REDUCTIVE PERCOLATION LEACHING OF A COPPER-COBALT ORE PART II: FERROUS ION AS REDUCING AGENT

By

Nontobeko Nxumalo, Petrus Basson, Mpumelelo Ndhlalose

Mintek, South Africa

Presenter and Corresponding Author

Nontobeko Nxumalo

ABSTRACT

Oxidised copper-cobalt ore deposits from the Central African Copperbelt contain cobalt(III) oxide minerals such as heterogenite (CoOOH) and stainierite (Co_2O_3), which require reduction of Co(III) to soluble Co(II) for dissolution in acidic sulphate solutions. Reducing agents commonly used in hydrometallurgical plants include sodium metabisulphite ($Na_2S_2O_5$; SMBS), sulphur dioxide (SO_2), ferrous ion (Fe(II)) and pulverised copper metal (Cu°). Several studies have been conducted on the subject matter showing that these reductants can improve cobalt recovery up to 90% when applied in tank leaching. There are limited studies focusing on reductive cobalt recovery from economically marginal ores, which are only treatable by low cost processes such as heap leaching. This study investigated the effect of ferrous ion as a reducing agent in the percolation leach of a copper-cobalt oxide ore.

A copper-cobalt ore sample from the Katanga Province of the Democratic Republic of the Congo (DRC) was used for the testwork. The ore sample contained 952 ppm cobalt, 2.33% copper, 4.05% iron and 1.27% carbonate, with 92% acid-soluble copper. The ore sample was crushed to 100% passing 25 mm with 80% passing (P_{80}) 18 mm. The percolation leach tests were conducted in Φ 160 mm (inside diameter), 6 m (height), water-jacketed, polypropylene columns.

The addition of ferrous ion in the irrigant improved the extent of overall cobalt dissolution by up to 41 percentage points. About 50% of the cobalt could be leached within 9 days with the addition of 3.7 kg ferrous / t ore in agglomeration. The extents of overall cobalt dissolution achieved were 40% in the absence of ferrous ion and up to 81% with ferrous in agglomeration and in the irrigant. The reductive conditions did not have an adverse effect on the copper dissolution, with the average extent of overall copper dissolution reaching 95%.

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

INTRODUCTION

Cobalt is generally recovered in low quantities as a by-product during other major metal extraction processes such as copper and nickel(1). The increase in the cobalt demand in recent years, mainly driven by the demand in lithium-ion batteries, has compelled operations to seek effective methods of recovering this valuable metal(6).

The Central African Copperbelt boasts approximately half of the world's cobalt reserves(1). The Democratic Republic of the Congo (DRC) is by far the world's largest producer of cobalt, accounting for roughly 70 percent of global production. The country has been the top producer of cobalt for some time, with a reported output of 130 000 metric tonnes in 2022, and is likely to remain a crucial cobalt producer for the near future(2)(4).

Oxidised copper-cobalt ore deposits from the Central African Copperbelt contain cobalt(III) oxide minerals such as heterogenite (CoOOH) and stainierite (Co_2O_3), which require reduction of Co(III) to soluble Co(II) for dissolution in acidic sulphate solutions. Reducing agents commonly used in hydrometallurgical plants include sodium metabisulphite ($Na_2S_2O_5$; SMBS), sulphur dioxide (SO_2), ferrous ion (Fe(II)) and pulverised copper metal (Cu^o). Several studies have been conducted on the subject matter showing that these reductants can improve cobalt recovery up to 90% when applied in tank leaching(3)(5). There are limited studies focusing on reductive cobalt recovery from economically marginal ores, which are only treatable by low cost processes such as heap leaching.

In this study, the effect of ferrous ion in agglomeration and in the irrigation solution on the rate and extent of cobalt dissolution from an oxidised copper-cobalt ore was investigated in 6 m (height) percolation leach columns. The achievement of satisfactory cobalt dissolution at mildly reductive conditions (solution potentials > 350 mV vs. Ag/AgCl; 3 M KCl) will be a reagent cost saving for cobalt producing heap leach operations. Ferrous ions are significantly less expensive than reductants such as sulphite and can be produced on site from scrap iron and sulphuric acid whilst other reductants / reagents are typically transported to site from a remote location(7).

EXPERIMENTAL

Ore Sample

The sample used in this study was a Cu-Co oxide ore from the Katanga Province in the DRC. The ore was jaw / cone crushed to 100% passing 25 mm. The crushed ore was blended and submitted for particle size distribution (PSD) analysis on 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, 850 µm, 600 µm, 425 µm, 300 µm, 212 µm, 150 µm, 106 µm, 75 µm, 53 µm and 38 µm. Thereafter the material was combined into four size classes: -25+16 mm, -16+6.7 mm, -6.7+1.18 mm and -1.18 mm for head analysis by size class.

Chemical Analysis

Solids

Solid head and column 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), as well as sequential / diagnostic copper leaching (acid and cyanide digestion method). 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.

Mineralogical Analysis

The solid head sample was submitted for mineralogical investigation. Automated image analysis, utilising Backscattered Electron (BSE) and Energy Dispersive X-ray (EDX) signals from a Scanning Electron Microscope (SEM), was used to create digital images in which each pixel corresponds to mineral species in the corresponding region under the electron beam. A QEMSCAN Particle Mineral Analysis (PMA) protocol was used for the analysis. This method was selected so as to attain the overall mineral assemblage of the sample, as well as the copper and cobalt deportments.

QEMSCAN: quantitative evaluation of minerals by scanning electron microscopy

Column Leach Tests

Five 6 m (height) column leach tests were conducted in 160 mm (inside diameter), water-jacketed, polypropylene columns. The experimental matrix is summarised in Table 1.

The columns were operated in open circuit, at 25 °C. Irrigation was carried out with synthetic raffinate at 10 $L/m^2/h$. The ore was agglomerated with synthetic raffinate and 98% H_2SO_4 to a total moisture content of 8% and a total amount of 10.8 kg/t H_2SO_4 in agglomeration. The effect of adding ferrous ion in the ore agglomeration step on the rate of cobalt dissolution was evaluated by using a 3.7 kg/t dosage (C5). The rest of the tests were conducted at varying ferrous concentrations in the irrigation solution. The ferrous concentrations tested were: 0 g/L (C1; base case), 0 mg/L to 400 mg/L (C2), 300 mg/L (C3 and C5), and 1.5 g/L (C4). The ferrous ion was added as 99% ferrous sulphate ($FeSO_4 \cdot 7H_2O$) (supplied by Associated Chemical Enterprises (ACE)).

Figure 1: 6 m Column Set-up

Table 1: 6 m Column Leach Test Matrix

Conditions	Units	C1	C2	C3	C4	C5
Crush size (100% passing)	mm	25	25	25	25	25
Column inside diameter (ID)	mm	160	160	160	160	160
Temperature	°C	25	25	25	25	25
Cure / rest duration	days	3	3	3	3	3
Leach duration	days	248	248	248	248	248
Agglomeration / Loading						
Loading bulk density (dry)	t/m^3	1.4	1.4	1.4	1.4	1.4
Moisture content	% w/w	8	8	8	8	8
Concentrated acid (98% H_2SO_4)	kg/t	10	10	10	10	10
Total acid (conc. + raffinate)	kg/t	10.8	10.8	10.8	10.8	10.8
Total iron (Fe(T))	kg/t	0.105	0.105	0.105	0.105	3.7
Ferrous (Fe(II))	kg/t	-	-	0.021	0.105	3.7
Ferric (Fe(III))	kg/t	0.105	0.105	0.083	-	-
Aluminium (Al)	kg/t	0.110	0.110	0.110	0.110	0.110
Magnesium (Mg)	kg/t	0.105	0.105	0.105	0.105	0.105
Irrigation Solution						
Irrigation flowrate	$L/m^2/h$	10	10	10	10	10
[H_2SO_4]	g/L	10	10	10	10	10
[Fe(T)]	g/L	1.5	1.5	1.5	1.5	1.5
[Fe(II)]	g/L	-	0 - 0.4(1)	0.3	1.5	0.3
[Fe(III)]	g/L	1.5	1.5 - 1.1(1)	1.2	0	1.2
[Al]	g/L	1.6	1.6	1.6	1.6	1.6
[Mg]	g/L	1.5	1.5	1.5	1.5	1.5

1) The ferrous concentration of the irrigation solution was increased from 0 to 400 mg/L, after 97 days of leaching.

All reagents were supplied by ACE as follows:

- Al : aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) (100-110%)
- Fe(II) : ferrous sulphate ($FeSO_4 \cdot 7H_2O$) (99%)
- Fe(III) : ferric sulphate anhydrous ($Fe_2(SO_4)_3 \cdot xH_2O$) (20-23% Fe)
- Mg : magnesium sulphate ($MgSO_4 \cdot 7H_2O$) (99-100.5%)
- H_2SO_4 : sulphuric acid (98%)

RESULTS AND DISCUSSION

Head Sample Characterisation

Particle Size Distribution

Figure 2 shows the particle size distributions of three, randomly-selected batches of the crushed head sample together with the average (by mass). The blending and splitting of the sample were satisfactory as confirmed by the narrow grouping of the PSD profiles. On average, the head sample had a P_{80} (80% passing) of 18 mm with 26% passing 1.18 mm and 13% passing 150 µm.

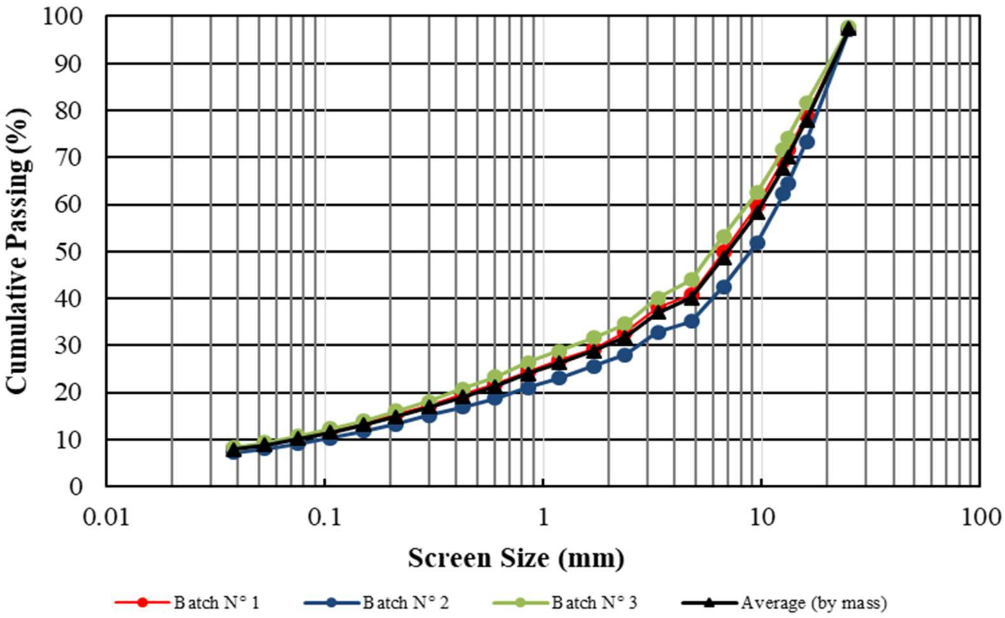

Figure 2: Particle Size Distribution of the Head Sample

Chemical and Mineralogical Analysis

Table 2 shows the chemical analysis and distribution of the major elements of the head sample. The average assays were calculated from the composite head sample and constituted head sample from particle size classes -25+16 mm, -16+6.7 mm, -6.7+1.18 mm and -1.18 mm.

Table 2: Major Element Mass Distribution of the Head Sample

Size Class	Mass	Co		Cu		Fe		CO_3
(mm)	(%)	(ppm)$^{(1)}$	(%)$^{(2)}$	(%)$^{(1)}$	(%)$^{(2)}$	(%)$^{(1)}$	(%)$^{(2)}$	(%)
-25+16	22.0	530	11.3	1.21	12.0	3.30	18.0	
-16+6.7	29.3	724	20.5	2.14	28.4	3.41	24.8	
-6.7+1.18	22.4	862	18.6	2.60	26.3	3.99	22.1	
-1.18	26.2	1956	49.6	2.81	33.3	5.40	35.1	
Overall	100	1035	100	2.22	100	4.04	100	
Composite		868		2.45		4.07		1.27
Average		952		2.33		4.05		1.27

1) Element content for size class or composite.
2) Element content for size class as a percentage of the total element content.

The ore sample contained 2.33% copper, 952 ppm cobalt, 4.05% iron and 1.27% carbonate. The element distributions show that 50% of the cobalt and 33% of the copper were contained in the -1.18 mm size class.

The sequential copper leach analysis indicated that the sample contained 92% acid-soluble copper, a marginal amount of cyanide-soluble copper (less than 1% of the total copper) and 7% non-soluble copper, which is in good agreement with the low sulphide sulphur concentrations assayed.

Copper occurred as malachite (53%), pseudo-malachite (20%), goethite Cu (9%), MnFeCuCoSilicate wad (8%), chrysocolla (6%), cuprite (1%) and very little (< 1%) of chalcocite, CuCoMn wad, Cu-bearing chlorite, bornite and chalcopyrite. Cobalt was present as MnFeCuCoSilicate wad (67%), heterogenite (28%) and Cu-Co wad (5%).

The chemical analyses of the other constituents of the head sample are presented in Table 3.

Table 3: Chemical Analysis of the Head Sample (other constituents)

Element	Unit	Size (mm)				Overall	Composite	Average
		-25+16	-16+6.7	-6.7+1.18	-1.18			
Mass	%	22.0	29.3	22.4	26.2	100		
Al	%	6.69	6.29	5.75	5.42	6.03	6.05	6.04
As	ppm	155	276	347	409	300	228	264
Ca	%	0.36	0.20	0.19	0.20	0.23	0.23	0.23
Cr	ppm	23	29	25	36	29	32	30
K	%	-	-	-	-	-	2.78	2.78
Mg	%	4.36	3.25	2.75	3.05	3.33	3.38	3.35
Mn	%	0.06	0.06	0.06	0.22	0.1	0.09	0.10
Na	ppm	-	-	-	-	-	218	218
Ni	ppm	120	115	118	162	129	141	135
Pb	ppm	108	231	306	431	273	335	304
Si	%	31.0	32.2	32.8	31.8	32.0	31.3	31.6
S(T)	%	-	-	-	-	-	0.03	0.03
S^{2-}	%	-	-	-		-	< 0.01	< 0.01
Ti	%	0.80	0.74	0.65	0.66	0.71	0.70	0.70
V	ppm	249	369	417	440	372	360	366
Zn	ppm	243	368	418	686	435	418	427

Column Leach Tests

The testwork comprised five column leach tests: C1, C2, C3, C4 and C5. The vertical broken line in the subsequent graphs denotes the end of the leaching stage; thereafter follows the water wash / rinsing stage.

Redox Potential and pH Profiles

Figures 3 and 4 display the redox potential and pH profiles of the irrigation solutions, respectively. The potential was between 600 mV and 650 mV for columns C1 and C2, which were conducted in the absence of ferrous iron (all the iron in the irrigation solution was ferric). However, 400 mg/L of ferrous was introduced into the irrigation solution for column C2 after 97 days; thus reducing the potential to about 480 mV. The average potential was 480 mV for columns C3 and C5, which were irrigated with 300 mg/L ferrous. Column C5 was irrigated with all iron as ferrous; thus at the lowest potential of 370 mV.

The H_2SO_4 concentration in the irrigant was kept constant at 10 g/L, which kept the pH relatively constant between 1 and 1.2. Initial pH of the PLS ranged from 2.5 to 3.2, with the lowest being that of column C5 which was agglomerated with 3.7 kg/t ferrous. The PLS pH profiles peaked between 3.8 and 4.0, and thereafter decreased steadily to between 1.4 and 1.6 after 248 days of leaching. The decrease in pH is likely due to the slower leaching of acid-consuming gangue minerals over time.

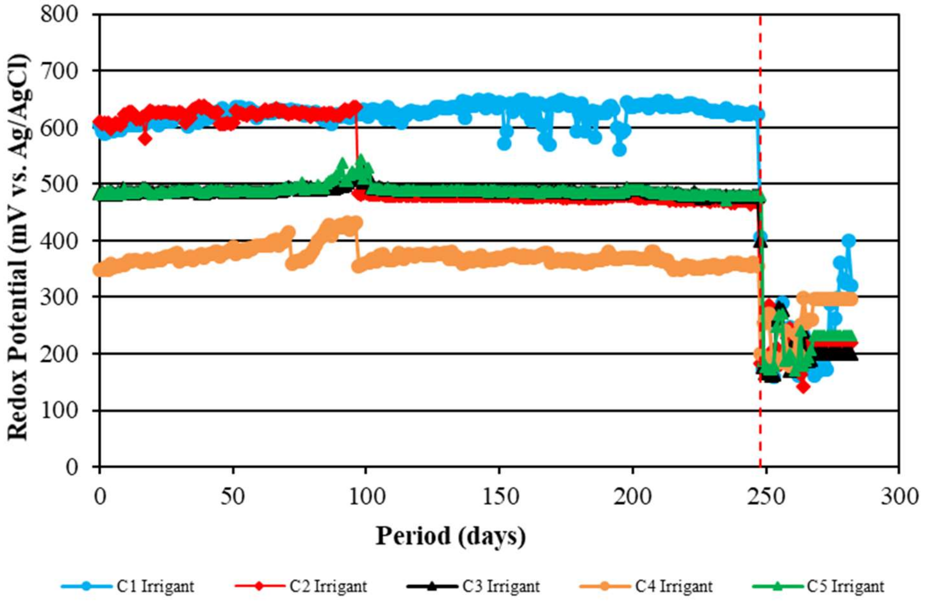

Figure 3: Redox Potential Profiles (Irrigant)

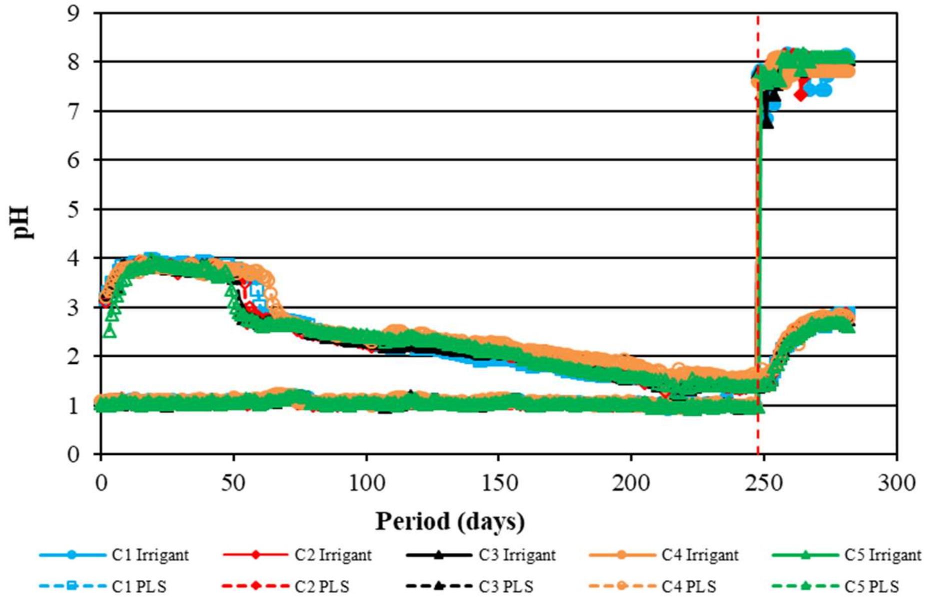

Figure 4: pH Profiles

Copper, Cobalt and Iron Dissolutions

Copper, cobalt and iron dissolution profiles are presented in Figures 5 to 7, respectively. These were plotted from the recalculated metal head grade and metal in solution analyses. 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 / rinsing and drain-down stages.

Similar copper dissolution profiles were observed for all the tests. The overall copper dissolutions were between 94% and 96% after 248 days of leaching.

Column C1, which did not have any ferrous in the irrigant, showed the lowest cobalt dissolution of 40%, the solution potentials were high (> 600 mV) and not conducive for cobalt dissolution. A notable improvement in the rate of cobalt leaching was observed for column C2 after 97 days, which corresponded with the addition of 400 mg/L ferrous in the irrigant. The addition of ferrous in the irrigant (300 mg/L to 1.5 g/L) improved the extent of overall cobalt dissolution by between 38 and 41 percentage points. The effect of adding ferrous in agglomeration on the initial rate of cobalt dissolution was more pronounced than that of adding ferrous in the irrigation solution. This is supported by the rapid initial cobalt dissolution for column C5 (at 3.7 kg ferrous / t ore in agglomeration), reaching 50% after 9 days. This is much higher than that of column C3 (300 mg/L ferrous in the irrigant) and column C4 (1.5 g/L ferrous in the irrigant) which were only at 11% and 16% dissolution respectively, after 9 days. The overall cobalt dissolutions after 282 days were: 40% for C1, 78% for C2, 80% for C3, 81% for C4 and C5.

The negative iron dissolutions depicted (up to 132 days) were because of iron precipitation (i.e. ferric) during the high pH period experienced in the ore beds. The profiles show a gradual increase in the iron in solution after 60 days, which corresponds to a rapid drop in pH to between 1.8 and 2.3. The overall iron dissolutions were between 11% and 14% after 282 days.

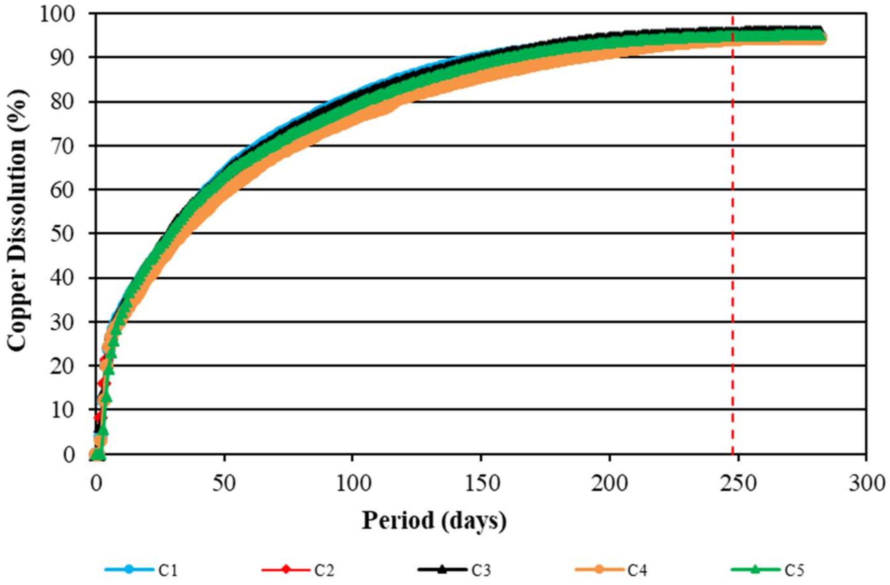

Figure 5: Copper Dissolution Profiles

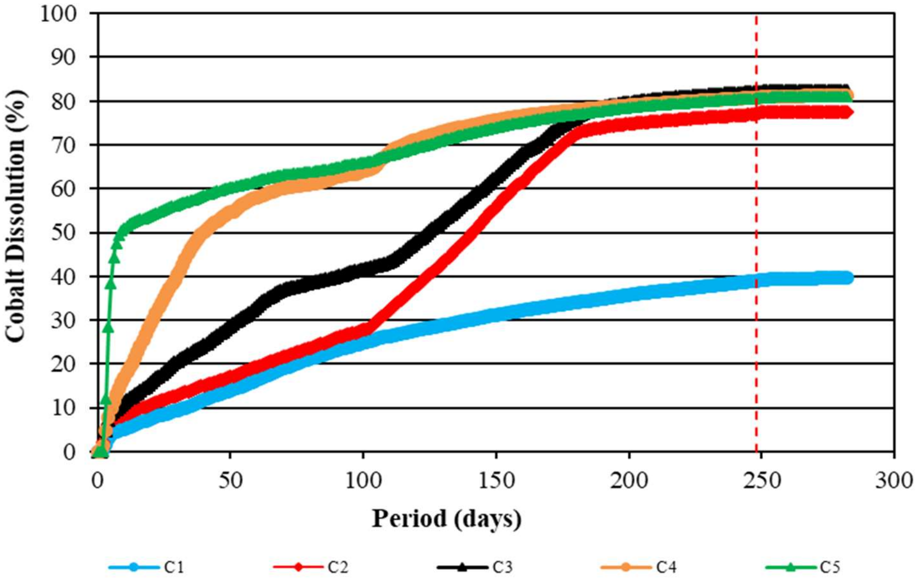

Figure 6: Cobalt Dissolution Profiles

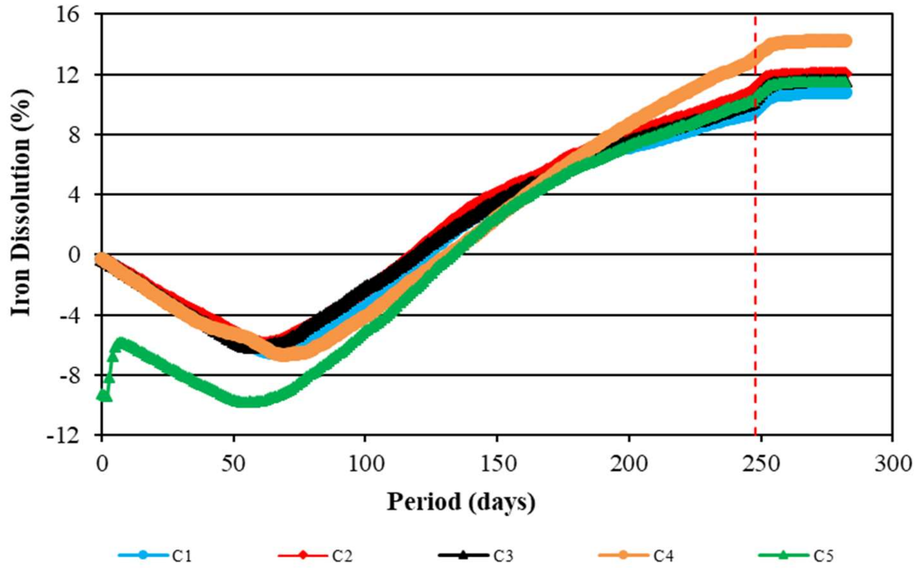

Figure 7: Iron Dissolution Profiles

Acid Consumption Profiles

The net acid consumption (NAC) profiles corresponding to the aforementioned metal dissolutions are depicted in Figure 8. These are defined as follows:

$$mNAC = mFEED - mPLS - mSX \tag{1}$$

With:

mNAC : net acid consumption, in kg H_2SO_4 / t (dry) ore
mFEED : acid in the irrigation solution, in kg H_2SO_4 / t (dry) ore
mPLS : acid in the PLS, in kg H_2SO_4 / t (dry) ore
mSX : acid in the raffinate solution after copper solvent extraction (SX), in kg H_2SO_4 / t (dry) ore (1.54 kg H_2SO_4 / 1 kg Cu extracted)

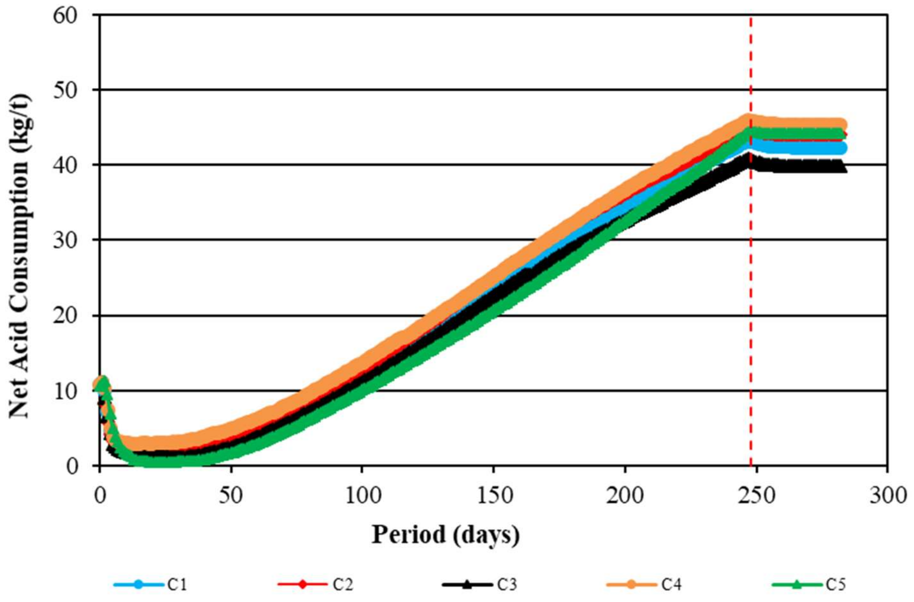

Figure 8: Net Acid Consumption Profiles

The acid consumption profiles were very similar, this was expected since the tests were conducted on the same ore sample and the same amount of acid was added in agglomeration and in the irrigation solutions. The average net acid consumption was 43 kg H_2SO_4 / t ore after 282 days**.**

CONCLUSIONS

The results presented in this paper demonstrate the ability of ferrous ion to enhance the dissolution of Co(III) minerals at solution potentials above 350 mV, by the addition of as little as 300 mg/L Fe(II) in the irrigation solution. A significant improvement in the initial rate of cobalt dissolution was achieved with the addition of Fe(II) in the agglomeration step. The addition of Fe(II) had no adverse effect on the copper dissolution, with the average extent of overall copper dissolution reaching 95% over a period of 282 days.

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