Versatic 10 Acid/NICKSYN™ Synergistic System versus D2EPHA-Cyanex 272 for the Recovery of Cobalt from Typical DRC/Zambian Copper-Cobalt Leach Liquors

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Summary

The production of a premium grade cobalt requires stringent control of impurity concentrations in the cobalt advance electrolyte, in order to obtain an electrowon Co with a purity of >99.3%. Typically such a Co refining circuit would, prior to the recovery and upgrading of the Co, entail oxidative precipitation of Fe and Al, Zn, Ca and Mn removal with di-(2-ethylhexyl)phosphoric acid (D2EHPA) followed by subsequent upgrading and recovery of cobalt with bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272).

This paper considers the Versatic acid/Nicksyn™ synergistic system as an alternative to the conventional solvent extraction (SX) unit operations with D2EHPA and Cyanex 272. This synergistic system provides not only an option for the recovery and efficient separation of Co from Ca and Mg, but also gives the option of selecting the degree of Mn co-extraction.

The technical and commercial aspects of the two refining circuits are compared in a desktop trade-off study, in which estimated cash flow differentials are used to evaluate the two flow sheets. A stochastic economic model was used to estimate the revenue, and operating and capital costs using discounted cash flow techniques.

Introduction

Copper processing circuits on the Copperbelt in Southern Africa require a bleed stream to avoid the build-up of impurities whilst also maintaining the water balance within the leach circuit. This bleed stream is typically the feed to a cobalt purification circuit, provided that cobalt is a targeted by-product.

Several metal species are usually present in such a bleed stream, including Cu, Co, Fe, Al, Mn, Zn, Ni and Mg. The treatment of this bleed stream for the production of a premium grade Co cathode requires stringent control of impurity concentrations in the Co advance electrolyte, in order to obtain an electrowon Co cathode with a purity of >99.3%. Discussions and reviews of some of the successful Co refining circuits are summarised in the literature (Cole & Feather, 2008), (Cole, Sole & Feather, 2006) and (Roux et al., 2007).

Typically such a Co refining circuit would, prior to the recovery and upgrading of Co, entail oxidative precipitation of Fe, precipitation of Al and most of the Cu, Zn, Ca and Mn removal with D2EHPA, followed by the subsequent recovery and upgrading of Co with Cyanex 272.

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This paper considers, as an alternative to the aforementioned circuit, the use of a synergistic system to replace both the D$_2$EHPA and Cyanex 272 solvent extraction (SX) unit operations. The SX circuit using the Nicksyn™ reagent in combination with Versatic 10 acid would not only provide for a more effective approach for the recovery and upgrading of Co and its effective separation from Mg and Ca, but also allows control over the degree of Mn co-extraction.

Although the Nicksyn™ extractant would also recover Ni, the Ni content in the Copperbelt ores is typically very low. Any Ni present could be removed from the advance electrolyte via conventional ion exchange (IX) technology.

The comparison outlined in this paper should not to be regarded as definitive, but rather as a general guideline as each operation and application is unique.

**Theory**

A typical cobalt bleed stream composition (after Fe and Al removal) is shown in Table 1.

*Table 1: Bleed stream composition (g/L) post Fe and Al removal.*

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Mg</th>
<th>Mn</th>
<th>Ca</th>
<th>Ni</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>3 - 8</td>
<td>2 - 3</td>
<td>0.1 – 1.5</td>
<td>0.6</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

Selected metal distribution equilibria for pH versus extraction using various organic extractants are shown in Figure 1.

![Figure 1](image-url)
In the case of a phosphinic acid solvent extractant (Cyanex 272), the extraction of manganese prior to cobalt is evident from the order of extraction of the metals shown in Figure 1(a):

\[ \text{Mn} > \text{Co} > \text{Mg} > \text{Ca} > \text{Ni} \]

When this extractant is used for the recovery and upgrading of cobalt from such a stream, often operating in a closed loop with electrowinning (EW) to produce high grade Co metal, the Mn is quantitatively extracted and reports to the EW circuit. Although some Mn precipitates at the anodes as manganese dioxide \((\text{MnO}_2)\), the majority of the Mn has to be bled from the EW circuit and the Co is recovered from this bleed stream via selective precipitation. However, the treatment of this bleed stream for Co recovery is costly, as the Co has to be recycled to the various Co purification circuits and hence additional Co losses are incurred.

In addition, all the Cu and Zn present in solution would be co-extracted by Cyanex 272 (Du Preez et al., 2007) and if optimum Co recovery is targeted, some Mg will be co-extracted (while Ca will be rejected). The Mg co-extraction would have to be either scrubbed from the organic, or bled from the electrowinning circuit.

To cope with the Mn and Zn present in the feed stream, D₂EHPA is employed as an extractant. As indicated by the order of metal extraction depicted in Figure 1(b), these metals are preferentially extracted before Co in the following order:

\[ \text{Zn} > \text{Ca} > \text{Mn} > \text{Co} > \text{Ni} \]

If relatively efficient Mn extraction is targeted, Ca will co-extract to an even larger extent, and some Co will be co-extracted. This loss of Co would have to be limited via scrubbing of the loaded organic.

In contrast to these two systems, the extraction of metals from a similar stream using a synergistic mixture of 0.5 M Versatic 10 acid (V10) plus 0.5 M Nicksyn™ in Shell Sol D70 is illustrated in Figure 1(c). The order of extraction of the metals is as follows:

\[ \text{Cu} > \text{Ni} > \text{Zn} > \text{Co} > \text{Mn} > \text{Ca} \approx \text{Mg} \]

The synergistic effect of Nicksyn™ when added to V10 acid has been extensively reported in the literature (Du Preez & Kotze, 2013), (Du Preez & Preston, 2004) and (Du Preez et al., 2007) and some of the results are summarised in Figure 2. The \( \Delta pH_{50}^{\text{Ca-Co}} \) increased from 0.56 pH units, when a 0.5 M V10 acid alone is used, to 2.01 units when 0.5 M V10 acid mixed with 0.5 M Nicksyn™ is used. Similarly the \( \Delta pH_{50}^{\text{Mn-Co}} \) increased from 0.05 to 0.35 pH units.

Any Ni present in the feed solution will be co-extracted with the Co, which is extracted in preference to Mn, with the option to reject Ca and Mg almost quantitatively. Although this extractant would also extract all Cu and Zn from the feed stream, these impurities (Cu, Zn and Ni) could be removed from the advance electrolyte via conventional IX technology.
Mn removal is therefore not required via oxidative precipitation in the Fe precipitation step as it is in the conventional system, instead it can be rejected using the synergistic system. Scrubbing of the loaded organic would need to be incorporated to minimise Mn co-extraction.

![Graphs](image)

**Figure 2:** Synergistic effect of Nicksyn™ on the extraction of metals from sulphate solution using 0.5 M V10 acid alone or with 0.5 M Nicksyn™ in Shellsol D70 for (a) Co-Ca and (b) Co-Mn separation

Alternative processing routes considered for Mn removal from the bleed stream prior to Co recovery includes oxidative precipitation of MnO₂ or Mn₂O₃ in the Fe removal circuit using sulphurous acid (Muzadi & Kotze, 2013) followed by the selective precipitation of Co hydroxide. Although these unit operations have been optimised in laboratory test work, they would incur significant capital and operating costs, and cobalt losses could be 1% to 5%.

**Basis for trade-off study**

For both, the V10/Nicksyn™ synergistic system and the D₂EHPA / Cyanex 272 circuit (Figure 3 and Figure 4 respectively), conceptual process design criteria were developed and cost estimation was completed to determine the likely capital and operating differential costs for these two circuits.

All areas common to both circuits were excluded from the analysis. These plant areas include ore receiving, crushing, milling, classification, leach, Cu-SX, and Fe/Al removal.

Probability distributions were applied to the key system variables used in the model in order to describe the inherent uncertainty associated with them. The difference in Co revenue between the circuits, although not large, was included in the analysis.

**D₂EHPA-Cyanex 272 Refining Circuit (Figure 3)**

This base-case circuit incorporates Zn, Ca and Mn removal via D₂EHPA followed by the recovery and upgrading of Co with Cyanex 272. The loaded strip liquor/advance electrolyte is subsequently polished with an aminomethylphosphonic acid chelating resin to remove any deleterious impurities (Cu and Zn) which would not be not captured by the Cyanex 272. The loaded resin is stripped completely with a strong
acid and the eluate is recycled to the front-end of the circuit. Stripped resin is converted to the Na form prior to loading. The concentrations of Mn, Mg and/or Na are controlled by means of a bleed stream from the spent electrolyte.

![Figure 3: D2EHPA-Cyanex 272 Refining Circuit Block Flow Diagram](image)

**V10/Nicksyn™ Synergistic Refining Circuit (Figure 4)**

The proposed circuit configuration, shown in Figure 4, involves replacing both the D2EHPA and Cyanex 272 solvent extraction unit operations with a V10/Nicksyn™ synergistic system.

![Figure 4: V10/Nicksyn™ Synergistic Refining Circuit Block Flow Diagram](image)

After the oxidative precipitation of Fe and Al, the Co in the bleed stream is recovered and upgraded using a V10/Nicksyn™ synergistic mixture. Owing to the inherent characteristics and selectivity of the synergistic system, the Zn, Cu and Ni are co-extracted into the advanced electrolyte. Similarly to the previous circuit, Cu and Zn are removed with an aminomethylphosphonic acid resin. However, in addition to these elements, Ni is removed with a chelating resin containing the bis-picolylamine functional group. In both instances, the loaded resin is first stripped with a weak acid to recover the majority of the co-loaded Co, followed by a strong acid strip to remove the remaining metals. The weak acid eluate is recycled to the front-end of the circuit, whereas strong acid eluate is routed to neutralisation. The concentrations of Mn, Mg or Na are controlled with a bleed from the advanced electrolyte which also serves to convert the aminophosphonic resin to the Co form after elution.

**Financial model results**

The financial valuation was done on a bare-bones basis, in real terms and did not consider the effects of taxes, interest, financing models or any escalation. The costs shown are not to be regarded as definitive, but rather differential or incremental cost estimates, since all common items have been excluded from the analysis.

Based on preliminary process flow diagrams and mass balances, equipment lists were produced for both circuits. Capital costs for major equipment items were estimated using a database of recently completed projects or studies. After applying typical factors to estimate the supply and erection costs for the civil, structural, platework, piping, electrical, control and instrumentation disciplines, capital costs were obtained for both circuits.
Operating cost estimates were based on the outcomes of preliminary mass balances. Calculation of reagent consumption rates for both circuits was based on a number of calculations, assumptions, benchmarks, public domain data, vendor data and test work results. The reagent costs were derived from the estimated rates of consumption for key reagents and using DRA’s extensive reagent cost database. The cost for specialised reagents were obtained directly from reagent/chemical suppliers. Power, labour and general maintenance costs were not considered due to the small differential expected between the options.

Based on the expected probability ranges assigned to capital, reagent consumption and reagent supply rate estimates, Figure 5 provides a scatter plot of estimated capital and operating costs for both options. The graph shows the outcomes from Monte Carlo simulations, where each data point represents a simulation outcome. The error bars represent the 90% confidence band.

![Figure 5: Operating and capital cost differential estimates (bars show the 90% confidence range for simulated outputs)](image)

Figure 6 shows output probability distribution for the differential NPV$_{10\%}$, real between the two circuits. The positive number is in favour of the V10/Nicksyn™ option.
Figure 6: Differential NPV(10%, real) between the two circuits. The positive differential is in favour or the V10/Nicksyn™ option.

Conclusions

Based on the modelling exercise, the use of a V10/Nicksyn™ system to replace both the conventional D₂EHPA and Cyanex 272 solvent extraction (SX) unit operations is expected to provide both capital and operating costs benefits, but may result in a small drop in Co recovery. Despite the marginal reduction in metal output, and based on the design criteria used in the model example, the synergistic circuit is estimated to provide a pre-tax NPV improvement of between US$20m and US$70m over a 10 year life of mine.

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References
