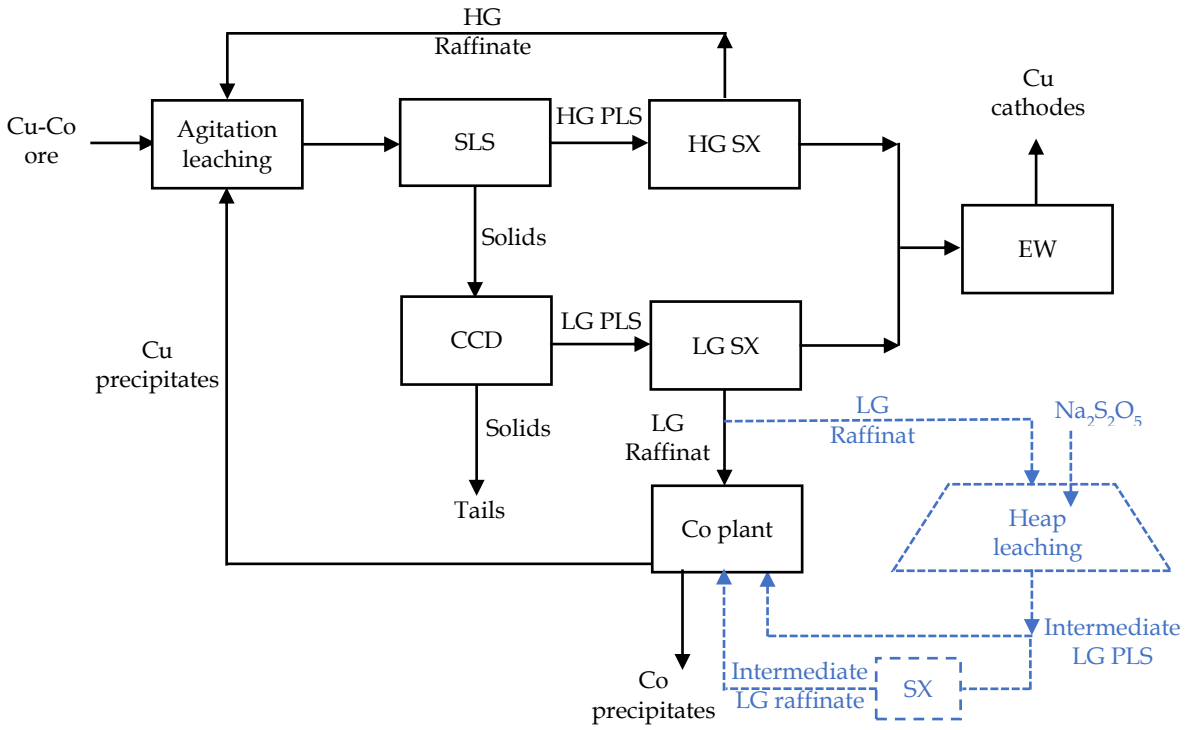

Figure 1: Cobalt heap leaching in Split Circuit concept flowsheet.

CHARACTERIZATION OF THE ORE

Chemical Analysis

The ore used for this work is considered a waste for the agitation leaching plants in the DRC, where 1.5% is considered as cut-off grade. We will deliberately call it: *low-grade copper ore*. The sample collected was analyzed and the results are presented in Table I.

Table I: Chemical analysis of ore.

Species	Proportion (%)	Species	Proportion (%)
Total copper	1.2	SiO_2	66
Oxide copper	0.9	Al_2O_3	4.19
Total cobalt	0.4	MgO	3.02

Chemical Analysis by Size Fractions

Table II presents the chemical analysis by size fraction, after the size distribution analysis was conducted on the sample destined for heap leaching.

Table I: Chemical analysis by size fractions.

Size (mm)	Mass (kg)	Cu (%)	Co (%)	Fe (%)	Mn (%)
12.25	161	1.14	0.12	1.34	0.04
6.30	126	1.42	0.37	1.24	0.04
4.75	51	1.12	0.34	1.29	0.05
3.35	58	1.56	0.38	1.65	0.07
2.36	46	1.26	0.34	1.53	0.06
-2.36	75	1.53	0.46	1.89	0.16
1.18	53	1.62	0.39	1.69	0.09
-1.18	727	1.15	0.50	1.75	0.15
Total	1297	1.24	0.42	1.62	0.11

The copper and iron were evenly distributed amongst the various fractions while the cobalt and manganese content tended to be more concentrated in fines.

CHARACTERIZATION OF LEACHING SOLUTION

The leaching solutions used in these tests were the LG and HG raffinates collected from an operating plant. Their respective characteristics are provided in Table III. While the targeted leaching solution was the LG raffinate, we also considered the HG raffinate with the aim of evaluating the impact of the acid content on the leaching efficiency.

Table III: Chemical analysis of low- and high-grade raffinates.

Designation	Acid (g/L)	Cu (g/L)	Co (g/L)	Fe (g/L)	Mn (g/L)
Low-grade raffinate	16	0.25	2.35	0.45	0.65
High-grade raffinate	20	2.42	3.14	0.91	0.73

The two raffinates originated from solvent extraction (SX) of the LG and HG PLS. The HG raffinate is recycled to the agitation leaching section and the LG raffinate is used for cobalt hydroxides production. In the hydroxide production plant, impurities such as iron, aluminium, manganese and then copper are removed by step-wise precipitation at pH 3.5 and 5.3, respectively, before precipitating the cobalt at pH 7.5.

AGITATION LEACHING TESTS

Preliminary tests were conducted to determine the maximum leaching efficiency of cobalt, while evaluating also the quantities of the reducing agent needed to solubilize the trivalent cobalt and the acid to be used.

The first test was conducted without the use of the reducing agent and the second with the use of the reducing agent. The pH and oxidation–reduction potential (ORP) were maintained constant at 1.8–2

using sulfuric acid and 350 mV using SMBS, respectively, during the entire test period. Both tests were conducted over six hours. Figures 2 and 3 illustrate the results.

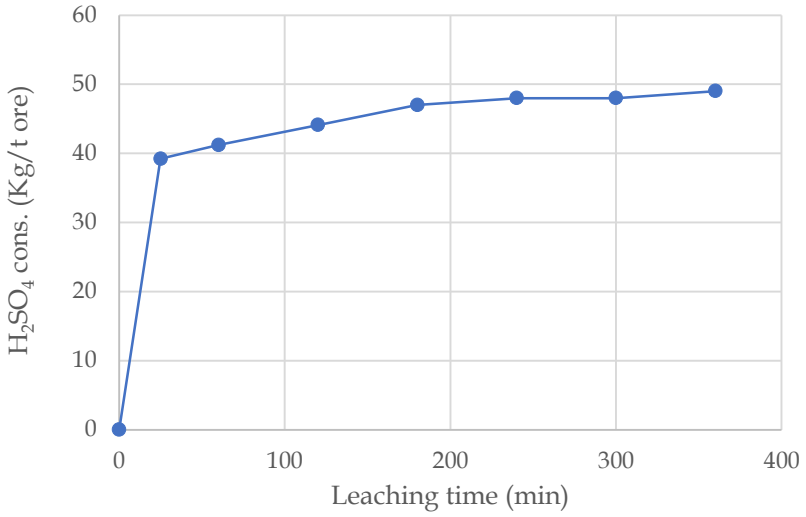

Figure 2: Acid consumption to maintain pH 1.8–2 during the agitation test without the use of SMBS.

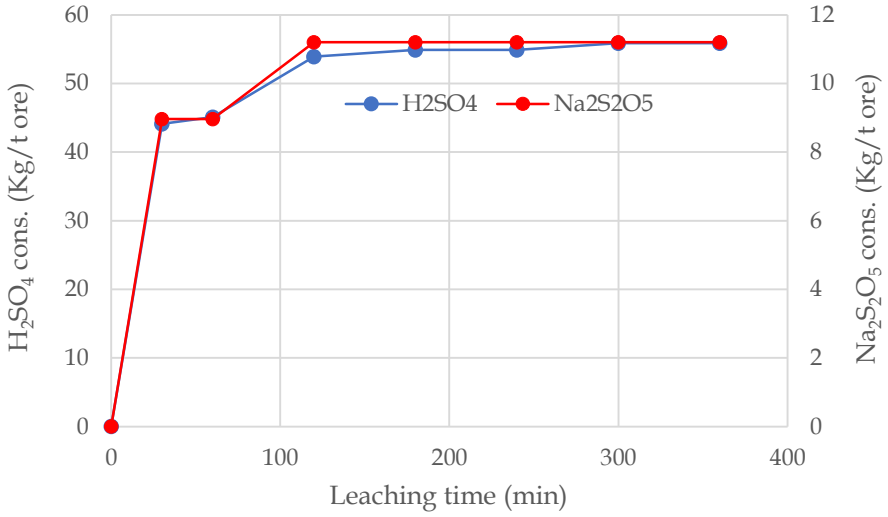

Figure 3: Acid to maintain pH 1.8–2 and SMBS consumption during the agitation test with the use of SMBS.

Figure 4 shows that without the use of SMBS we could only achieve 30% Co leaching efficiency, while this was increased to 84% after the use of SMBS at 11.2 kg/t ore. These tests suggested that about 54% of the Co contained in the ore was in the trivalent form and required the use of the reducing agent to be dissolved. The acid consumption increased from 49 to 56 kg/t ore due to the increase of cobalt dissolution.

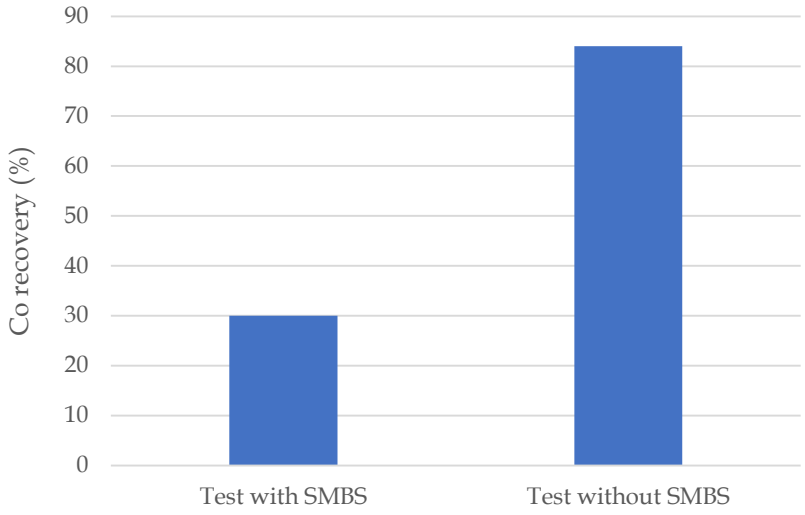

Figure 4: Cobalt leaching efficiency during the agitation test without and with the use of SMBS.

COLUMN HEAP LEACHING TESTS

Conditions

The following parameters were considered as variables for the heap leaching tests:

- reducing agent;
- size fraction of ore;
- application rate of leaching solution;
- acid concentration of leaching solution.

The conditions investigated are summarized in Table IV. For each test, 10 kg ore was leached in a 20.5 cm diameter by 50 cm high laboratory column. The solid SMBS was placed at 95% of the total height of ore, and recovered with ore into the column.

Table IV: Column heap leaching tests conditions.

Test ID	Ore size range (mm)	Application rate (L/h/m²)	Leach solution	SMBS mass (g)
Test 1	−19 +1.18	10	LG raffinate	–
Test 2	−19 +1.18	10	LG raffinate	112
Test 3	−19 +1.18	20	LG raffinate	112
Test 4	−19 +6	10	LG raffinate	112
Test 5	−19 +1.18	10	HG raffinate	112

Evaluation of Impact of Reducing Agent

These tests were conducted to evaluate the cobalt leaching efficiency in both the absence and presence of reducing agent. Figure 5 provides the results. Only 25.7% Co could be leached over 168 h (at pH > 1) in the absence of SMBS. This was increased to 66.3% with the use of SMBS—more than double.

Evaluation of Impact of Application Rate

Figures 6 provides the results of the two tests in which different application rates (10 and 20 L/h/m²) were used. Increasing the leaching solution application rate from 10 to 20 L/h/m² decreased Co extraction from 66.1 to 56.5%. The 10% point reduction was attributed to the increased rate of SMBS (placed in solid form on top of the ore in the column) washing from the column. We therefore used 10 L/h/m² as the application rate for the rest of the tests.

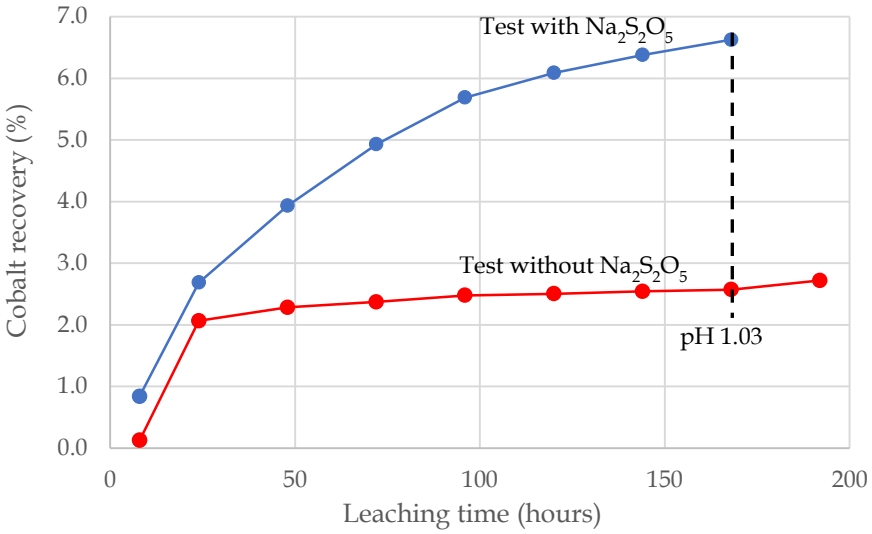

Figure 5: Effect of reducing agent on cobalt leaching efficiency.

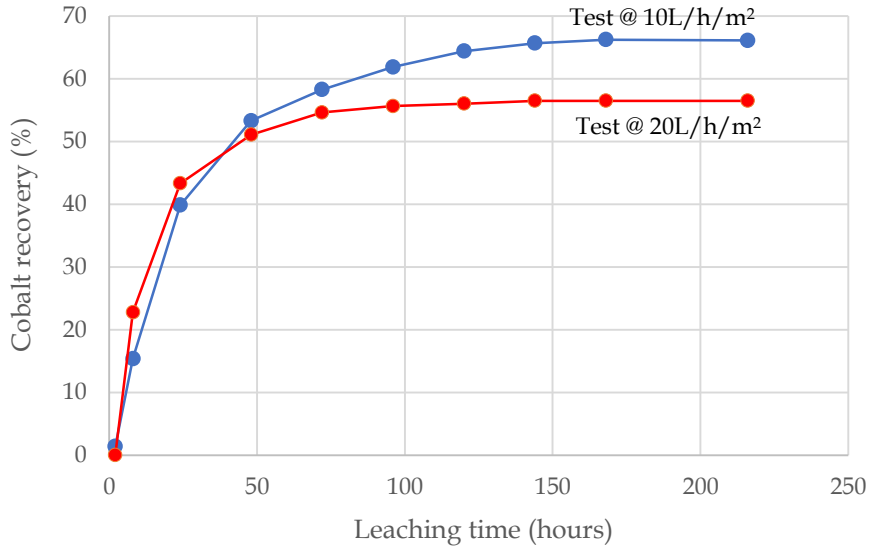

Figure 6: Effect of application rate on cobalt leaching efficiency.

Evaluation of Effect of Fines

We considered two size fractions for this test: with fines (−19 +1.18 mm) and without fines (−19 +6 mm). The results are presented in Figure 7. The cobalt leaching efficiency was, respectively, 66% and 38% for the two fractions: the test with fines yielded the higher recovery, probably because the cobalt is more concentrated in fines and the retention time of SMBS was higher (due to lower column permeability) than with coarse particles fraction. The finer particles also provided more surface area and a greater extent of exposure to the leach solution.

Evaluation of Effect of Acid Concentration

Figures 8 provides the results of tests conducted with acid concentrations of 16 and 20 g/L. The leaching efficiencies were 66.1% and 70.8% for the low and high acid solutions, respectively. The difference (5% points) in Co extractions was not very significant when the acid concentration was increased from 16 to 20 g/L in the leaching solution.

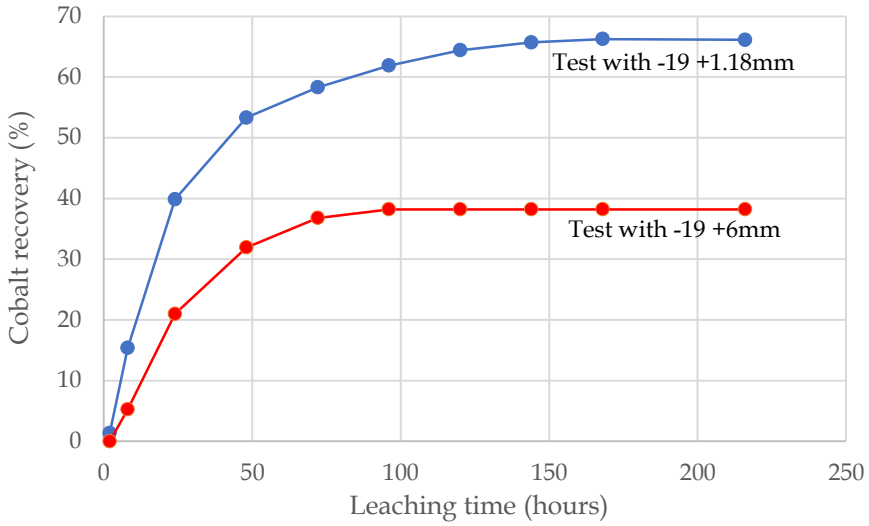

Figure 7: Effect of particles size on cobalt leaching efficiency.

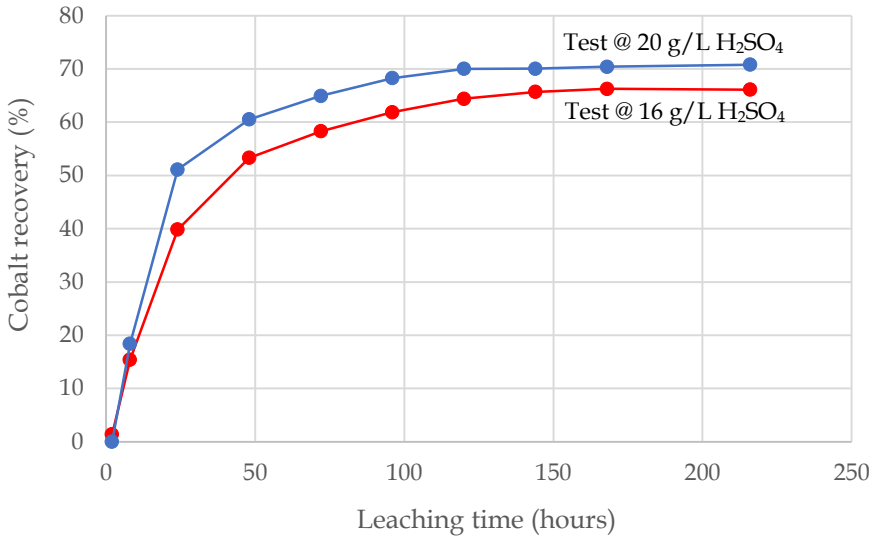

Figure 8: Effect of leaching solution acid content on the cobalt leaching efficiency.

SUMMARY OF HEAP LEACHING RESULTS AND DISCUSSION

The results from the laboratory column heap leaching tests are summarized in Table V.

Table V: Summary of metals extractions from different tests.

Test ID	Cum. Co extraction (%)	Cum. Cu extraction (%)
Test 1	27.2	82.2
Test 2	66.3	79.2
Test 3	55.1	81.6
Test 4	38.2	22.9
Test 5	70.0	63.6

The following observations were made from the results summarized in Table V:

- Test 1 yielded low cobalt leaching efficiency due to absence of SMBS.

- Test 2 yielded good leaching efficiency of both cobalt and copper for the leaching solution targeted in our study (LG raffinate). The higher copper extraction achieved with LG raffinate, in comparison with Test 5 where the HG raffinate was used, is attributed to the lower copper content of the LG raffinate.
- The increased of the application rate in Test 3 compared with Test 2 had a negative effect on the cobalt extraction, which decreased due to the increased wash out of SMBS from the column.
- Test 4 yielded low cobalt and copper extraction due to coarse particle size distribution.
- Although Test 5 yielded the highest cobalt extraction, Tests 2 and 3 gave the highest copper extractions. We considered that Test 2 gave the best result because the LG raffinate and cobalt extraction were targeted. Test 5 considered the HG raffinate with the aim of evaluating the impact of the acid content into the leaching solution and cobalt extraction was lower in Test 2.

ECONOMIC ANALYSIS

An economic analysis was performed that compared Case 1, where the LG raffinate is sent directly to cobalt precipitation, with Case 2, where the LG raffinate goes first to heap leaching before the produced intermediate LG PLS is sent to cobalt precipitation. We did not include Case 3, which is similar to Case 2, except for the capital expenditure required for SX: it considered building a 2E–1S SX (two extract, on strip stage) plant to extract the leached copper from the intermediate LG PLS before sending the produced intermediate LG raffinate to cobalt precipitation. Table VI provides the average compositions of the solutions considered in the three cases.

Table VI: Compositions of the solutions to cobalt plant.

Designation	Flow (m^3/h)	Acid (g/L)	Cu (g/L)	Co (g/L)	Fe (g/L)	Mn (g/L)	pH
LG raffinate	900	16.0	0.25	2.35	0.45	0.65	0.83
Intermediate LG PLS	900	4.0	2.78	2.88	0.65	0.70	1.42
Intermediate LG raffinate	900	7.8	0.23	2.88	0.65	0.70	1.10

The following assumptions of the reagents make-up and precipitation efficiencies were made when we completed the modelling of cobalt plant with the two feeds:

- Limestone was made up to 20% solids;
- MgO was made up to 20% solids;
- In Fe, Al, Mn (FAM) removal at pH 3.5, the precipitation efficiencies were:
  - 99% Fe;
  - 99% Mn;
  - 0% Cu;
  - 2% Co.
- In Cu removal at pH 5.3, the precipitation efficiencies were:
  - 99% Cu;
  - 10% Co (i.e., 10% of the Co fed to the circuit).
- In Co removal at pH 7.5, the precipitation efficiency was:
  - 100% Co.
- $[H_2SO_4] = 10^{(-pH)}/98$ (this is concentration in g/L), therefore:
  - pH 3.5 = 30.99 mg/L H_2SO_4;
  - pH 5.3 = 0.4911 mg/L H_2SO_4; and,
  - pH 7.5 = 0.003099 mg/L H_2SO_4.
- Copper precipitates as $Cu(OH)_2$ (not as a basic sulphate);
- Similarly, cobalt precipitates as $Co(OH)_2$ (not as a basic sulphate);
- Iron precipitates as $Fe(OH)_3$ (not as a basic sulphate);

- Manganese precipitates as $Mn(OH)_2$;
- The thickeners have an underflow solids density of 40%;
- SO_2/air additions are the same for all cases.

The above compositions of solutions and assumptions were used to generate simple mass balances. The results are presented in Table VII.

Table VII: Results of the cobalt plant modelling.

Case	Feed flow (m3/h)	FAM limestone (t slurry/h)	Cu limestone (t slurry/h)	Co MgO (t slurry/h)	$Co(OH)_2$ produced (t/h)	Co produced (t/h)
1	900	99.29	4.6	7.89	2.91	1.85
2	900	37.8	27.2	9.62	3.55	2.25
3	900	58.32	4.9	9.68	3.57	2.26

Table VIII provides the results of the economic evaluations of the two first cases. Only operating cost benefits were considered in the above evaluation.

Table VIII: Evaluation and economics of a case study.

Designation	Case 1	Case 2
Operating days per year	360	
Copper price (USD/t)	6985	
Cobalt price in $Co(OH)_2$ (USD/t)	65437.5	
Sulfuric acid price (USD/t)	275	
Limestone price (USD/t)	64.29	
Magnesia price (USD/t)	1160	
SMBS (USD/t)	630	
SMBS (t/h)	–	8.39
Limestone (t/h)	20.8	13.0
Magnesia (t/h)	1.58	1.92
Cobalt production (t/h)	1.85	2.25
Copper production (t/h)	0.17	1.94
Acid savings (t/h)	–	0.52
SMBS (USD million/a)	–	−45.7
Limestone (USD million/a)	−11.5	−7.2
Magnesia (USD million/a)	−15.8	−19.3
Cobalt production (USD million/a)	1046.0	1272.1
Copper production (USD million/a)	10.3	117.1
Acid savings (USD million/a)	–	1.2
Revenue benefit (USD million/a)	1028.9	1318.2
Overall benefit (USD million/a)	–	289.4

CONCLUSIONS

- The use of LG raffinate as leaching solution for a low-grade copper ore presents the benefits of using cost-free acid, reducing the neutralization chemicals costs and increasing the copper and cobalt production from a mined ore. In the case study example, the operating costs benefits are estimated in the order of USD 289 million/annum.

- There are, however, some capital costs, that we did not consider for Case 2, for introduction of the heap leaching plant within the existing circuit. The overall operating cost benefit is, however, so considerable that the extra capital cost should not eliminate this option.
- The introduction of solid SMBS in the heap, as the cobalt reducing agent, helped to more than double the cobalt extraction from the ore, compared with the case without it. Despite its cost, the increase in metals production and acid savings provide an overall benefit.
- The concept is relatively simple and could be easily incorporated into an existing flowsheet. A new copper SX plant is an option to consider, for Case 2, if the copper content in the final product (cobalt salts) presents any problem due to increased co-precipitation.

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