DESIGN CONSIDERATIONS FOR THE COBALT RECOVERY CIRCUIT OF THE KOL (KOV) COPPER/COBALT REFINERY, DRC

By

KG Fisher* and LG Treadgold**

* Bateman Minerals & Metals
  Bartlett Road, Boksburg,
  Gauteng, 1462. South Africa

** Consulting Metallurgist
  1740 South Otterbein Avenue,
  Suite 28, Rowland Heights,
  California, 91748. USA

Presented by

Graham Fisher
graham.fisher@batemanengineering.com
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1. INTRODUCTION

In the late 1990’s Gécamines, the DRC state-owned copper/cobalt mining company, started a campaign to attract investors or partners to join with them in the rehabilitation of their existing mines and ageing processing facilities. This was prompted by their production decline from 470 000 tpa of copper in 1987, to less than 24 000 tpa in 2000.

In February 2006, DCP Sarl (a joint venture between Nikanor Plc’s subsidiary GEC and the state owned Gécamines) were granted the rights to operate the KOV copper-cobalt mine near the town of Kolwezi in Katanga Province, together with two nearby smaller mines and the Kolwezi Concentrator plant. The exploitation permits allowed DCP to mine the deposits for a 30-year period, renewable thereafter for 15-year extensions. At the same time, similar concessions were granted to other investors in the region. Katanga Mining Limited (previously Kinross Forrest) were given the rights to the old Gécamines refinery at Luilu together with the nearby Kamoto Concentrator, Kamoto underground mine and other mines.

The indicated mineral resource for the KOV ore bodies is a massive 172 million tonnes at 4.84% copper and 0.49% cobalt, mostly present as oxides but with some sulphides at depth. The pit had lain dormant and flooded for almost 10 years due to lack of funding before DCP, in 2006/7, commenced re-development of the mine and design of a complete new hydrometallurgical facility with capacity to produce up to 250 000 tpa annum of LME Grade ‘A’ copper cathode and 30 000 tpa of cobalt as a hydroxide salt. This new refinery was to be built on land adjacent to the old Luilu refinery.

In January 2007, Nikanor and Katanga Mining merged to form a single company under the Katanga Mining name, with the potential to produce up to 400 000 tpa copper and 40 000 tpa cobalt. The merged plant now known as KOL (Kamoto Operating Limited), which is currently being designed, will utilise most of the new DCP refinery flowsheet, including the cobalt processing facility.

This paper describes the various factors that had to be considered in the process selection for the cobalt recovery circuit. DCP’s process selection for copper has been described in a paper by Treadgold and Parker1.

2. THE WORLD COBALT MARKET

2.1. COBALT USES

Cobalt is a metal with certain unique properties and is used in several specific industrial and military applications, including:

- Superalloys in gas turbine engines;
- Magnets and magnetic alloys;
- Corrosion- and wear-resistant alloys;
- High-speed steels and cemented carbides;
- Catalysts for the petroleum and chemical industries;
- Drying agents and colorants for paints, varnishes, inks and ceramics;
- Batteries, particularly re-chargeable for electric vehicles and portable electronic equipment;
- Steel-belted radial-ply tyres.

(Readers can refer to the Cobalt Development Institute website for more information on cobalt and its uses – www.thecdi.com)

Most of these markets are growing and so the cobalt price has increased in recent years from below $20 to over $50 per pound, while consumption has risen from around 35 000 tpa to 60 000 tpa; and could increase to over 100 000 tpa by 2020. There are several new projects apparently coming on line in the next few years but the DCP/KOL project is by far the largest.

2.2. COBALT PRODUCTS

Cobalt is traded in various forms, ranging from concentrates through various intermediates to high-purity metal. Many of the concentrates and intermediates are ultimately refined to metal. Products that could logically be produced by DCP/KOL include:
2.3. THE KATANGA CONTEXT

One of the unique features of copper ore bodies in the Katanga region of the DRC is the high level of contained cobalt. In the case of the KOV and Kamoto ores, the copper to cobalt ratio is about 10:1 and, with the additional cobalt from the smaller mines, KOL’s potential cobalt production is almost 40 000 tpa. In current terms, this would be over half of world annual consumption.

At the Feasibility Study stage (prior to the Nikanor/Katanga merger), it was felt by DCP that finding off-takers for some 30 000 tpa would prove difficult and that the cobalt price could be low due to the supply surplus, so it was planned to produce only an impure cobalt oxide initially, by precipitation with lime and calcining, for sale to toll refiners. Subsequently, there has been some re-thinking resulting in the flowsheet being modified to produce a higher grade hydroxide that would be more attractive to buyers and incur less transport costs. However, the potential extra revenue to be earned from cobalt metal production was recognised and allowance is being made in the design for future installation of facilities to produce up to 12 000 tpa cobalt cathode.

Many other DRC and Zambian cobalt projects are faced with a similar conundrum – what type of product to make and what grade? The larger the project is, the more difficult the solution becomes, since production of high purity cobalt metal is not an easy task. A paper by Roux et al compares several current studies and projects with this problem.

The following discussion reviews the pros and cons of some process options potentially applicable to the DCP/KOL project.

3. PROCESSING HISTORY OF KOV AND LUILU

Historically, oxide and mixed oxide/sulphide ores from the KOV/Kamoto area were processed through Kamoto and Kolwezi Concentrators, to produce oxide and sulphide flotation concentrates which were then treated at the Gécamines Luilu and Shituru refineries via a conventional roast-leach-electrowin process. Copper and cobalt recoveries for this route are indicated in Table 1.

<table>
<thead>
<tr>
<th>Concentrator</th>
<th>Recovery</th>
<th>Copper</th>
<th>Cobalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td>75%</td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td>Sulphides</td>
<td>85%</td>
<td>75%</td>
<td></td>
</tr>
<tr>
<td>Refinery</td>
<td></td>
<td>91%</td>
<td>58%</td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>77%</td>
<td>44%</td>
</tr>
<tr>
<td>Sulphides</td>
<td>68%</td>
<td>26%</td>
<td></td>
</tr>
<tr>
<td>Oxides</td>
<td>68%</td>
<td>26%</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Gécamines historical recoveries

Luilu refinery was first built in 1960 and expanded in the 1970’s to a capacity of 175 000 tpa copper cathode and 8 000 tpa cobalt cathode. Cobalt was recovered from a de-copperised bleed stream from the leach/EW circuit by the traditional DRC/Zambian process of precipitation with lime (known as PPS - “Purification by Precipitation Section”), followed by re-leach and electrowinning to produce cathode metal. Simplified flowsheets for the old refinery and the PPS circuit are given in Figures 1 & 2 below.

The cobalt process selection for DCP’s new refinery was made against the background of this well-known and established process.
4. COBALT PROCESS OPTIONS

4.1. PROCESS REQUIREMENTS

The extent of impurity removal required depends on the final product to be produced, but it is normal to have to remove most of the following elements prior to producing cathode metal. Obviously, care has to be taken to avoid adding them with the reagents used in the process:

- Fe, Mn, Al, Cu, Zn, Pb, Cd, Ni and
- Ca, Mg and other sundry metals, plus
- Certain undesirable metalloids (As, Se, Te) and non-metals (e.g. Cl⁻ and organics).
4.2. POSSIBLE PROCESSES
Some processes considered possibly viable for DCP include the following:

- Precipitation with limestone (CaCO₃) and/or lime (Ca(OH)₂) – for copper, aluminium and zinc removal; together with:
  - Air/O₂ injection – for iron removal,
  - Air/SO₂ injection – for manganese (and iron) removal.
- Sulphide precipitation with NaHS or H₂S, or with SO₂ and elemental sulphur - for zinc, nickel and copper removal;
- Cementation onto cobalt – for copper clean-up;
- Solvent extraction (SX) – for copper, zinc and lead, manganese and nickel;
- Ion exchange (IX) – for copper, zinc and nickel;
- Precipitation with soda ash (Na₂CO₃) – for cobalt carbonate production;
- Precipitation with caustic (NaOH) – for cobalt hydroxide production;
- Precipitation with magnesia (MgO) for cobalt hydroxide production;
- Evaporation/crystallisation – for cobalt sulphate production;
- Re-leach of cobalt precipitate (ahead of EW);
- Cobalt Electrowinning – for final metal production – divided or undivided cells;
- Vacuum de-gassing – for cathode metal hydrogen removal.

4.3. OTHER PROCESSES
Processes considered impractical in the DCP/KOL context include:

- Resin in Pulp (RIP);
- Molecular Recognition Technology (MRT);
- Superoxidants (Caro’s acid and ozone);
- Hydrogen reduction – for final metal production;
- Thermal (furnace) refining.

Many of the above processes are discussed below.

5. PROCESS DESCRIPTIONS

5.1. SELECTIVE IMPURITY PRECIPITATION WITH LIME & LIMESTONE

5.1.1. General Principles
A raffinate bleed stream is an essential component of a leach/SX circuit required to maintain the overall water balance – compensating for inputs such as wash water, flocculants and reagents.

According to the DCP/KOV Metsim® mass balance, the analysis of this bleed stream sent to cobalt recovery will be typically as follows:

- Cobalt = 5 - 6 gpl
- Nickel = 0.05 gpl
- Aluminium = 0.8 gpl
- Copper = 0.4 gpl
- Zinc = 0.1 gpl
- Sulphuric Acid = 15.7 gpl
- Iron = 1.3 gpl
- Manganese = 1.0 gpl

This stream is a very high flow (~700 m³/h) and relatively dilute because of water balance issues.

Selective precipitation with lime is an obvious contender for DRC projects, as it is an “easy” process and well known to the local workforce. Plants using this process include Luilu (see ref. 2), Shituru, Chambishi and Nkana. The Chambishi plant has been well documented, initially by Aird et al. and subsequently by Rao et al. These plants tend to do bulk impurity precipitations in one or two steps, followed by cobalt hydroxide precipitation. Further purification is then done after re-leaching the hydroxide intermediate.
Figure 3 below, from DCP’s testwork at Mintek, shows how impurity metals can be selectively precipitated from this stream by incrementally raising the pH with lime. Note that most of the target metals come down before cobalt – with the important exception of manganese.

This graph ultimately formed the basis of the KOL cobalt circuit design. The reactions are typically as follows:

\[
\begin{align*}
\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \quad \text{or} \quad \text{CaCO}_3 + \text{H}_2\text{SO}_4 & \rightarrow & \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \\
\text{CuSO}_4 + 2\text{H}_2\text{O} & \rightarrow & \text{Cu(OH)}_2 \downarrow + \text{H}_2\text{SO}_4 \\
\text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} & \rightarrow & 2\text{Al(OH)}_3 \downarrow + 3\text{H}_2\text{SO}_4 \\
\text{ZnSO}_4 + 2\text{H}_2\text{O} & \rightarrow & \text{Zn(OH)}_2 \downarrow + \text{H}_2\text{SO}_4
\end{align*}
\]

\[ Fig 3: \text{Metal precipitation with } \text{Ca(OH)}_2 \text{ versus pH, at } 35^\circ \text{C} \]

The main problem with this process is the relatively high cobalt losses that occur due to co-precipitation. This can be limited by good reactor agitation, careful pH control and lime addition, small incremental steps and recycles; all of which avoid localised over-dosing of lime and high pH “hot spots”.

The second problem is the large amount of gypsum that is produced and the associated problems of precipitation and scaling. Gypsum is only soluble to around 500 ppm, so most precipitates.

5.1.2. Neutralisation and Iron/Aluminium Precipitation

The incoming bleed stream contains over 15 gpl acid, so the first requirement is to neutralise this. Milled limestone (CaCO₃) is employed in preference to milk of lime (Ca(OH)₂) because it is cheaper and less hazardous – Ca(OH)₂ normally being made by slaking burnt lime (CaO). The downside of limestone is a longer residence time and larger reactors.

If the solution pH is then raised to pH3.2 and air (oxygen) injected, ferrous iron is oxidised to ferric which precipitates as a “hydroxide” whose form depends on temperature. Some 60% of the aluminium also precipitates as hydroxide.

Reactions are basically as follows, plus gypsum precipitation:

\[
\begin{align*}
2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 & \rightarrow & \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \\
\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} & \rightarrow & 2\text{Fe(OH)}_3 \downarrow + 3\text{H}_2\text{SO}_4 \quad \text{(hydroxide precipitation)} \\
4\text{FeSO}_4 + 6\text{H}_2\text{O} + \text{O}_2 & \rightarrow & 4\text{FeO.OH} \downarrow + 4\text{H}_2\text{SO}_4 \quad \text{(goethite precipitation)} \\
\text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} & \rightarrow & 2\text{Al(OH)}_3 \downarrow + 3\text{H}_2\text{SO}_4
\end{align*}
\]

Note that the nature of the iron precipitate is temperature dependent, as Figure 4 below indicates, and for reasons of filterability – Fe(OH)₃ being difficult - the feed may be heated to encourage goethite formation.
An interesting point is the capacity of low temperature ferric hydroxides to collect non-metallic impurities such as arsenic, antimony, selenium and tellurium oxides. Hematite, although offering good filtration characteristics, has very little impurity removal capacity and this may be an important factor if the up-stream process was a pressure leach.

5.1.3. Manganese Precipitation with Air/SO₂

The use of air/SO₂ or O₂/SO₂ mixtures to oxidize and precipitate manganese has been extensively documented by several authors including Zhang et al. [5,6] and Krause [7]. Recently Mintek (Mouton et al.) summarised much of their recent work on this topic and gave some design information. Unfortunately however no commercial cobalt plant has yet employed the process at full scale, so there is some uncertainty as to how to scale up the reactor design from laboratory work. A recent paper by Van Rooyen [9] attempts to explain the scale-up problems.

For KOL, manganese is a major impurity and the air/SO₂ process was successfully demonstrated during DCP’s testwork at Mintek. From this work, design criteria were developed and subsequently confirmed on their 2m³ reactor. Although it may yet prove necessary to make some adjustments when the plant is operating, the advantages of this process compared to the alternative of SX (see later) were considered sufficient to justify its selection. The key criteria are pH (best between pH3 and pH4); and the O₂:SO₂ ratio which in the laboratory is optimum just above 4 mol/mol but, in practice, is affected by the oxygen utilization efficiency achieved by the sparge and agitator design. A further complication arises if the SO₂ used is from the acid plant sulphur burner; in which case the gas strength is only ~12%.

Reactions are gypsum formation, plus:

\[
2\text{FeSO}_4 + \text{O}_2 + \text{SO}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 \quad (\text{which precipitates as Fe(OH)}_3 \text{as above)}
\]

\[
\text{MnSO}_4 + \text{O}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2\downarrow + 2\text{H}_2\text{SO}_4
\]

At KOL, the neutralisation, iron, aluminium and manganese removal will all be done in a single train of reactors. The neutralisation and bulk of the iron removal is done first with air alone at pH <3.2, followed by manganese with air/SO₂ at pH<4. The total gypsum/Fe/Mn/Al precipitate is rejected to waste.

The advantages of this process are that it is cheap and simple, and faster for iron than air alone. Cobalt co-precipitation is minimal at pH3-4. The disadvantages are that it is unproven on a large scale, generates more acid which requires more lime, and is hazardous due to the use of SO₂.

5.1.4. Copper Precipitation

As Figure 3 shows, copper precipitates with lime between pH4 and pH6 but only towards the end does a significant amount of cobalt co-precipitate, so the reaction is best performed in two stages. Normally this is done at pH5.2 and pH6, with the first precipitate being a copper product and the second being high in cobalt is recycled to the head of the process. DCP/KOL have adopted a slightly different approach:
1) At pH4.7 – the precipitate from which is aluminium hydroxide with minor copper hydroxide and is recycled to iron removal, so that the 1% – 5% of co-precipitated cobalt can be re-dissolved and recovered; and the recycled aluminium re-precipitated.

2) At pH6 – the precipitate from which is copper hydroxide with minor cobalt hydroxide and is recycled to copper leach for copper and cobalt recovery.

Note that a significant amount of zinc is precipitated, but not all. Also some traces of copper remain which must be removed downstream if the final cobalt product is to be cathode metal.

5.2. COBALT PRECIPITATION

5.2.1. Precipitation with Lime

Figure 3 shows that cobalt precipitates as the hydroxide, or a basic sulphate (hydrate), between pH6 and pH8.5. Some separation from manganese and magnesium can be achieved by doing a two-stage precipitation, similar to copper above; restricting the reagent dose to precipitate only ~85% of the cobalt in the first stage. A significant amount of manganese remains in solution and is precipitated in the second stage and recycled to iron removal.

$$\text{CoSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Co(OH)}_2 \downarrow + \text{H}_2\text{SO}_4$$

The problem with using lime to precipitate cobalt hydroxide, if this is the end product, is that a large amount of gypsum is also precipitated which reduces the cobalt content of the product from a potential 60% to around 20%. Apart from this being unpalatable to the buyers, there is a major (unnecessary) cost associated with the transport of the gypsum fraction to destination.

5.2.2. Precipitation with Sodium Hydroxide

Sodium hydroxide (caustic) can be used instead of milk of lime. The main difference is that soluble sodium sulphate is formed instead of insoluble gypsum.

$$\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$$

$$\text{CoSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Co(OH)}_2 \downarrow + \text{H}_2\text{SO}_4$$

Compared to milk of lime, this gives a much cleaner hydroxide product of lower mass, but the disadvantages are:

- Caustic is more hazardous to handle;
- Expensive high-grade caustic is required to avoid adding impurities, especially chlorides;
- Large tonnage of caustic required (>2 mol NaOH per mol cobalt), and logistical difficulties shipping to DRC;
- Large quantity of sodium sulphate reporting to end solution and tailings dam (and overflow);
  Tailings dam has to be lined (high cost) - not lined for gypsum.

For these reasons, particularly the environmental sodium issues, DCP/KOL rejected the caustic route.

5.2.3. Precipitation with Sodium Carbonate

Sodium carbonate (soda ash) is a commonly used precipitant. The product is a basic cobalt carbonate, and sodium sulphate remains in solution:

$$3\text{CoSO}_4 + \text{Na}_2\text{CO}_3 + 4\text{H}_2\text{O} \rightarrow \text{CoCO}_3 \downarrow + 2\text{Co(OH)}_2 \downarrow + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

$$\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$$

The pros and cons are very similar to caustic above, although the reagent is cheaper and safer. Again, the main drawback is the sodium sulphate impact on the tailings dam and environment.

The prospect of producing a sodium sulphate bi-product was discounted by DCP, since the solution stream is too large to evaporate and there is no market for sodium sulphate in the DRC.

5.2.4. Precipitation with Magnesia

Magnesia has been successfully used to precipitate cobalt and nickel hydroxides and many current cobalt projects are proposing to use this route:
MgO + H₂O → Mg(OH)₂
CoSO₄ + Mg(OH)₂ → Co(OH)₂↓ + MgSO₄

The advantages of magnesia are:
- Cleaner product than lime, ~60% cobalt;
- Like sodium sulphate, magnesium sulphate is soluble but, unlike sodium it can be precipitated from the end solution with lime at pH10.2; hence no impact on environment and tailings dam.

Disadvantages or problems are:
- For KOL, large quantity (up to 30 000 tpa) of high-grade MgO required - difficult to secure supply;
- Grades of magnesia vary markedly in their effectiveness due to their origin and different activities; also prone to ageing;
- It is an expensive reagent, imported from USA or Australia;
- The precipitate, although filterable, retains much H₂O and requires extensive drying;
- Associated CaO forms gypsum which reports to product;
- MgO does not all dissolve; at least 2% reports to cobalt product and is highly undesirable.

DCP and Mintek have done extensive testwork to find the best magnesia material and to optimise the reaction conditions to give the purest product with lowest Mg/Co ratio. A two-stage precipitation as in 5.2.1 above will be employed, with the second stage (lime) precipitate being recycled.

5.2.5. Hydroxide Re-leach
The re-leach of cobalt hydroxide precipitate to generate fresh loaded electrolyte for cobalt EW is an important step in the impurity removal chain if the end product is cathode. Some projects have made the mistake of re-leaching at low pH (2-3) to ensure maximum cobalt re-solution and minimise losses. In practice, a pH >6 is adequate to dissolve most of the cobalt whilst leaving troublesome copper and zinc behind in the residue.

5.3. SOLVENT EXTRACTION FLOWSHEETS

5.3.1. General
With the future production of electrowon cathode in mind, serious consideration was given to the use of Solvent Extraction (SX) to remove several impurities. Many projects are planning to follow the SX route, even to the extent of having three or four SX plants in series – each employing a different reagent. The following three established processes were all considered by DCP:

5.3.2. Copper SX
The early flowsheets for DCP had a conventional primary copper SX for the copper leach circuit, from which the raffinate bleed was taken for cobalt recovery, as per Figure 5 below. After neutralisation, the bleed passed to copper SX2 which was the first stage of cobalt impurity removal. The organic would be LIX984N® which is often the reagent of choice for this application.

![Fig 5: Conventional Copper Leach – SX - EW circuit](image-url)
In line with several copper leach/SX/EW plants, DCP/KOV have recently changed the SX configuration – converting to high-grade and low-grade SX as shown in Figure 6. This arrangement is more efficient in terms of metal and acid recovery; and the bleed to the cobalt circuit contains less copper than conventional SX. Having a secondary copper SX in the bleed was then considered overkill for a relatively small amount of copper. Precipitation with lime can achieve the same result.

![Diagram of Hi-grade / Low-grade Leach – SX - EW circuit](image)

**Fig 6: Hi-grade / Low-grade Leach – SX - EW circuit**

### 5.3.3. Zinc and Manganese SX

**Zinc extraction:**
Zinc removal using D₂EHPA® has been successfully used in several cobalt plants, including Chambishi, Nkana and Kasese. The D₂EHPA selectivity series is:

\[ Fe^{3+} > Zn > Ca > Cu > Mg > Co > Ni \]

At Kasese (Uganda) the zinc is extracted from a pH3.5 solution in a two-stage extraction circuit. Loaded organic is treated in a two-stage scrub circuit to recover co-extracted cobalt and then stripped in a two-stage strip circuit with 50 gpl sulphuric acid. The loading/stripping equilibrium is represented simplistically as follows:

\[ ZnSO_4 + 2HL \leftrightarrow ZnL_2 + H_2SO_4 \]  
(\text{the organic ligand is L})

The reagent is relatively cheap and stable and the process is quite efficient and simple with no interstage pH control required since the acid generated is minor (1 acid for every zinc extracted).

**Manganese extraction:**
It is also possible to extract manganese with D₂EHPA (refer to a paper by Cole 10) using a higher O:A ratio and interstage pH control.

Problems with D₂EHPA in this application are the poisoning effect of Fe³⁺ ions, which requires a HCl strip, and the affinity of the reagent for calcium – which has a tendency to precipitate in the scrub or strip stage.

Zinc SX was discounted for DCP/KOL because of the size of plant that would be required for a flow of 700 m³/h and because hydrochloric acid is not readily available in the DRC. However, it may have a role to play in the purification of the low flow / high concentration electrolyte stream in a future EW circuit.

### 5.3.4. Cobalt SX for Nickel Separation

Cyanex 272® reagent is widely used for separation of nickel from cobalt – which is perhaps the most critical step en-route to high-grade cobalt cathode. The Cyanex 272 selectivity series is:

\[ Fe^{3+} > Zn > Cu > Co > Mg > Ca > Ni \]

At Kasese, cobalt is loaded onto the extractant at 40°C in a four-stage extraction train. Loaded organic is treated in a single scrub stage to remove co-extracted nickel and magnesium, following which the cobalt is stripped into spent cobalt electrolyte from electrowinning in a three-stage strip section. Loaded electrolyte leaving the stripping stage contains 50 gpl cobalt. The loading/stripping equilibrium is represented simplistically as follows:

\[ CoSO_4 + 2HL \leftrightarrow CoL_2 + H_2SO_4 \]
The process works well but in this case the reagent is expensive. It is also prone to oxidation degradation problems, although the addition of BHT antioxidant can control this. Furthermore, strict interstage pH control is required since the amount of acid generated is major (one acid for every cobalt extracted).

The neutralising agent can be NaOH or NH₄OH, both of which would lead to serious environmental problems in the DCP/KOL context. The sodium issues are very similar to 5.2.2 above and the use of ammonia in the DRC was not considered appropriate (availability of ammonia and disposal of NH₄SO₄). Hence the process was discounted for DCP.

A benefit with Cyanex 272 is its ability to separate cobalt from calcium and magnesium. Further, unlike D₂EHPA, any co-extracted Fe³⁺ can be readily stripped with 150 gpl H₂SO₄.

5.3.5. New SX Reagents for Cobalt/Nickel Separation

Recently there has been much interest in the new thio-based extractants including Cyanex 301 and 302 in which the active oxygen atoms are replaced by sulphur. These reagents have the ability to separate cobalt (and nickel) from manganese and magnesium and a novel Cyanex 301 circuit is being employed on INCO’s Goro project (refer to paper by Mihaylov et al11).

However, the 301 reagent is easily oxidised and decomposes to 272 in two stages, the first of which is reversible. Hence the flowsheet includes a nitrogen sparge ahead of extraction and utilises Bateman pulsed columns, which are totally enclosed and allow an inert atmosphere, instead of conventional mixer-settlers.

Careful control is also required to ensure that no ferric ion or copper is in the feed, since they are irreversibly extracted and will poison the reagent. Stripping at Goro is with 6N hydrochloric acid (although sulphuric can be used), which brings with it another set of potential problems. A paper by Flett12 gives a good overview of cobalt SX technology including 301, together with some of the other available processes.

In short, DCP concluded that new technology such as Goro would not be appropriate for the DRC especially for a major revenue stream like cobalt.

5.4. SOME OTHER PROCESSES

5.4.1. Sulphide Precipitation

Sulphide precipitation has been used in many applications to purify a cobalt stream. For example at Lulu there are two sulphide precipitations:

1) Nickel sulphide precipitation using NaHS and cobalt granules
2) Zinc sulphide precipitation using H₂S generated in situ from NaHS and dilute sulphuric acid.

\[ \text{ZnSO}_4 + \text{H}_2\text{S}(g) \rightarrow \text{ZnS} \downarrow + \text{H}_2\text{SO}_4 \]

At Shituru, a side-stream from the cobalt EW circuit is treated with elemental sulphur and SO₂ for nickel removal:

3) \[ \text{NiSO}_4 + \text{S}^2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NiS} \downarrow + 2\text{H}_2\text{SO}_4 \]

These processes can be useful since they are very effective at removing the troublesome impurities in cobalt EW as saleable by-products but the sulphide precipitates, zinc especially, are difficult to filter. Sulphide precipitations also result in high cobalt losses to the precipitate.

The major drawback however is the hazardous nature of the process – especially the use of H₂S which has caused fatalities. Sulphide precipitation was considered too hazardous in the DRC context.

5.4.2. Superoxidants

The use of Caro’s acid, H₂SO₅, or ozone for separation of cobalt from nickel has been investigated extensively. A paper by Owusu13 describes the Caro’s Acid process and one by Dunn et al14 reports favorable test results on both processes. However, there are no large scale commercial operations.

The production and use of ozone or Caro’s acid (direct addition of strong H₂SO₅ to hydrogen peroxide) would not be appropriate in the DRC. Further it should be noted that the product is insoluble trivalent cobaltic hydroxide – and many end users do not want this.
5.4.3. Ion Exchange

Ion exchange (IX) undoubtedly has a role to play in the production of high-grade cobalt. The chemistry is basically the same as solvent extraction, but in IX the organic resin is based on a macroporous polystyrene matrix and operates as a fixed solid bed in a series of reactor vessels. The flow through the IX vessels is strictly limited (a few bed volumes per hour) to provide residence time and avoid breakthrough, so IX is best suited to relatively small flow rates of concentrated cobalt solution – specifically impurity polishing of cobalt advance electrolyte. Two IX applications are currently finding favour in cobalt projects:

1) Purolite S950 for copper removal;
2) Dow XFS4195 for nickel removal and sometimes copper.

Both of the above processes are provided for in the KOL “future” cobalt EW circuit.

The Purolite resin is relatively cheap, but the XFS4195 can present a major cost in terms of first fill and operating expenditure. A practical difficulty is the automatic operation of the valves as the duty of the vessels is changed (lead – lag – elute – regenerate – wash - standby).

5.4.4. Molecular Recognition Technology

Molecular Recognition Technology (MRT) is similar to IX but employs specially made SuperLig® resins. The process has been trialed with some success for selective recovery of cobalt or impurity removal from cobalt but, due to the expensive resins and resin usage, the economics are unfavorable in comparison to other processes. For details of Cu/Fe removal from a cobalt stream, refer to a paper by Izatt et al.

5.4.5. Resin in Pulp

A number of resin-in-pulp flowsheets have been proposed for nickel/cobalt. The process is analogous to the CIP process used in the gold industry. Instead of activated carbon, a resin similar to IX is used to load the target metal. It was considered for DCP/KOL to extract a portion of the cobalt from the dilute bleed stream prior to hydroxide precipitation; and transfer it into a high strength solution, suitable for cobalt EW.

It was rejected because it is unproven on a large scale; and because of the uncertain economics and practicalities associated with resin degradation and losses.

5.5. COBALT ELECTROWINNING

5.5.1. Cobalt EW Background

Most current cobalt projects are directed towards the production of cobalt cathode because of the high price that good quality metal commands. However few people appreciate how difficult it is to make cobalt cathode in significant quantities. Plating cobalt is fraught with difficulties, unlike copper, nickel and even zinc.

The fundamental problem is the highly stressed nature of the deposit, the stress increasing with deposition time and other factors until the deposit "peels" itself off its stainless steel cathode blank. Various tricks of the trade are employed in an effort to keep the cobalt on the cathode for sufficient time to grow to a reasonable thickness (~3mm). Zambian and DRC plants grow the cathodes with no edge strips, so as to allow the cathode to grow right around the edges whereby it cannot peel off. The downside of this is the major manual effort (hammer and chisel) required to strip these deposits from the cathode blanks.

At INCO’s Port Colbourne, to avoid the above problems, cobalt is electrowon from the purified electrolyte as “rounds”, which are 1” diameter cobalt discs, deposited onto stainless steel mandrel sheets. The mandrels are produced by applying dielectric heat-cured epoxy paint to a blank stainless steel cathode following a suitable pattern using a silk screening process. The paint lasts 8-10 cycles after which it must be re-applied. The mandrel surface is also periodically sandblasted, exposing virgin metal, to maintain deposit adhesion. The process is described in a paper by Agnew et al.

A similar process – “crowns” - is employed by Falconbridge. Both processes are patented.
5.5.2. Divided versus Undivided Cells
Many cobalt plants use undivided cells, whereas in nickel electrowinning divided cells are normally used, in which the cathodes are enclosed by a porous membrane or “bag”. This gives some control over the competitive side-reaction of hydrogen evolution at the cathode by withdrawing the spent electrolyte (high in acid) from the anode compartment for return to cobalt re-leach or SX.

At the Port Colbourne plant, the anodes are bagged and not the cathodes as in nickel. This allows improved flow of catholyte and control of pH in the cathode compartment. Certain current cobalt projects plating full sheet cathodes are now attempting the use of divided cells with anode bags. However, an adherent deposit is essential to avoid damage to the bags by “peelers”.

A major benefit of anode bag technology is that the acid/oxygen mist produced at the anode is captured together with the anolyte and withdrawn to a collection/separation/scrubber system. This results in a significant improvement to the cellhouse atmosphere.

Developments on this front will be watched with interest.

5.5.3. Electrowinning from Pulp
An interesting variation of cobalt EW is practised at the Shituru plant in the DRC. After partially re-leaching the intermediate cobalt hydroxide (hydrate), the entire slurry is sent direct to the electrolysis cells, which operate at pH6.2 - 6.4. As acid is produced in the cell it is immediately consumed by the cobalt hydroxide in the slurry, thereby maintaining pH and cobalt tenor.

Unfortunately, the cobalt cathode is physically and chemically inferior to normal EW cathode. The process is described in a paper by Twite et al.17

6. NEW DCP/KOL REFINERY FLOWSHEET
The new DCP/KOL operation is designed to significantly improve on the recoveries of both copper and cobalt as compared to the old plant, mainly by leaching the ore directly and eliminating the concentrator step and its associated losses.

The following Figure 7 depicts the cobalt process flowsheet eventually chosen by DCP (prior to the Katanga/Nikanor merger). As can be seen, the new cobalt section is similar to old Luilu minus the sulphide precipitations, despite there being many other interesting and potentially suitable cobalt processing options to choose from.

![Fig 7: New Refinery Simplified Cobalt Flowsheet](image)

Note that after the Nikanor/Katanga merger, although the old and new plants will be merged, it is planned to retain this basic flowsheet for the KOV oxide ore, including the new cobalt section.
7. CONCLUSIONS

There are a number of processes available to the designers of a cobalt recovery circuit. Each has its pros and cons. For the massive DCP/KOL project, the end product will be a hydroxide intermediate produced with tried and tested technologies – apart from manganese precipitation with SO$_2$/O$_2$. Environmental and logistical issues weighed against some of the newer technologies.

DCP/KOL decided against using the established SX processes at this stage, mainly to keep the process simple but also to avoid the sodium sulphate environmental problems and the risks of having multiple SX reagents on the same site.

When the operation is established, the cobalt refining circuit will be extended to produce up to 12 000 tpa electrowon cathode and will utilise IX and/or SX for impurity polishing.

The redevelopment of the KOV and Kamoto mines in conjunction with the establishment of a new refinery and refurbishment of the old Luilu refinery will place KOL as one of the major copper and cobalt producers in the world and will contribute significantly to the economy of the Katangan region of the DRC and its people.

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