

REDUCTIVE PERCOLATION LEACHING OF A COPPER-COBALT ORE PART I: SODIUM SULPHITE AS REDUCING AGENT

By

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ABSTRACT

The Democratic Republic of the Congo (DRC) contains approximately half of the world's cobalt reserves, with an estimated production of 130 000 tonnes, accounting for nearly 70% of primary global cobalt production in 2022. Although mineralogical composition varies with depth and location, cobalt occurs typically in trivalent form as heterogenite (CoOOH) in the oxidised zone of deposits. It therefore needs to be reduced to the divalent state (Co(II)) before it can be leached in acidic sulphate solutions. In this study, the effect of sodium sulphite (Na_2SO_3) as a reducing agent in the ore agglomeration step was investigated on the rate of leaching of cobalt from heterogenite in 1 m (tall) leach columns.

An ore sample that originated from the DRC was used for the testwork. The sample contained 0.29% cobalt, 3.6% copper, 3.53% iron and 6.81% carbonate. The sample was crushed to 100% passing 25 mm with 80% passing 20 mm, 30% passing 5 mm and 13% passing 150 μm . Percolation leach tests were performed in Φ 160 mm (inside diameter), 1 m (tall), water-jacketed, polypropylene columns.

The leach results showed that cobalt dissolutions were sensitive to the Na_2SO_3 dosage used in agglomeration, increasing from 43% (0 kg SO_3 / t) to 62% (5 kg SO_3 / t) with open circuit irrigation of the orebed. Cobalt dissolution was further enhanced to 79% by operating in closed circuit with recycled Cu-SX raffinate, at the same reductant dosage (5 kg SO_3 / t) in agglomeration. Increasing the curing time from 3 days to 7 days had no effect on cobalt dissolution. Specific reagent consumptions were between 0 and 2.74 kg SO_3 / kg Co leached. The addition of sodium sulphite in agglomeration at dosages of up to 5 kg SO_3 / t ore had little effect on copper dissolution, with overall dissolutions of 90% to 95% achieved.

Keywords: Cobalt, Copper, Percolation, Reductive leach, Heap leaching

INTRODUCTION

Cobalt (Co) is a transition metal with unique physical properties, which makes it essential for high-technology applications such as high-strength materials, magnets and rechargeable batteries⁽²⁾. Due to its relatively low concentration in ores, cobalt is usually produced as a by-product of other metals, such as copper (Cu) and nickel (Ni). It occurs in a wide variety of deposit types, mostly Cu-Co sediment-hosted deposits⁽¹⁾⁽⁶⁾. Since cobalt is often not the primary focus of the mining operation, recoveries tend to be low, with cobalt regularly reporting to tailings or smelter slags⁽⁵⁾. Mount Cobalt mine in Queensland, Australia, and Bou Azzer mine in Morocco are examples where cobalt is the primary target metal⁽²⁾.

The Democratic Republic of the Congo (DRC) contains approximately half of the world's cobalt reserves, with an estimated production of 130 000 metric tonnes, accounting for nearly 70% of primary global cobalt production in 2022⁽⁷⁾. Although mineralogical composition varies with depth and location, cobalt occurs typically in trivalent form as heterogenite (CoOOH) in the oxidised zone of deposits⁽⁴⁾. It therefore needs to be reduced to the divalent state (Co(II)) before it can be leached in acidic sulphate solutions.

From the standard potentials of the redox reactions below, it can be seen that sulphite ions (SO₃²⁻), meta-bisulphite ions (S₂O₅²⁻), aqueous sulphur dioxide (SO_{2(aq)}), metallic copper (Cu) and ferrous ions (Fe²⁺) can all reduce heterogenite to soluble cobaltous ions (Co²⁺) since these are all lower than that for the CoOOH / Co²⁺ redox couple⁽⁷⁾.



Iron(III) oxides such as goethite (FeOOH) and limonite may also be present in copper-cobalt oxide ore deposits. On reaction with acid, these oxides release ferric ions into solution resulting in increased ferric-to-ferrous ratios and, as a result thereof, solution potentials as high as 650 mV (vs. Ag/AgCl; 3 M KCl). Such oxidative conditions may be kinetically unfavourable for the leaching of heterogenite by reductive dissolution in acidic sulphate solutions.

In this study, the effect of sodium sulphite (Na₂SO₃) as a reducing agent in the agglomeration step was investigated on the rate of leaching of cobalt from heterogenite in 1 m (tall) leach columns. The effect of Na₂SO₃ dosage, curing time and mode of operation (open or closed cycle) were investigated.

EXPERIMENTAL

Materials

The sample used in this study was a Cu-Co oxide ore from the DRC. The ore sample was jaw / cone crushed to 100% passing 25 mm. The crushed ore was blended and split into 30 kg batches. Three batches were randomly selected and screened using the following sieve sizes: 25 mm, 16 mm, 13.2 mm, 12.5 mm, 9.5 mm, 6.7 mm, 4.75 mm, 3.35 mm, 2.36 mm, 1.7 mm, 1.18 mm, 0.850 mm, 0.600 mm, 0.425 mm, 0.300 mm, 0.212 mm, 0.150 mm, 0.106 mm, 0.075 mm, 0.053 mm and 0.038 mm. After screening, the sizes were combined into 4 size classes (-25+6.7 mm, -6.7+3.35 mm, -3.35+1.18 mm and -1.18 mm) for head assay.

Chemical Assays

Solids

Solid head and leach residue samples were analysed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for: aluminium (Al), calcium (Ca), copper (Cu), cobalt (Co), chromium (Cr), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), silicon (Si), titanium (Ti), vanadium (V) and zinc (Zn). Carbonate (CO_3^{2-}) was determined by combustion technique (LECO). Potassium (K) and sodium (Na) were assayed by Atomic Absorption Spectroscopy (AAS). Total sulphur (S(T)) and sulphide sulphur (S^{2-}) were analysed by combustion technique (LECO).

Solutions

Daily pregnant leach solution (PLS) samples were analysed for copper and iron by AAS. Monthly accumulated PLS samples were analysed by ICP-OES for: Al, arsenic (As), Ca, Cu, Cr, Fe, lithium (Li), Mg, molybdenum (Mo), Ni, Pb, Si, Ti, V and Zn as part of the ICP base metal suite. Ferrous ion (Fe (II)) and sulphuric acid (H_2SO_4) concentrations were determined by titration methods.

All reported redox potentials were recorded against a 3 M KCl, Ag/AgCl reference electrode.

Mineralogy

The solid head sample was submitted for mineralogical investigation. The mineralogical information was obtained by Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) on a 100% -0.3 mm sample for individual size classes.

Column Leach Tests

Leach tests were performed in 1 m (tall) columns (Figure 1). All tests were conducted in Φ 160 mm (inside diameter), single sectioned, water-jacketed, polypropylene columns. The experimental matrix is summarised in Table 1.

During agglomeration, sodium sulphite (Na_2SO_3) was dissolved in 7 g/L H_2SO_4 solution and sprayed onto the ore while rolling on a plastic sheet to a total moisture content of 8%. All the columns were operated at 25 °C. Dosages of 0, 0.5, 1 and 5 kg SO_3 / t were added as Na_2SO_3 .

Tests were performed in open circuit (C1, C2, C3, C4 and C6) with 7 g/L H_2SO_4 in water (Rand Water Board) at 6 L/m²/h or in closed circuit (C5) with return raffinate. Test C5 was irrigated with 7 g/L H_2SO_4 in water, and the PLS was accumulated in batches. Copper removal by batch solvent extraction (SX) was then performed on the PLS. The acid concentration of the raffinate was adjusted to 7 g/L and the solution recycled back to the column.

The effect of curing time was evaluated by increasing the curing period from 3 days (C1, C2, C3, C4 and C5) to 7 days (C6).



Figure 1: 1 m Column Set-up

Table 1: Experimental Test Matrix

Condition	Units	Test					
		C1	C2	C3	C4	C5	C6
Temperature	°C	25	25	25	25	25	25
Moisture content in agglomeration	% w/w	8	8	8	8	8	8
Acid in agglomeration	kg H ₂ SO ₄ / t	24	24	24	24	24	24
Reductant in agglomeration	kg SO ₃ / t	0	0.5	1	5	5	5
Curing time	days	3	3	3	3	3	7
Acid in irrigation	g/L	7	7	7	7	7	7
Irrigation rate	L/m ² /h	6	6	6	6	6	6
Mode (of irrigation)		Open	Open	Open	Open	Closed	Open

All reagents were supplied by Associated Chemical Enterprises (ACE) as follows:

- H₂SO₄: sulphuric acid (98%)
- SO₃: as sodium sulphite (Na₂SO₃) (min. 97%)

RESULTS AND DISCUSSION

Particle Size Distribution (PSD)

Figure 2 shows the PSD's of three randomly selected 30 kg batches of the head sample, and the average PSD by mass. The narrow grouping between the profiles indicate that the blending and splitting of the head sample were performed satisfactorily. On average, the head sample had a

P₈₀ (80% passing) of 20 mm with 30% passing 5 mm, 20% passing 1 mm, 13% passing 150 µm and 11% passing 75 µm.

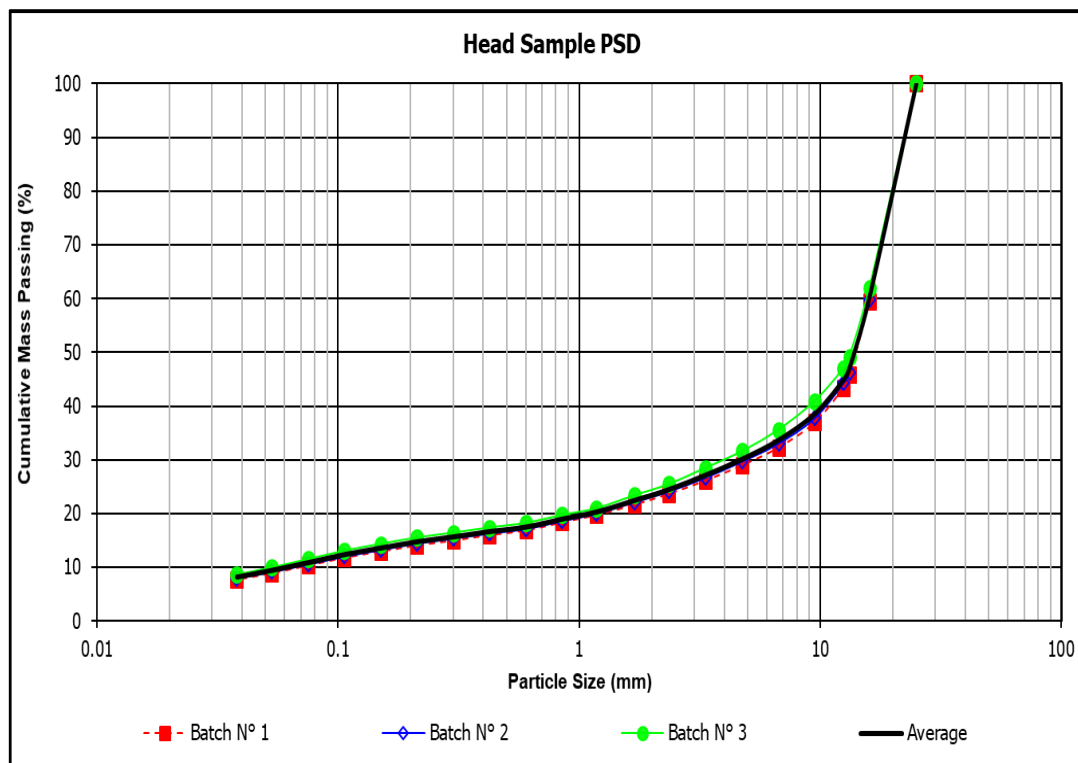


Figure 2: Head Sample PSD

Chemical Head Assays and Mineralogical Analysis

Table 2 shows the constituted chemical analysis of the head sample. The sample contained 3.6% copper, 0.29% cobalt, 3.53% iron and 6.81% carbonate (CO₃²⁻).

Table 3 shows size-class chemical analysis and the constituent distributions in the different size classes of the head sample. Copper (67%), cobalt (55%), iron (61%) and carbonate (82%) occurred primarily in the coarsest size fraction (-25+6.7 mm).

QEMSCAN analysis showed that copper deported as malachite (71.7%), chrysocolla (19.9%), pseudo-malachite (4%), chalcocite (4%) and very little chalcopyrite (< 1%). Cobalt occurred as heterogenite.

Table 2: Chemical Analysis of the Head Sample (Major Constituents)

Cu (%)	Co (%)	Fe (%)	CO ₃ ²⁻ (%)
3.60	0.29	3.53	6.81

Table 3: Size Class Chemical Analysis and Distributions of Major Constituents

Size Class (mm)	Cu		Co		Fe		CO ₃ ²⁻	
	(%) ¹	(%) ²	(%) ¹	(%) ²	(%) ¹	(%) ²	(%) ¹	(%) ²
-25+6.7	3.64	67.0	0.24	54.7	3.26	61.3	8.43	82.2
-6.7+3.35	3.90	7.02	0.29	6.40	3.81	7.01	5.60	5.34
-3.35+1.18	4.67	8.89	0.37	8.68	4.57	8.89	5.01	5.05
-1.18	3.05	17.1	0.44	30.3	3.97	22.8	2.50	7.43
Total	3.60	100	0.29	100	3.53	100	6.81	100

1) Constituent content for the ore size class.

2) Constituent content for the ore size class as a percentage of the total constituent content.

1 m Column Leach Tests

PLS pH and Potential Profiles

The PLS pH profiles are presented in Figure 3. The pH of the breakthrough solutions ranged from 1.5 to 2.7, after which levels increased to between pH 4 and pH 4.5. Thereafter the levels decreased, and remained within the range pH 1.4 to pH 2 from Day 95 up to the end of the leaching period. The high PLS pH that was experienced for a significant period of the leach was in all likelihood due to the high carbonate content (6.81%) of the ore sample. A water wash was implemented on Day 181 for all the tests except test C6 (Day 177), corresponding to the immediate pH rise at that point.

The PLS potential profiles are shown in Figure 4. The profiles for tests C1, C2 and C3 were similar over the first 20 days of leaching. However, a small decrease in corresponding potential with increased reductant dosage in agglomeration over the range 0 to 1 kg SO₃ / t is noticeable. It can also be seen that tests C2 (0.5 kg SO₃ / t) and C3 (1 kg SO₃ / t) remained at lower corresponding potentials for some time when the potential of test C1 (0 kg SO₃ / t) increased to about 550 mV. This may be explained by longer duration wash out of residual reductant in the orebed. Increasing the reductant dosage further from 1 to 5 kg SO₃ / t ore (C4, C5 and C6) resulted in a more pronounced decrease in corresponding potential, e.g. by at least 100 mV, as can be seen during the first 30 days of leaching. Over time the potential profiles of tests C1, C2, C3, C4 and C6 reached levels of up to about 650 mV.

The PLS potential for test C5 (5 kg SO₃ / t), which was operated in closed circuit with recycled raffinate solution, remained low in comparison with the other columns.

Cobalt and Copper Dissolution Profiles

Cobalt and copper dissolution profiles are presented in Figures 5 and 6, respectively. These were plotted from the recalculated metal head grade and metal in solution assays. The recalculated head grade entails a 100% element mass balance (i.e. element out / element in) with respect to both solid and solution phases over the leach, water wash and drain-down stages.

The use of a reductant in agglomeration at dosages of 0.5 kg SO₃ / t (C2) to 1 kg SO₃ / t (C3) achieved noticeable improvement of initial and overall cobalt dissolution, with significant further enhancement at a dosage of 5 kg SO₃ / t (C4 and C6). Moreover, raffinate recycling in conjunction with 5 kg SO₃ / t in agglomeration rendered the highest overall cobalt dissolution of 79% (C5) compared with the other tests (43% to 61%; Table 4). From Figure 5 it can be seen that test C5's rate of cobalt dissolution became 'negative' directly after introduction of the recycled raffinate solution. This is due to the fact that the raffinate entering the orebed contained a higher cobalt concentration than the solution in the bed at that time. Once this volume was 'pushed' out of the bed, daily cobalt dissolution calculated as $\Sigma(\text{mass of cobalt})_{\text{PLS}} - \Sigma(\text{mass of cobalt})_{\text{irrigation}}$ became positive again. Hereafter, the rate of cobalt dissolution showed a marked increase as is evident from the steeper dissolution profile. Closed circuit operation with Cu-SX raffinate solution could return unreacted sulphite ions beneficially for the leach, and / or even other reductants that have accumulated in solution such as ferrous ions (Equation 6). This presents a plausible explanation for test C5's lower PLS potentials (from Day 35 onwards) compared with those for tests C4 and C6, which were operated in open circuit with acidified water only.

Similar dissolution profiles for tests C4 (5 kg SO₃ / t, 3 days curing) and C6 (5 kg SO₃ / t, 7 days curing) indicated that curing for longer than 3 days had no effect on initial and overall cobalt dissolutions.

The addition of reductant in agglomeration up to 5 kg SO₃ / t had little effect on copper dissolution during the initial stages of leaching. Overall copper dissolutions were similar and ranged between 90% and 95% (Table 4), with a slightly higher dissolution achieved for the test operated in closed circuit (C5).

Reductant and Acid Consumptions

Specific reductant consumptions, in kg SO₃ / kg Co (leached), were calculated from the reductant dosage used in agglomeration, the recalculated cobalt head grade and overall cobalt dissolution. The values are listed in Table 4.

Table 4 also includes acid consumptions that were calculated as follows:

Total Acid Consumption (TAC):

$$mTAC = mFEED - mPLS \quad (7)$$

Net Acid Consumption (NAC):

$$mNAC = mFEED - mPLS - mSX \quad (8)$$

mTAC: total acid consumption, in kg H₂SO₄ / t (dry) ore

mFEED: acid in the irrigation solution and agglomeration, in kg H₂SO₄ / t (dry) ore

mPLS: acid in the PLS, in kg H₂SO₄ / t (dry) ore

mSX: acid in the raffinate solution after copper solvent extraction (SX), in kg H₂SO₄ / t (dry) ore
(1.54 kg H₂SO₄ / 1 kg Cu extracted)

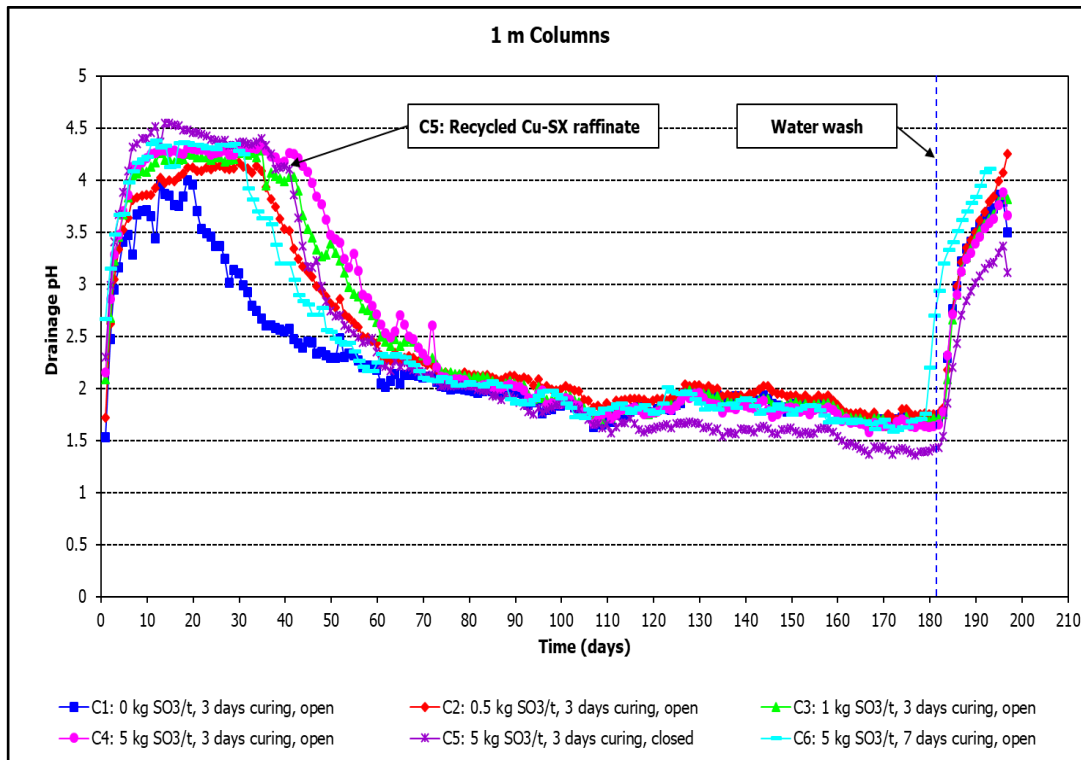


Figure 3: PLS pH

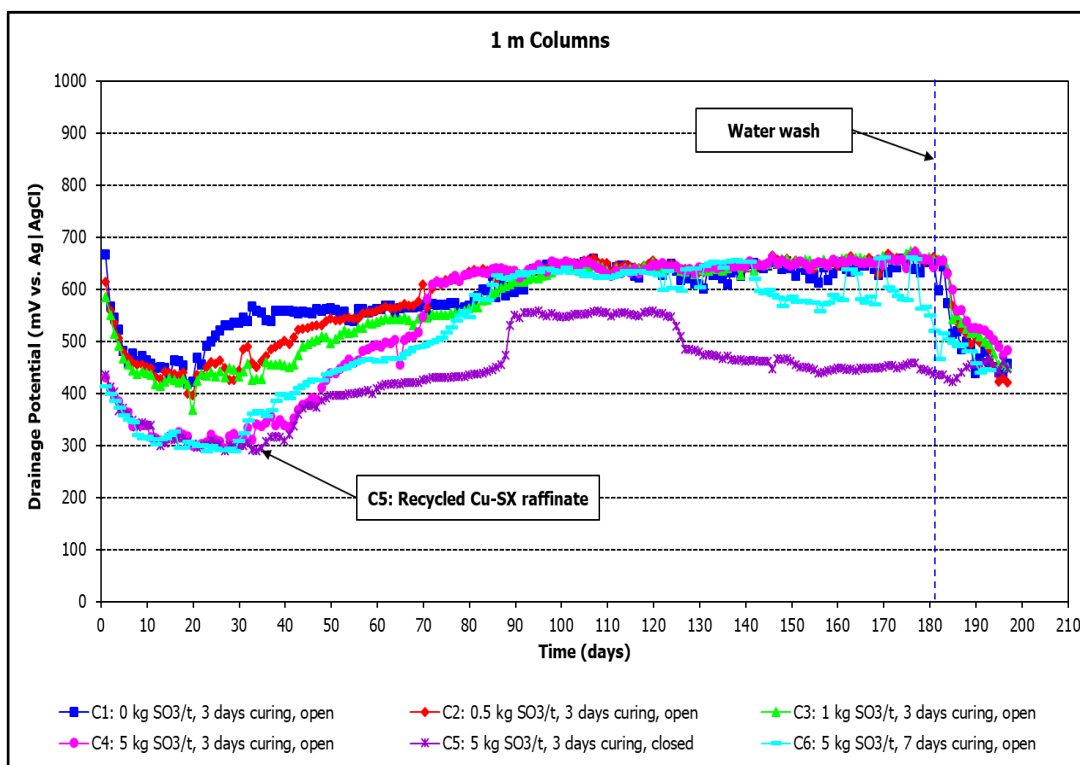


Figure 4: PLS Potential

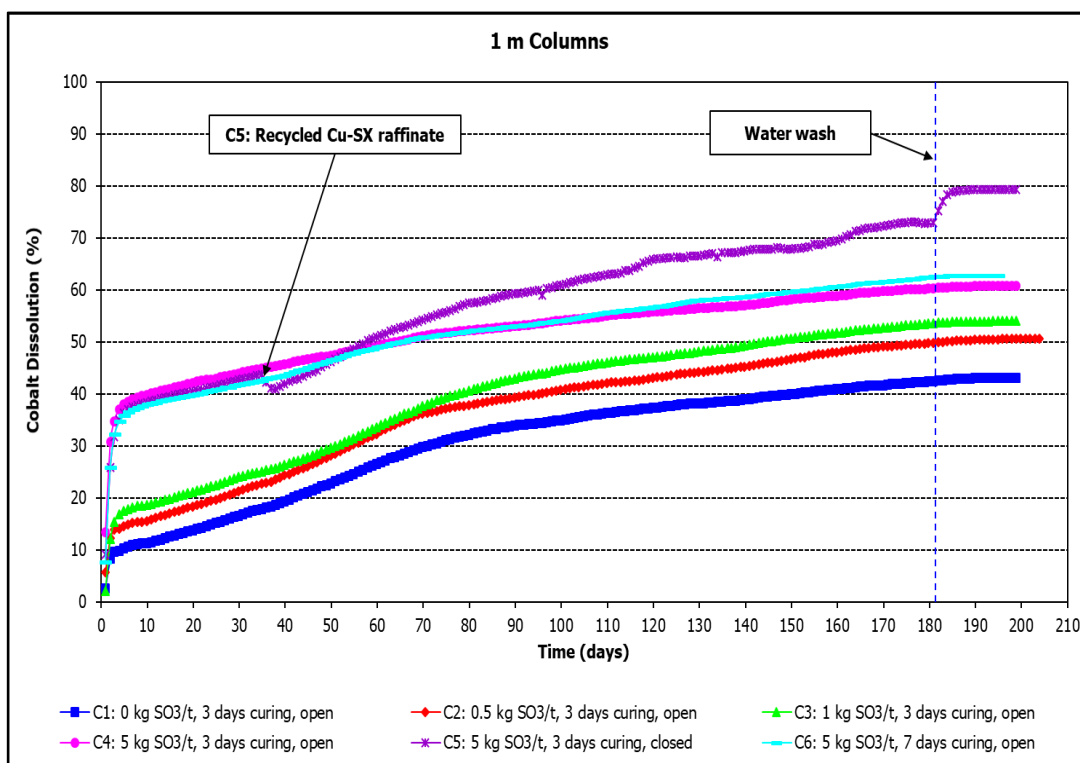


Figure 5: Cobalt Dissolution vs. Time

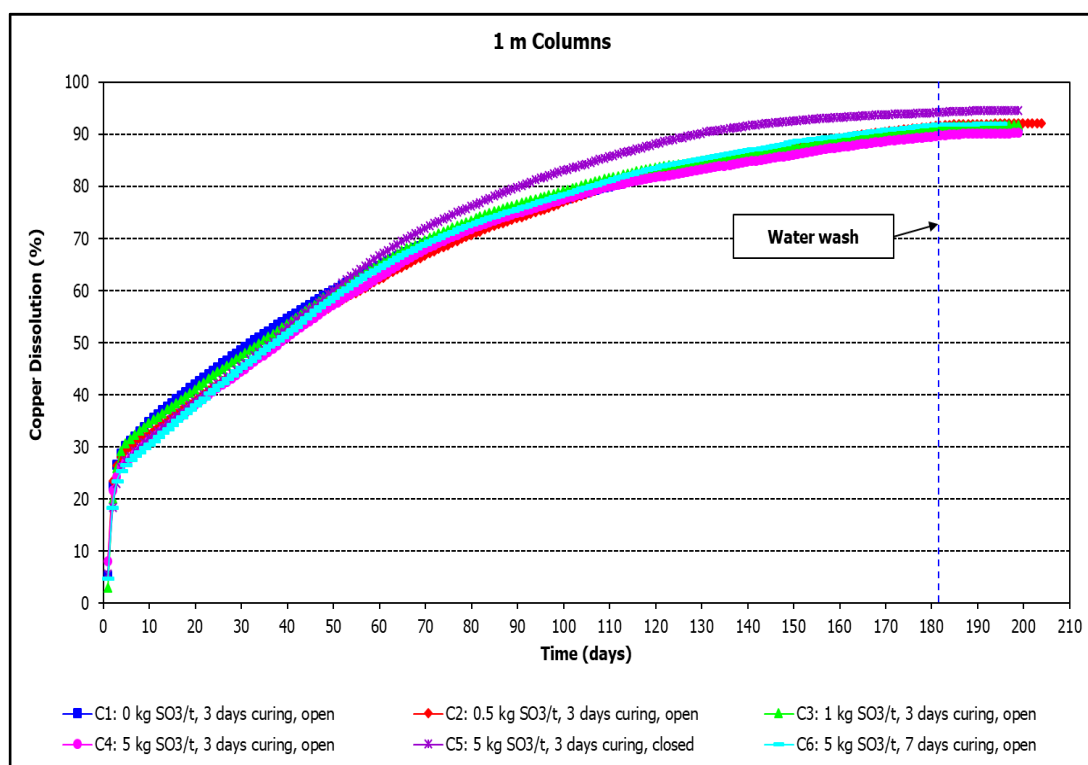


Figure 6: Copper Dissolution vs. Time

Table 4: Cobalt Dissolutions, Copper Dissolutions, Acid and Reductant Consumptions

Test	Conditions (dosage; curing; mode)	Metal Dissolution		Reagent Consumption		
		Co (%)	Cu (%)	TAC (kg H ₂ SO ₄ / t)	NAC (kg H ₂ SO ₄ / t)	Reductant (kg SO ₃ / kg Co)
C1	0 kg SO ₃ / t; 3 days; open	43.1	91.0	162	111	0
C2	0.5 kg SO ₃ / t; 3 days; open	50.6	92.1	161	109	0.37
C3	1 kg SO ₃ / t; 3 days; open	54.0	91.8	163	113	0.65
C4	5 kg SO ₃ / t; 3 days; open	60.8	90.3	157	109	2.74
C5	5 kg SO ₃ / t; 3 days; closed	79.4	94.6	128	76	2.00
C6	5 kg SO ₃ / t; 7 days; open	62.8	92.1	147	109	2.66

CONCLUSIONS

Enhanced cobalt recoveries were achieved in 1 m column leach tests by the addition of a reductant (Na_2SO_3) in the ore agglomeration step prior to leaching. This potentially provides a simple and practical way of improving cobalt recoveries during heap leaching of Cu-Co ores, where cobalt is in the form of heterogenite.

Cobalt dissolutions were sensitive to the reductant dosage, increasing from 43% (0 kg SO_3 / t) to 62% (5 kg SO_3 / t) in open circuit. Cobalt dissolution was further enhanced to 79% by operating in closed circuit with recycled Cu-SX raffinate, at the same reductant dosage (5 kg SO_3 / t) in agglomeration. Increasing the curing time from 3 days to 7 days had no effect on cobalt dissolution. Specific reagent consumptions were between 0 and 2.74 kg SO_3 / kg Co leached.

The addition of sodium sulphite in agglomeration at dosages of up to 5 kg SO_3 / t ore had little effect on copper dissolution, with overall dissolutions of 90% to 95% achieved.

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REFERENCES

1. Dehaine, Q., Filippov, L.O., Filippova, I.V., Tijsseling, L.T. and Glass, H.J., 2019a. Processing of a complex carbonate-rich Cu-Co mixed ore via reverse flotation, in: Flotation'19. MEI, Cape Town.
2. Fisher, K.G., Cobalt processing developments. Bateman Engineering Projects. The Southern African Institute of Mining and Metallurgy, 6th Southern African Base Metals Conference 2011: 237-258.
3. Outotec HSC Chemistry 6.1 software.
4. Schmidt, T., Buchert, M. and Schebek, L., 2016. Investigation of the primary production routes of nickel and cobalt products used for Li-ion batteries. *Resour. Conserv. Recycl.* 112, 107-122.
5. Slack, J.F., Kimball, B.E. and Shedd, K.B., 2017. Cobalt. In: Schulz, K.J., DeYoung, J.H., Seal, R.R. and Bradley, D.C., (Eds.), *Critical Mineral Resources of the United States*.
6. Smith, C.G., 2001. Always the bridesmaid, never the bride: cobalt geology and resources. *Transactions of the Institution of Mining and Metallurgy Section B-Applied Earth Science* 110, B75-B80.
7. U.S. Geological Survey, Mineral Commodity Summaries, January 2023.