19-24:Template Journal 6/25/09 11:54 AM Page 337

A cobalt solvent extraction investigation in Africa's Copper Belt

by T. Könighofer*, S.J. Archer†, and L. Bradford‡

Synopsis

Processing of copper-cobalt orebodies in Africa's Copper Belt has received much recent attention with various flowsheet options being developed specifically for the refining of cobalt. The upfront leach and copper refining routes are well understood whereas the refining of cobalt is more complex, requiring numerous impurity removal steps to produce high purity metal. This paper describes an investigation into one of the possible processing steps in the refining of cobalt, namely, cobalt solvent extraction.

The paper emphasizes the importance of upstream impurity removal to achieve the required cobalt solvent extraction feed composition. 18% (v/v) Cyanex 272 in an aliphatic diluent is used as the organic phase. The pH profiles in the various stages are evaluated in order to obtain a raffinate containing <10 mg/ℓ cobalt and with a low magnesium content reporting to the stripping section. The pH profile is also used to minimize the impurity deportment to the cobalt electrolyte. The effect of adding a preneutralization stage before feeding the organic phase to the extraction circuit is investigated. Zinc build-up in the stripping stages is also looked at.

It is recommended for the purpose of this study that four extraction stages at an O:A ratio of 1 with a pH profile from 4.9 to 5.7 be employed. The pH is controlled with 40 g/ℓ NaOH. A preneutralization stage is required, where the organic phase is contacted with 10 M NaOH. Two scrubbing stages are recommended at an O:A ratio of 40, using the cobalt electrowinning advance electrolyte as the scrub liquor. Three strip stages are to be employed at an O:A ratio of 0.67.

Introduction

The high commodity prices in recent years have spawned many investment opportunities in this market. The sub-Saharan Copper Belt, extending from Zambia to the Democratic Republic of the Congo, is rich in copper and cobalt. Recovery of copper from these deposits results in dissolution of cobalt as well as impurities, and in most operations the dissolution of cobalt is promoted by altering the copper leach conditions. Producing copper from the leach liquor is relatively easy and well understood. However, the purification and production of premium grade cobalt metal from a copper-circuit bleed stream is more complex and a variety of flowsheet options can be considered.

The interest shown in producing cobalt metal is attributed to the high price that can be obtained for premium grade cobalt metal, which was $34/lb in August 2008 (audited by Pricewaterhouse Coopers LLP)[1]. The composition of premium and standard grade cobalt metal is shown in Table I.

The difficulty in producing premium grade cobalt metal is the ability to maintain low levels of impurities in the cobalt electrowinning electrolyte in order to achieve a metal that contains >99.83% cobalt. The metal impurities in a cobalt electrowinning process have high upgrade ratios and as such a solution composition, as shown in Table II, is required to meet the metal specification.

In a copper-processing circuit a bleed stream is required to avoid a build-up of impurities. This bleed stream is the feed to the cobalt circuit and contains various metals, such as iron, aluminium, magnesium, zinc, nickel, manganese and trace amounts of copper.

Typical process unit operations to purify the copper bleed in order to achieve the cobalt electrolyte compositions include precipitation of iron and aluminium, copper ion exchange, impurity solvent extraction, zinc ion exchange and cobalt solvent extraction. Figure 1 shows a simplified flowsheet option incorporating cobalt solvent extraction as one of the process steps in the production of cobalt metal[2,7]. Cobalt solvent extraction is used to selectively extract cobalt from a purified solution, which typically contains less than 15 g/ℓ cobalt and transfers it into a concentrated electrolyte containing 50 g/ℓ cobalt.

* *TWP Matomo Process Plant (Pty) Ltd, South Africa.*

† *MDM Technical Africa (Pty) Ltd, South Africa.*

‡ *Metorex Ltd, South Africa.*

© *The Southern African Institute of Mining and Metallurgy, 2009.* *SA ISSN 0038–223X/3.00 + 0.00. This paper was first published at the SAIMM Conference,* Hydrometallurgy 2009, *24–26 February 2009.*

A cobalt solvent extraction investigation in Africa's Copper Belt

Table I

Composition of premium and standard grade cobalt metal

Element	Premium grade (99.83% Co), mg/kg	Standard grade (99.73% Co), mg/kg
Ni	<1000	<1500
Fe	<50	<100
Cu	<30	<50
Mn	<20	<50
Si, P, Sn, Sb, As, N	<10	<20
Al	<10	<10
Pb, S	<30	<60
Zn	<50	<100
Cd	<50	<50
Ag	<5	<5
Se, H	<5	<10
Mg	<10	<30
Bi	<1	<5
C	<100	<200
O	<200	<250

Table II

A typical cobalt electrowinning solution composition

Element	Concentration, mg/ℓ
Zn	<3
Cu	<2
Fe	0
Ni	46
Element	Concentration, g/ℓ
Mn	2.5
Mg	7
Co	55
Na	16

A typical copper-circuit bleed stream composition feeding the cobalt purification circuit is compared to the purified cobalt solvent-extraction feed stream in Table III and shows the extent to which the bleed-stream cation is required. The flowsheet considerations for each element are indicated.

The focus of the paper is on the testwork programme and considerations for the cobalt solvent-extraction component of the process flowsheet and uses Ruashi Phase II as a case study performed at MINTEK research facility.

The objectives of the testwork are to:

- Produce a raffinate stream containing <10 mg/ℓ cobalt in order to minimize cobalt losses
- Limit the amount of magnesium, reporting to the cobalt electrowinning to less than 5% of that contained in the feed to the cobalt solvent-extraction circuit
- Test preneutralization with 10 M NaOH[3]
- Determine the zinc build-up within the cobalt solvent extraction strip circuit.

Theory

In the cobalt solvent-extraction circuit Cyanex 272 in an aliphatic diluent is primarily employed to recover cobalt from solution. Cyanex 272 is a phosphinic acid extractant and metals are extracted through a cation exchange mechanism. It should be noted that a variety of metals can be extracted by this reagent depending on the pH of the aqueous solution with which it is in contact.

The overall reaction occurring in solvent extraction is:

$$\overline{2AH^+} + M^{2+} \leftrightarrow \overline{A_2Mn^{2+}} + 2H^+ \quad [1]$$

where A represents $R_2P(O)O^-$ and the overbar represents a species in the organic phase.

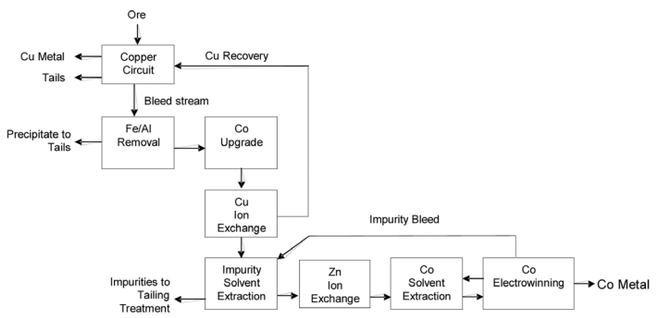

Figure 1—A flowsheet option for Co metal production

Table III

Typical copper circuit bleed and cobalt solvent extraction feed compositions

Element	Copper circuit bleed mg/l	Cobalt solvent extraction feed mg/l	Flowsheet considerations for undivided-cell cobalt electrowinning
Co	2000	8000	Cobalt upgrade reduces purification equipment size
Zn	<50	<2	Preferential plating resulting in a stressed deposit
Cu	175	<2	Preferential plating resulting in a stressed deposit.
Fe	1200	<2	Difficulty in stripping from organic phase.
Ni	<30	<25	Cobalt metal contamination
Mg	2000	1100	Increases electrolyte viscosity
Al	700	10	Crystal-lattice inclusion in cobalt cathode
Mn	1400	30	Manganese dioxide formation at anode—requires electrolyte bleed. At high concentrations permanganate forms in cobalt electrowinning circuit that oxides the organic phase.

19-24:Template Journal 6/25/09 11:54 AM Page 339

A cobalt solvent extraction investigation in Africa's Copper Belt

During extraction the forward reaction is predominant, whereas for striping the reverse reaction is favoured due to LeChatelier's principle.

Occasionally to achieve better pH control and to alleviate water balance issues, the stripped organic phase is contacted with NaOH at high concentration before being introduced into the extraction circuit[6]:

$$R_2P(O)OH_{org} + NaOH_{(aq)} \leftrightarrow R_2P(O)ONa_{org} + H_2O_{(aq)} \quad [2]^5$$

Test work

Batch test work

The order of metal extraction for Cyanex 272 with increasing pH is well established[4] and is as follows: $Fe^{3+}>Zn^{2+}>Al^{3+}>Cu^{2+}>Mn^{2+}>Co^{2+}>Mg^{2+}>Ca^{2+}>Ni^{2+}$. It is, however, necessary to obtain case specific data using the actual solution for verification purposes and as a basis for further test work. The metal extraction from a feed solution using 18% (v/v) Cyanex 272 in an aliphatic diluent at ambient temperature is shown in Figure 2.

It can be seen that the pH for optimum separation of cobalt from magnesium and nickel, while still extracting a high proportion of cobalt, is between 5 and 5.5. Zinc is quantitatively extracted, even at low pH values. Manganese is preferentially extracted, accentuating the need to purify the feed to the cobalt solvent-extraction circuit.

Once the pH for extraction is selected, distribution isotherms can be produced in which the feed solution is contacted with the organic phase at varying phase ratios at a constant temperature and pH. Distribution isotherms for the extraction of cobalt at pH 5.5 and an operating line are shown in Figure 3. An organic-to-aqueous (O:A) phase ratio of 1 is assumed to produce an operating line that achieves a maximum cobalt loading of about 7.5 g/ℓ in the organic phase at pH 5.5 from a feed liquor containing 7.5 g/ℓ cobalt.

The McCabe-Thiele plot method is used to predict the number of stages required in the extraction circuit. Figure 3 shows the McCabe-Thiele plot at an O:A phase ratio of 1 with pH controlled at 5.5. It can be seen that a cobalt content of less that 10 mg/ℓ can be achieved in 4 stages.

The 18% (v/v) Cyanex 272 is then 'max-loaded' to produce a loaded organic that would represent that obtained on the pilot and full-scale plant. This loaded organic is used for conducting stripping distribution isotherms in the laboratory.

The loaded organic phase and strip solution (8 g/ℓ sulphuric acid) is contacted at various O:A phase ratios at ambient temperature. At high O:A phase ratios contacts are maintained at a pH of <3.5 (as expected on the full-scale plant) with addition of 50 g/ℓ H_2SO_4.

The McCabe-Thiele plot method is used to predict the number of stages required for stripping. Figure 4 shows the McCabe-Thiele plot at an O:A phase ratio of 0.67. It can be seen that three stages are required to strip the loaded organic of cobalt.

Continuous test work

Based on the batch test work, the start-up conditions for the piloting campaign are chosen. The continuous test work utilizes 11 stages in the cobalt solvent-extraction circuit, namely 5 extraction stages, 3 scrub stages and 3 stripping stages as shown in Figure 5. 40 g/ℓ NaOH solution is employed for pH control in the extraction stages and a pH profile as shown in Table IV is recommended for start-up.

The pH profile in the extraction stages increases from pH 4.8 in the aqueous phase of E1 to a value of 5.5 in the raffinate (E5). This profile ensures that a raffinate of <10 mg/ℓ cobalt is achievable by choosing extraction conditions that are favourable for cobalt (see Figure 2). The

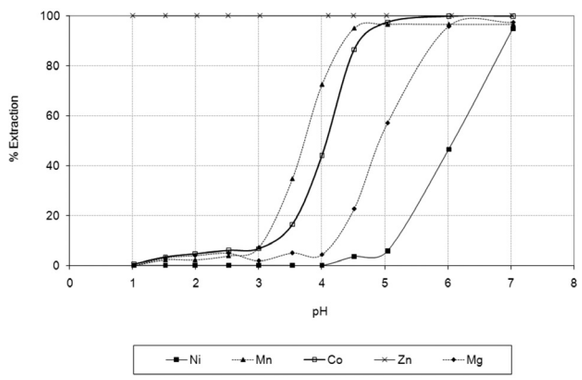

Figure 2—pH dependence of metal extraction at ambient temperature (with 18% (v/v) Cyanex 272)

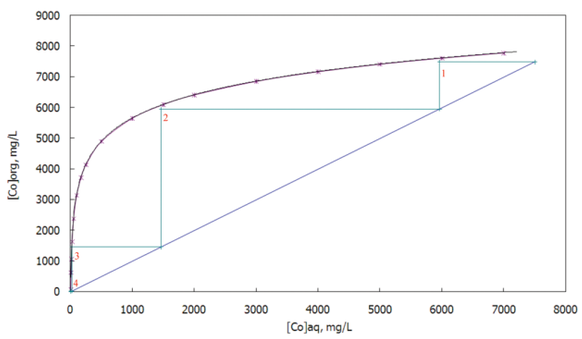

Figure 3—Distribution isotherm for the extraction of cobalt by 18% (v/v) Cyanex 272 at pH 5.5 and ambient temperature

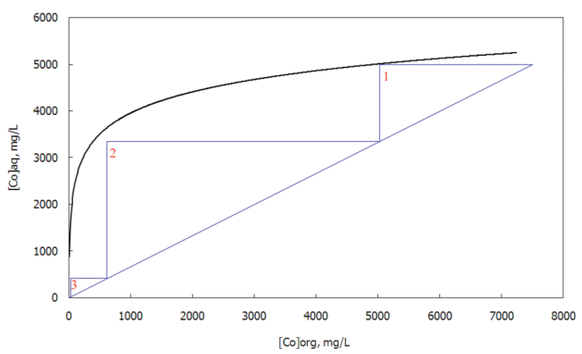

Figure 4—Distribution isotherm for the stripping of cobalt from 18% (v/v) Cyanex 272 using 8 g/ℓ H_2SO_4

A cobalt solvent extraction investigation in Africa's Copper Belt

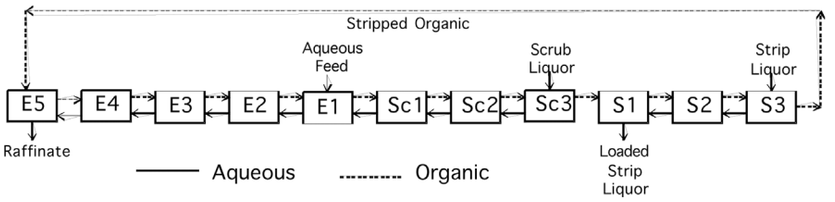

Figure 5—Schematic of cobalt solvent-extraction circuit for continuous test work

Table IV

pH profile used for start up of pilot-plant campaign

Stage	pH
E1	4.8 (controlled)
E2	4.5 (controlled)
E3	5.2 (controlled)
E4	5.4 (controlled)
E5	5.5 (controlled)
Sc1	4.5
Sc2	4.5 (monitored)
Sc3	4.5 (monitored)
S	3.5 to 4.0 (controlled)
S2	(not controlled)
S3	(not controlled)

co-extraction of magnesium is also enhanced but as the organic phase approaches E1 the pH is lowered, thus forcing a portion of the magnesium from the organic phase before it exits the extraction circuit.

The scrubbing stages operate at a high O:A ratio of approximately 40:1 and a pH slightly lower than the extraction circuit using scrub liquor that contains 55 g/ℓ cobalt (the advance electrolyte). These conditions provide a large driving force to scrub impurities from the loaded organic phase by displacing them with cobalt in the scrub liquor. The cobalt in the scrub liquor is not intended to load the organic phase to a maximum, but rather to replace impurities. The cobalt-depleted scrub liquor is normally directed to the extraction circuit but can be removed from the circuit for separate treatment if water balance issues are of concern. pH control in these stages is not required as scrub liquor is pre-adjusted to the desired pH value. The extracted cobalt does not exchange hydrogen ions, but rather other metal impurities, and the pH therefore remains constant.

The stripping circuit receives spent electrolyte containing approximately twice the amount of hydrogen ions (produced in the electrowinning cells) required for stripping cobalt from the organic. Thus pH adjustment is required only in S1 to make up for any deficit in hydrogen ions. S2 and S3 are not controlled providing that the organic is completely stripped of metal species before being recycled to the extraction circuit.

Extraction circuit

The extraction efficiencies for cobalt and magnesium and the pH in the final extraction stage (E5) are shown in Figure 6. A reproducible extraction efficiency of 100% for cobalt is achieved for the second half of the campaign. The co-extraction of magnesium averaged 13%, hence substantiating the need for scrubbing in order to achieve less than 5% magnesium reporting to the stripping circuit.

Initially cobalt is lost to the raffinate, i.e. low cobalt extraction efficiencies. The initial low cobalt extraction efficiency is attributed to low pH in the final extraction stage (E5). The low pH is due to the release of hydrogen ions (see Equation [1]) from the organic phase during loading and 40 g/ℓ NaOH is insufficient for neutralization in this stage. A preneutralization stage, where the organic phase is contacted with 10 M NaOH, is employed to achieve better pH control in the final stages of the extraction circuit (see Equation [2]). Once the preneutralization stage is incorporated in the cobalt-solvent extraction circuit, the required raffinate tenor of < 10 mg/ℓ cobalt is consistently achieved. The pH profile automatically increases to 4.9 in E1, to 5.7 in E4. Cobalt slippage occurred even when utilizing 5 extraction stages. The extraction circuit can be reduced to 4 stages if a preneutralization stage is introduced.

The behaviour of magnesium in the aqueous solution in the extraction stages is shown in Figure 7. Results show that the magnesium concentration increases from E1 to E3. The concentration of magnesium falls from E3 to E4. At high pH values magnesium loads more readily onto the organic phase and is scrubbed off at lower pH values and higher cobalt concentrations present in stage E1. This results in an aqueous-phase recycle that builds up magnesium in the extraction circuit until it eventually leaks out of the circuit via the raffinate stream.

Figure 8 shows the magnesium concentration in the organic phase in the circuit. The concentration of magnesium in E4 is high as it is co-extracted into the organic phase, hence the low concentration of magnesium in the aqueous solution in E4. The loaded scrub liquor exists at Sc1 in the

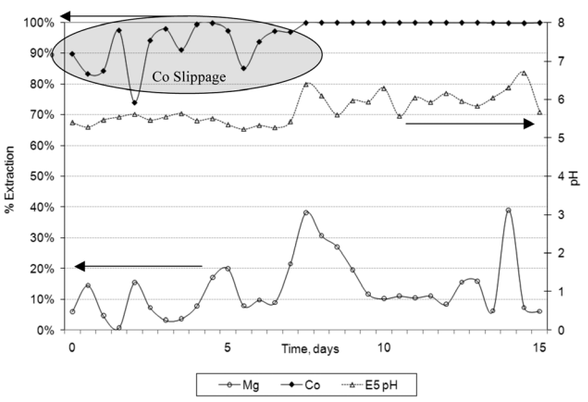

Figure 6—Extraction efficiencies of Co and Mg and pH values in the final stage of extraction

19-24:Template Journal 6/25/09 11:54 AM Page 341

A cobalt solvent extraction investigation in Africa's Copper Belt

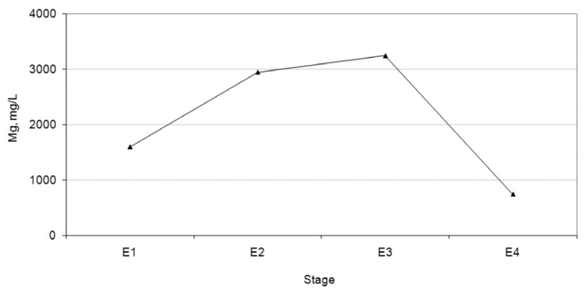

Figure 7—Magnesium concentration in the aqueous phase in the extraction circuit

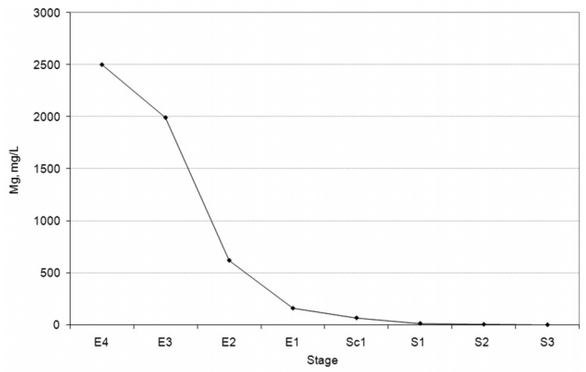

Figure 8—Magnesium concentration in the organic phase

aqueous solution. The concentration of magnesium in the organic phase in the scrub circuit is lowered as the magnesium is displaced by the cobalt in the scrub liquor. The scrub stage operates at a slightly lower pH than the extraction stages, thereby allowing magnesium to be scrubbed.

Scrubbing circuit

The cobalt solvent-extraction circuit is started up utilizing 3 scrub stages and in the later phase of the test work is reduced to one stage. As a result of the high phase ratio in the scrub section, and due to the limited duration of the pilot campaign, it is not possible to fully optimize the scrubbing performance. This should be conducted during the full-scale plant operation. The objective of achieving less than 5% of magnesium in the feed to the cobalt solvent extraction circuit from reporting to the strip section is achieved with three scrub stages; the results are summarized in Table V.

Figure 8 shows that the magnesium concentration in the organic phase on Sc1 is 50% of that at E1, thus showing the effectiveness of the scrubbing stage.

Figure 9 shows the cobalt concentration of the organic phase in E1 and the final scrub stage (Sc1). The results show that the cobalt concentration in the organic phase is generally slightly lower in E1 than in Sc1. This is attributed to cobalt from the scrub liquor displacing magnesium on the organic phase in the scrub circuit.

Stripping circuit

A phase ratio of 0.67 is employed in the strip circuit, which ensures that all loaded metal species are completely stripped from the organic in S3 and that a Δ 5g/ℓ of cobalt is achieved across the strip stages. The pH in S1 is maintained at 3.5 with the addition of 30 g/ℓ sulphuric acid. This pH value is ideal for cobalt electrowinning.

Figure 10 shows the build-up of zinc in the stripping circuit. The concentration of zinc in the feed to the cobalt solvent extraction is maintained below the analytical detection limit. Figure 11 shows that zinc does not leak into the cobalt electrowinning circuit via the loaded strip liquor but rather that it remains in the strip circuit. A pH value of 3.5 in S1 is conducive to maintain the zinc loaded on the organic phase, thus preventing it from leaking into the

Table V

Percentage magnesium extracted, scrubbed and reporting to the strip liquor

Number of scrub stages	% Magnesium extracted	% Magnesium scrubbed	% Magnesium reporting to strip circuit
3	18	68	5
1	15	39	6

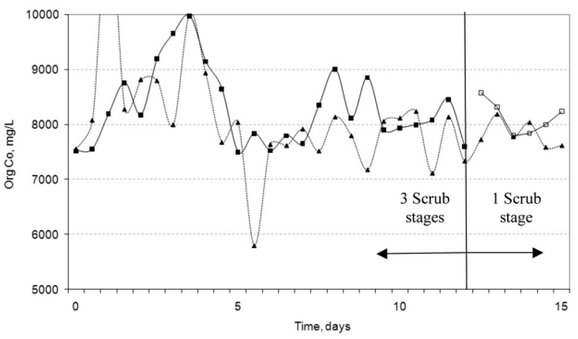

Figure 9—Comparison of cobalt concentration in organic phase of E1 and final scrub stage (Sc1)

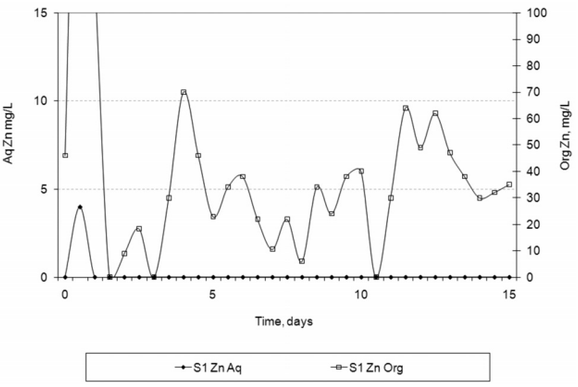

Figure 10—Zinc concentrations in aqueous and organic phase in S1

19-24:Template Journal 6/25/09 11:54 AM Page 342

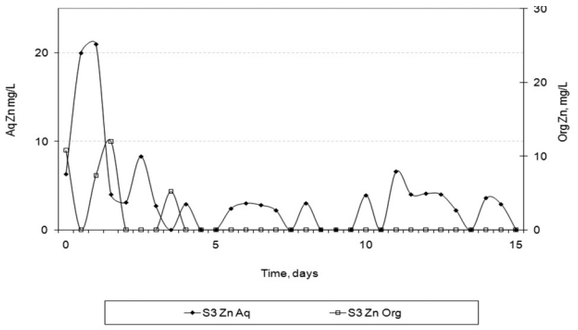

Figure 11—Zinc concentration in aqueous and organic phase in S3

Table VI

Optimum operating conditions for cobalt solvent extraction

Extraction	
Number of stages	4
Extractant	18% (v/v) Cyanex 272
Diluent	Aliphatic
O/A	1
pH profile	4.9 to 5.7
pH control	40g/l NaOH
Preneutralization	10 M NaOH
Scrubbing	
Number of stages	2
Scrub liquor	Advance electrolyte (~55 g/ℓ Co)
O/A	40
pH profile	4.5 (monitored)
Stripping	
Number of stages	3 (possibly a 4th)
Strip liquor	Spent electrolyte (50 g/ℓ Co)
O/A	0.67
pH control in S1	30 g/ℓ H_2SO_4

electrowinning circuit. Zinc is stripped in S2 and S3 due to the lower pH values in these stages, thus preventing zinc from exiting the strip circuit via the stripped organic, as seen in Figure 9. The zinc in the strip liquor exiting S2 is re-extracted in S1. This internal recycle of zinc gradually builds up, resulting in it eventually leaking into the cobalt electrowinning circuit or remaining loaded on the stripped organic phase, leading to a low extraction capacity of the organic phase and cobalt losses. A major concern is a spike of zinc existing in the loaded strip liquor due to pH deviations in S1. If the pH in S1 decreases to less than 3 then zinc will report to the cobalt electrowinning circuit, contaminating the electrolyte leading to the production of off-specification cobalt cathode.

Impurity species build-up in the loaded strip liquor during the pilot-plant campaign. It is thus recommended for a full-scale plant to incorporate a small bleed stream from the strip circuit to remove these impurities in order to avoid accumulation to levels that would compromise the metal product quality. The strip-liquor bleed can be recycled upstream to remove zinc and recover cobalt.

Conclusions and recommendations

Extraction circuit

It is shown that by increasing the pH profile in the extraction stages results in a marked improvement in the recovery of cobalt resulting in less than 10 m g/ℓ of cobalt in the raffinate. The pH profile is inherently raised by preneutralization of the stripped organic with 10 M NaOH. Greater than 99% extraction for cobalt is achieved in the extraction circuit with the high pH profile. A pH profile of 4.9 in E1 to 5.7 in E4 and a phase ratio of 1.0 are recommended for optimum results for the feed solution tested. Magnesium scrubbing is also enhanced due to the decreasing pH profile from E4 to E1.

Scrubbing circuit

Scrubbing of magnesium is established during the pilot campaign although it is not optimized due to the high phase ratio in the scrub circuit and the short duration of the pilot campaign. The objective of <5% magnesium in the feed reporting to the loaded strip liquor is achieved with three scrub stages and is shown to be possible with one stage, provided that the co-extraction of magnesium is limited within the extraction circuit. 68% magnesium scrubbing is achieved within three stages across the scrubbing circuit while only 39% is achieved with one stage. It is therefore recommended to employ a minimum of two scrub stages that can be optimized during the operation of the full-scale plant.

Stripping circuit

100% stripping of cobalt in the scrubbed organic phase is achieved in 3 strip stages providing that the pH in S1 is maintained between 3.5 and 4.0 to achieve a delta of 5 g/ℓ cobalt across the strip circuit. The pH in stage S1 is controlled by the addition of 30 g/ℓ H_2SO_4. It is shown that zinc accumulates within the strip circuit. Although zinc in the feed was kept below the analytical detection limit to prevent contamination of the cobalt cathode, the zinc does not exit the strip circuit and over time builds up to concentrations that, with a slip in pH control in the strip circuit, will contaminate the loaded strip liquor and ultimately the cobalt metal. The build-up of zinc in the strip circuit will occur on the full-scale plant and provision must be made for controlled periodic stripping of the organic phase at a low pH. A fourth strip stage can be used for selective stripping of impurities. The strip liquor generated in a fourth stage can be recycled to the cobalt upgrade step (see Figure 1) to minimize cobalt losses.

The optimum operating conditions for cobalt solvent-extraction determined in the piloting campaign are given in Table VI.

References

1. http://cobalt.bhpbilliton.com/ 31 August 2008.
2. Sole, K.C., Feather, A.M., and Cole, P.M. Solvent Extraction in Southern Africa: An update of some recent hydrometallurgical developments, *Hydrometallurgy 78*, Elsevier, 2005. pp. 52–78.
3. Roux, L.M., Minnaar, E., Cilliers, P.J., Bellino, M., and Dye, R. Comparison of Solvent Extraction and Selective Precipitation for the Purification of Cobalt Electrolytes at the Luilu Refinery, DRC, *The South African Institute of Mining and Metallurgy Base Metal Conference*, Symposium Series S47, 2007. pp. 343–364.
4. Cyanex 272® Handbook, Solvent Extraction Reagent, Cytec Industries, pp. 1–37.
5. Daudinot, A.M.M. and Liranza, E.G. *Proceeding of the International Solvent Extraction Conference*, ISEC 2002, Johannesburg, pp. 964–969.
6. Bourget, C. and Jakovljevic, B. Operational Practices for Cyanex 272 Extractant Circuits, *Proceedings of ISEC 2008*, vol. I, pp. 447–452.
7. Cole, P.M. and Feather, A.M. Processing of African Copper-Belt Copper-Cobalt Ores: Flowsheet Alternatives and Options, *Proceedings of ISEC* 2008, vol. I, pp. 131–138. ◆