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Nickel-Cobalt-Copper Keynote

**FLOWSHEET OPTIONS FOR COBALT RECOVERY IN
AFRICAN COPPER–COBALT HYDROMETALLURGY CIRCUITS**

By

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ABSTRACT

The price of cobalt has increased by some 450% in the past two years, mainly due to increasing demand for lithium-ion batteries, which are in widespread use in consumer electronics and increasingly required for electric vehicles. There are limited alternatives to cobalt in these batteries at present. With an official production of 64 000 t in 2017, the Democratic Republic of Congo produces more than half of the world's cobalt, which is eight times more than that of its closest competitor.

African Copperbelt operations have traditionally focused on copper production; however, it has now become imperative to also consider cobalt recovery from these ores. A plethora of processing routes are possible. Most hydrometallurgical flowsheets recover cobalt from the raffinate of the low-grade copper solvent-extraction circuit, although dedicated cobalt leaching, which typically requires reductive conditions, is now considered. Downstream purification processes include sequential precipitation with a variety of reagents, solvent extraction, and ion exchange. Product choices include hydroxide, carbonate, sulphate, and metal cathode.

This review assesses technical and economic advantages and limitations of various approaches to the hydrometallurgical processing of cobalt in an African context.

Keywords: Cobalt, hydrometallurgy, flowsheet development, Africa

INTRODUCTION

Owing to recent decisions and proposals by an increasing number of countries around the world to phase out diesel and petrol vehicles from 2025 onwards and replace them with electric vehicles[1,2], the demand for metals associated with battery components for electric vehicles—cobalt, nickel, lithium, and graphite—has escalated remarkably. These metals are also used in the burgeoning consumer electronics industry, such as in batteries for mobile phones, laptops, portable medical equipment, and other devices, and in emerging applications in small-scale storage of renewable energy in homes (the Tesla Powerwall is the best example) and grid-scale electrical storage, typically exceeding 100 kWh[3]. Lithium-ion batteries (LiB) provide an ideal combination of low mass, high energy density, long life, low maintenance, and scalability[4].

There are two main types of LiBs[5]: non-rechargeable (primary) batteries and rechargeable (secondary) batteries. Rechargeable LiBs have received most attention and have a market value almost ten times that of the non-rechargeable types[6] (Figure 1). The largest market is in portable consumer goods; however, although continued growth is expected, it is anticipated that the electric vehicle market will grow significantly and outstrip that of consumer goods within the next ten years. Figure 2 shows one of many forecasts for the LiB battery market[7].
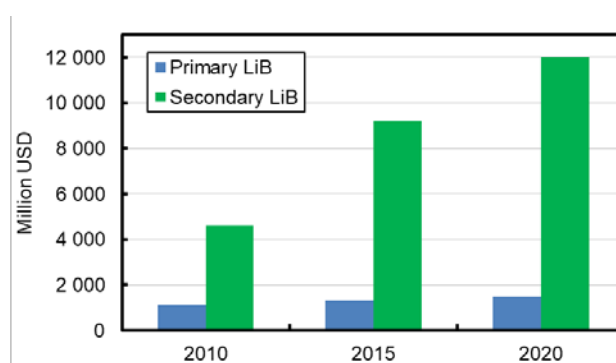

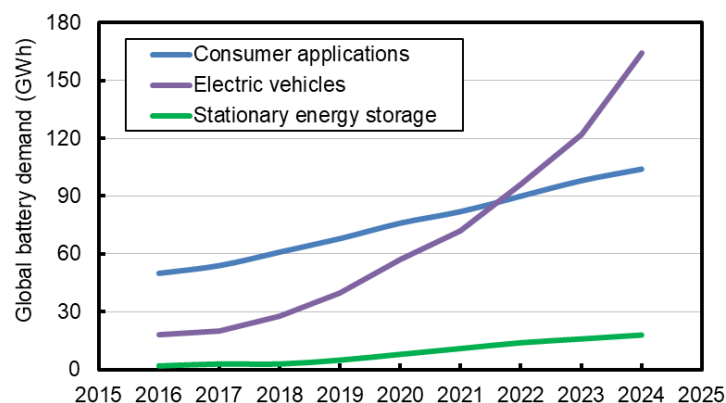**Figure 1: Global market share of primary and secondary lithium-ion batteries[6]**

Figure 2: Projected market growth of lithium-ion batteries[7]

The most widely employed cathode material is $LiCoO_2$, typically comprising ~28 mass% of an LiB[4]. Battery compositions vary widely, and much R&D in lithium-ion technology is associated with different formulations for the electrolyte and the cathode. Many of the more promising formulations for cathode chemistry, including those of $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, $LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{0.9}Co_{0.1}O_2$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $LiNiCoAlO_2$, and $LiFePO_4$, incorporate cobalt.

For cobalt, in particular, supply-chain considerations are important. Some 98% of the world's cobalt is a byproduct of the mining of copper or nickel. With an official production of 64 kt in 2017[8], the Democratic Republic of Congo (DRC) (Figure 3) produces more than half of the world's cobalt, eight times more than its closest competitor (Figure 4)[9,10]. Reliability of supply is, however, compromised by geopolitics, corruption, poverty, use of child labour and artisanal mining, armed militias, and poor infrastructure[11]. Figure 5 shows the variation in the London Metal Exchange (LME) price of cobalt since 2005[12]. Although the dramatic price hike of the past two years, and particular, recent months, has yielded an escalation of some 450%, much higher prices—exceeding USD 110,000/t—were, in fact, breached during the global financial crisis of 2007/8.
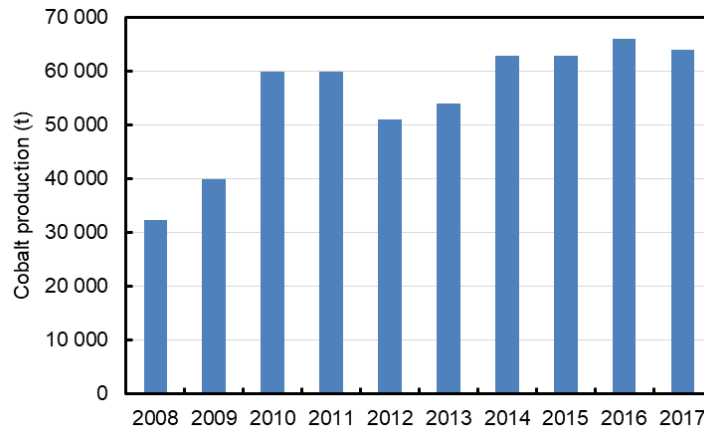
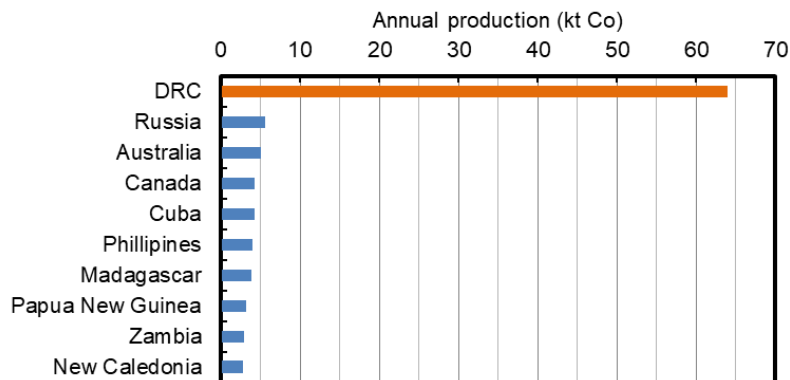**Figure 3: Annual cobalt production of Democratic Republic of Congo[8]**

Figure 4: Top ten cobalt-producing countries in 2016[10]
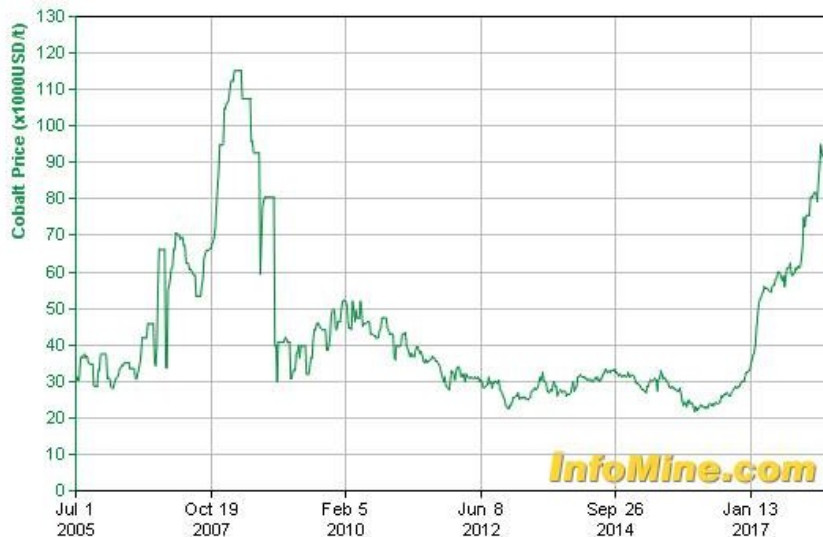
Figure 5: Variation in cobalt price from July 2005 to June 2018[12]

This disproportionate reliance on one main source of cobalt supply, particularly in view of the DRC government's recent changes to mining legislation with regard to strategic metals and the introduction of taxes of 50% on super profits,[13] means that there is increasing focus on alternative sources, albeit that they may be of considerably inferior quality in most respects. To remain competitive, take advantage of the current cobalt price, reduce operating costs, and improve product quality, DRC operations are focusing intently on flowsheets for cobalt recovery from their existing copper circuits. This review discusses various flowsheet options for the hydrometallurgical processing of cobalt from primary African Copperbelt sources and the technical and economic advantages of different product choices.

COBALT PROCESSING OPTIONS FOR THE AFRICAN COPPERBELT

The African Copperbelt stretches from Zambia through to the DRC, as shown in Figure 6. It is rich in cobalt and copper, estimated to comprise over one-third of the global reserves for cobalt and one-tenth for copper[14]. The main minerals of the oxide zone that is the current focus of most operations are malachite ($CuCO_3 \cdot Cu(OH)_2$), chrysocolla (($Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$), and heterogenite ($CoO(OH)$), with siliceous dolomite ($CaMg(CO_3)_2$) and quartz (SiO_2) as the main gangue minerals[14]. Copper production is via the well-known hydrometallurgical process that comprises leaching of the ore in sulphuric acid, solution purification using solvent extraction (SX) and metal recovery as copper cathode by electrowinning (EW)[15,16]. Cobalt metal has been produced since the late 1940s in DRC and since the early 1990s in Zambia[17]; other products are currently preferred.
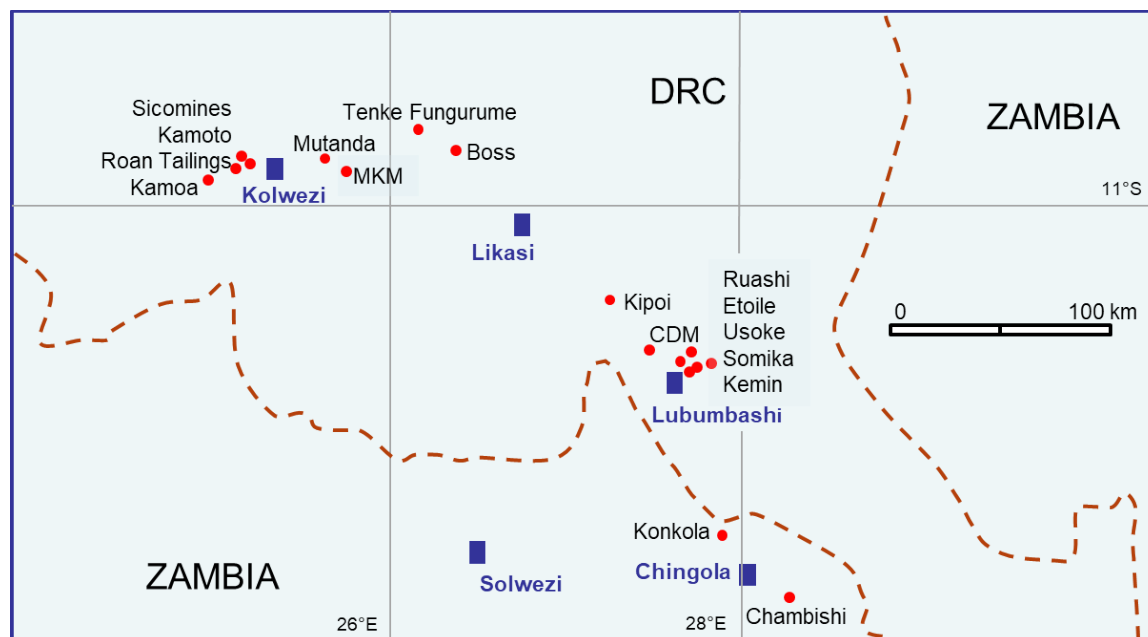
Figure 6: Location of major cobalt operations and projects in the African Copperbelt

All DRC operations carry out leaching under ambient conditions, usually by agitated tank leaching or, less often, by heap leaching. Under these conditions, acid-soluble minerals of both copper and cobalt report to the pregnant leach solution (PLS). Co(III) minerals, such as heterogenite, require the use of a reducing agent to solubilise the cobalt: sodium metabisulphite (SBMS) or sulphur dioxide (SO_2) are typically employed[18,19]. The high grades of these ores produce PLS tenors of 15–20 g/L Cu, while cobalt can range up to 3 g/L. Modern copper extractants are extremely selective for copper over all other base metals (although small amounts of iron(III) can be chemically complexed), so very little copper, but almost all cobalt, report to the raffinate. To conserve sulphuric acid, most plants employ split high-grade (HG)/low-grade (LG) SX circuits[20], in which the HG raffinate is recycled to leaching and the LG raffinate is used for washing of the solid leach residue and then a bleed or the entire stream treated for cobalt recovery.

A typical LG raffinate composition is as follows (g/L): Cu 0.2–0.5; Co 2–3; Fe 1–2; Mn 1; Al 1; H_2SO_4 10–15. All cobalt flowsheets first consider the removal of Fe(III), Al, and most Mn from the LG raffinate by precipitation with lime at pH 3–4.5 (so-called FAM removal) in a series of stirred tanks. Residual Cu can similarly be precipitated at pH 5–5.5 using lime. The FAM cake reports to tailings; the copper cake is recycled back to the process. Washing efficiency is obviously of paramount importance to minimise soluble losses of Co to the precipitation cakes, particularly in the FAM step.

The resulting overflow can then be treated in a variety of ways, depending on the flowsheet or product preference, the product purity required, and the prevailing economic conditions and constraints. The usual product choices include cobalt hydroxide, carbonate, sulphate, or metal. The main process routes for the various products are discussed in the sections that follow.

Separation of Copper and Cobalt Circuits in the Leaching Step

Two main approaches are taken with respect to the leaching step: copper and cobalt are usually leached simultaneously, but some flowsheets use sequential leaching. At Ruashi, Tenke Fungurume, Boss, and Kamoto Copper (Figure 7(a)), as examples, copper and cobalt are simultaneously dissolved in the primary leach using acid and SO_2 (added as SMBS) for reduction of Co(III) minerals. The downstream thickener overflow (O/F) advances to an HG copper SX circuit and this raffinate is recycled to the leach. The thickener underflow (U/F) is fed to a counter-current decantation (CCD) train to wash out entrained copper and cobalt values from the leach residue that reports to tailings, while the O/F from the first CCD stage is fed to an LG copper SX circuit. The raffinate from the LG Cu SX is bled to cobalt recovery.

A more complicated circuit is used by Roan Tailings Reclamation (RTR) (commissioning in 2018) to separate the copper and cobalt leach steps (Figure 7(b)). The reclaimed tailings feed is repulped in raffinate to leach copper. Any acid-soluble Co will also leach. The O/F from the subsequent thickener reports to a primary Cu SX circuit and the raffinate is recycled to the copper leach. The thickener U/F reports to a cobalt leach step where SO_2 is added to solubilise the Co(III) minerals. The slurry from the cobalt leach is washed in a CCD circuit to produce an U/F for tailings disposal; the O/F from the first CCD stage becomes the feed to the cobalt recovery process. The filtrate after iron removal feeds an LG Cu SX circuit that is integrated with the main copper circuit.

While the second configuration is more complicated and capital-intensive, it does offer savings in terms of acid consumption: less Cu reports to the LG SX circuit.

(a)

(b)
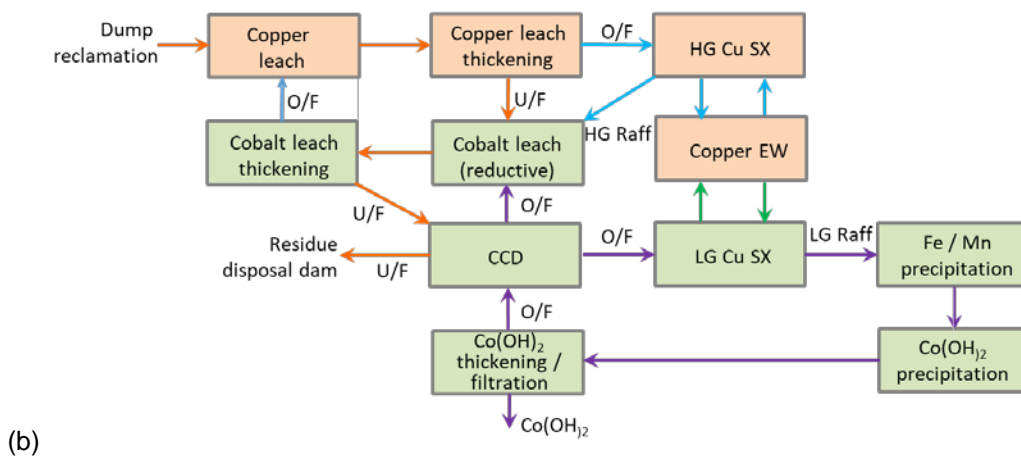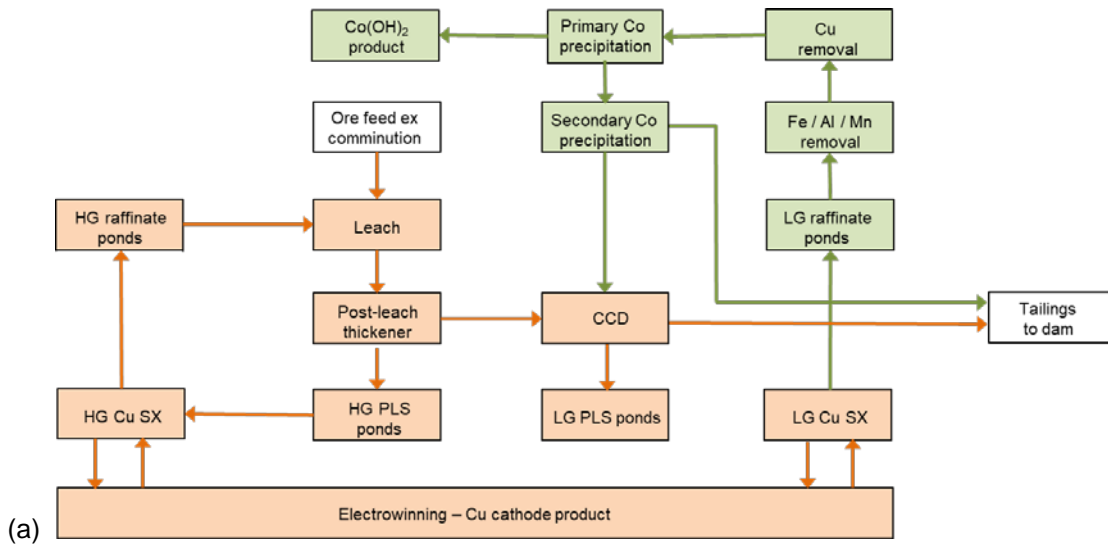
Figure 7: (a) Flowsheets used at Kamoto Copper, Tenke Fungurume, and Ruashi with simultaneous leaching of copper and cobalt; (b) Roan Tailings Reclamation flowsheet in which copper and cobalt leaching steps are separated.

Impurity Removal by Precipitation and Oxidation

The most widely employed flowsheets use a sequence of metal hydroxide precipitation steps to remove impurities from the cobalt-containing liquor, as well as produce a cobalt hydroxide product. Figure 8 shows the selectivity of metal ion precipitation by hydroxide as a function of pH[21].

In the first step, iron, aluminium, and manganese are removed by a combination of oxidation and precipitation. Iron needs to be oxidised to the 3+ state and manganese to the 4+ state. This can be done with air, but the kinetics are very slow. Mixtures of air and SO_2 have been shown to increase to rate of oxidation by an order of magnitude. Practically, it is sensible to implement such oxidation using aqueous SO_2 or SMBS, together with air[22-24]. Once oxidation is complete, the three metals will precipitate with lime at pH 3.5. Iron and aluminium removal can be further enhanced by the presence of phosphate that often occurs in these ores as pseudomalachite ($Cu_5(PO_4)_2(OH)_4$); iron and aluminium phosphates begin precipitating at lower pH values than the hydroxides.

In the second step, copper is removed by simple precipitation with lime at pH 5.5–6. There is some coprecipitation of cobalt but, because the copper cake is recycled to the leach plant, there is no overall cobalt loss.
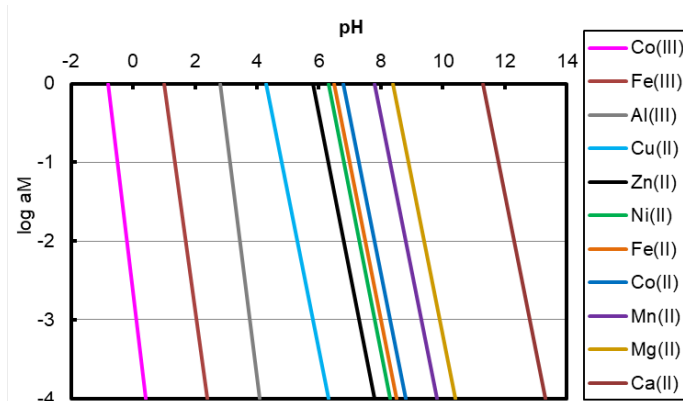

**Figure 8: Precipitation of base metal hydroxides as a function of pH[21]**

Product Recovery by Precipitation

Cobalt Hydroxide as a Product

$Co(OH)_2$ precipitates at pH 7.5, so pH 8–8.5 is required to achieve quantitative cobalt precipitation. All metals precipitated at lower pH (Figure 8) report quantitatively with Co and it is likely that all nickel and zinc present will precipitate and contaminate the cobalt hydroxide product. Magnesium only starts precipitating at around pH 10 so it is possible to use magnesia as the precipitant with only minor contamination by excess or unreacted MgO. Calcium precipitates at pH 11.3, but if lime (CaO) is used, the low solubility of $CaSO_4$ means that gypsum co-precipitates and will reduce the cobalt grade of the hydroxide product to below 20%. Several operators therefore employ a two-stage precipitation:

1. at pH 7.5 with MgO: to maximise cobalt product grade by minimising the presence of unreacted magnesia in the product;

2. at pH 8.5 with lime: to ensure overall cobalt recoveries exceeding 99%. This precipitate is recycled to the iron-removal stage or to the leach.

The precipitation of cobalt from aqueous solutions at pH 7.5–8 is not as simple as might first appear:

$$CoSO_4 + MgO + H_2O \rightarrow Co(OH)_2\downarrow + MgSO_4. \hspace{2cm} [1]$$
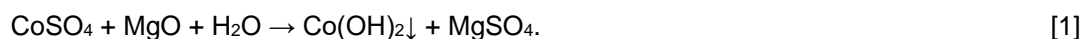
Such a reaction would be expected to produce a product that would grade 55–63% cobalt, given that the impurities are removed to levels that can readily be achieved. Cobalt is, however, present in solution as the hexa-aqua species and, when precipitated, a variable portion of the ligand water remains with the hydroxide. In addition, the precipitate is, in fact, a basic sulphate. The reaction can be better represented as follows:

$$5[Co(H_2O)_6]SO_4 + 4Mg(OH)_2 \rightarrow [Co(H_2O)_y]_5(OH)_8SO_4\downarrow + 4MgSO_4 + (30 - 5y)H_2O. \hspace{1cm} [2]$$
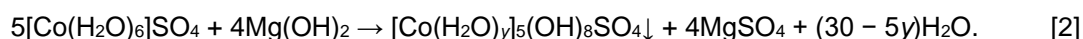
Evidence suggests that: (i) the basic sulphate contains only one sulphate ion because the sulphur analysis is normally in the range 3 to 6%; (ii) the amount of ligand water that is displaced depends on temperature and the choice of precipitant.

Until a few years ago, Chemaf's Usoke plant employed NaOH as a precipitant, but the high costs and very poor settling and filtration characteristics led to a move to MgO. Most other plants in the African Copperbelt use either lime or magnesia. With lime, the activity of the specific reagent influences the quantity of unreacted $Ca(OH)_2$ that reports to the product: fortunately, good quality sources are available from Zambia, Tanzania, and elsewhere in the region. Released calcium precipitates as insoluble calcium sulphate, which also reports to the product. For this reason, MgO is generally preferred, despite its considerably higher delivered price (hydrated lime: USD 400/t; MgO: USD 1400/t); however, MgO is itself insoluble, which can cause under-utilisation and magnesium contamination of the product. Furthermore, high-reactivity magnesia is not easily sourced in the region: the two suppliers most widely used for Congolese applications are Sibelco (Australia) and Martin Marietta (USA), so transport costs typically exceed the basic purchase price of the reagent.

The theoretical cobalt content of a dry pure cobalt hydroxide is 63.4% (the balance being hydroxide of no value). Typical moisture content for these types of filter cakes is around 50% or higher. Hydroxides do not filter as well as carbonates. Although valuable metal content in the hydroxide is significantly higher than in the carbonate, at least half of the mass transported to the buyer would be of no value unless the cake is dried further. Cobalt hydroxide is also prone to oxidation.

Cobalt hydroxide is produced using magnesia at Tenke Fungurume Mining (TFM), Mutanda Mining, Kamoto Copper, Sicomines, CDM (China Dongfang Mining), and MKM (La Minière de Kalumbwe Myunga) and will be at RTR. A generic flowsheet is presented in Figure 9. In 2010, Ruashi changed from producing $CoCO_3$ to $Co(OH)_2$ using MgO as precipitant.
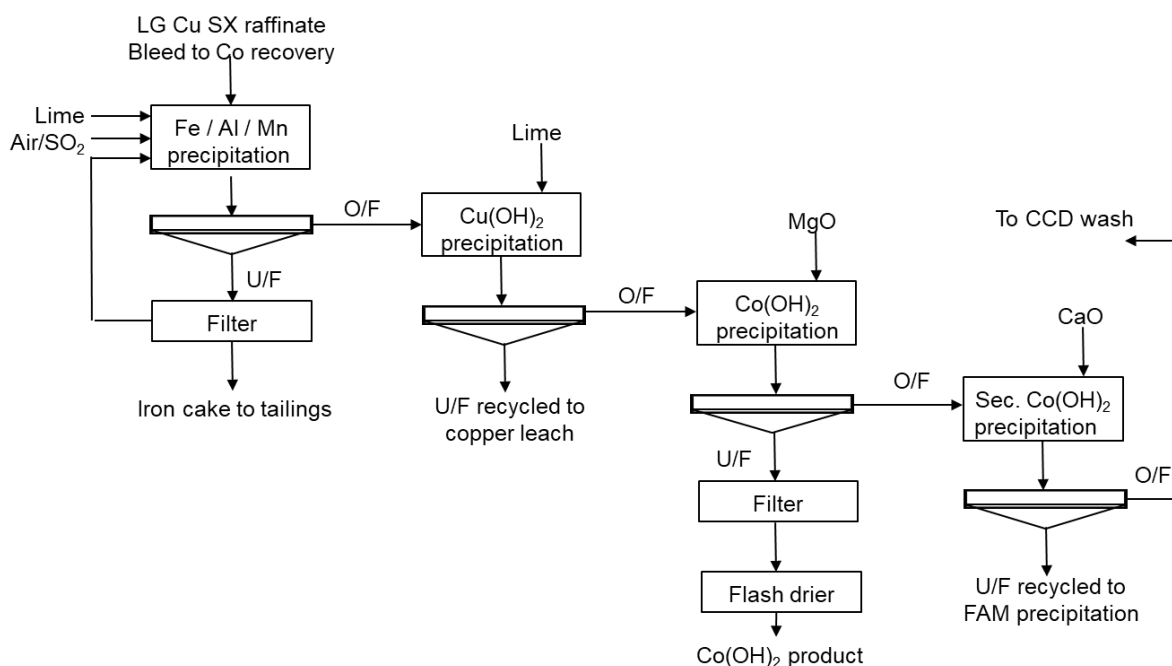
Figure 9: Generic cobalt recovery flowsheet by two-step magnesia and lime precipitation used by Tenke Fungurume, Mutanda Mining, Kamoto Copper, and Sicomines

The high cost of MgO is one of its most significant drawbacks. Build-up of Mg associated with the use of MgO in process streams can also increase their viscosity, which can, in turn, adversely affect downstream processes, such as solid–liquid separation, with associated effects on the Cu SX–EW circuits due to solids' carryover. The barren stream from cobalt purification must therefore be neutralised with lime to precipitate and bleed Mg before recycling the barren stream as process water. This generates an effluent stream that contains both $Mg(OH)_2$ and $CaSO_4 \cdot 2H_2O$ (gypsum).

Technology patented by Mintek[25] enables $Mg(OH)_2$ in this stream to be selectively recovered and recycled, thereby reducing consumption of fresh MgO. The process is based on the separation of fine $Mg(OH)_2$ particles from coarse gypsum particles using an elutriation classifier[26]. The technology has

been demonstrated on a semi-continuous basis, with the recovered Mg(OH)$_2$ used to precipitate Co from a 5.5 g/L solution. The reactivity of the recovered Mg(OH)$_2$ compared favourably with that of fresh MgO samples from two suppliers. A cake with a Co grade of 46% was produced using recycled Mg(OH)$_2$ and its contamination by Mg (1.3%) and Ca (1.3%) was relatively low.

Additionally, Glencore Technologies has published a paper[27] on the use of lime as a precipitant and the subsequent separation of gypsum from the Co(OH)$_2$ on the basis of particle size. This study suggested that, after screening at 38 μm, a cobalt cake with a grade of 47.5% could be achieved at a first-pass recovery exceeding 90%. The higher grade was achieved at lower pH, around 7.5, which reduced precipitation of Mg that was present as a soluble species from the ore leaching. Separated gypsum can be recycled to the iron-removal circuit or to the leach plant.

Table 1 shows comparative reagent costs for MgO and lime for a production of 10 kt/a contained cobalt without reagent recycle. On this basis, techno-economic assessment of either the Mintek or Glencore processes indicates that massive annual savings are potentially possible. These technologies remain to be validated at demonstration scale and for a significant operating period, but their commercial viability may significantly change the current scenario with respect to selection of precipitation reagent.

Table 1. Comparative operating costs of precipitation by magnesia and lime

Parameter	Magnesia precipitation	Lime precipitation
Cobalt production (t/a)	10 000	10 000
Magnesia usage (t/t Co)	0.75	0
Lime usage (t/t Co)	1	1
Magnesia price (USD/t)	1,400	1,400
Lime price (USD/t)	400	400
Annual reagent cost (USD)	14,500,000	4,000,000

Cobalt Carbonate as a Product

Cobalt carbonate can be precipitated from sulphate solution with a suitable carbonate base, such as Na$_2$CO$_3$, ideally at a temperature of 60°C. Limestone (CaCO$_3$) can be used, but utilisation using this insoluble reagent can be poor; in addition, calcium sulphate is co-precipitated, which contaminates the final product. Unlike hydroxide, the carbonate product is not prone to oxidation and is readily soluble in acidic solution. Soda ash is readily available in the Copperbelt region from Botswana at a typical delivered cost of USD 350/t.

The reaction with soda ash solution is:

$$CoSO_4 + Na_2CO_3 \rightarrow CoCO_3\downarrow + Na_2SO_4. \hspace{2cm} [3]$$

As indicated by the order of precipitation selectivity shown in Figure 10, the pH dependence of the reaction equilibrium allows some split between metals by pH control. Cobalt precipitates as a carbonate at pH 7.5: quantitative cobalt precipitation requires pH 8–8.5. At this pH, all the metals shown to the left of cobalt would be quantitatively precipitated, as well as significant quantities of those that occur after cobalt in the sequence. To achieve the chemical specifications for high-purity cobalt carbonate, significant removal of iron, copper, zinc, and manganese is required. Although magnesium and calcium limits are not typically specified, their presence in the product will lead to significant reduction in the cobalt content of the final product.

Boss Mining is the only operation currently employing soda ash for precipitation. Copper and cobalt are coprecipitated from a process bleed stream after iron removal: the product contains only ~11% Co, but has a moisture content exceeding 70%. Significant losses of both Cu and Co also report to the iron cake. An alternative process route is currently under investigation. It is notable that Ruashi moved away from the use of soda ash in favour of MgO and production of a Co(OH)$_2$ product in 2010.
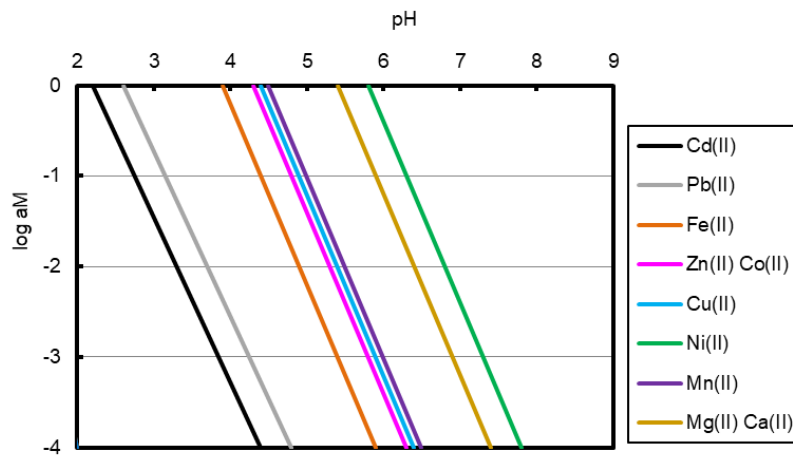
Figure 10: Precipitation of base metal carbonates as a function of pH

Purification by Solvent Extraction and Ion Exchange

Production of higher purity products requires more sophisticated technologies for purification of the cobalt streams[28]. Although not yet widely employed on the Copperbelt, most new projects are now considering the use of techniques such as SX and ion exchange (IX), particularly when targeting a cobalt metal product. Cobalt EW requires <1 mg/L Zn, <1 mg/L Cu, and <150 mg/L Ni in the advance electrolyte, a target not easily achieved with traditional technologies.

Chambishi Metals (Zambia) is the only Copperbelt refinery that currently employs both SX and IX process steps, as shown in Figure 11. In the main copper flowsheet, the primary SX raffinate is neutralised and then a second copper SX step employed to remove copper to low levels (<0.5 g/L). The LG raffinate is bled to the cobalt refinery process. Iron, aluminium, and any residual copper are precipitated at pH 3.6–3.8 using lime. Zinc and some manganese are then removed by SX with di(2-ethylhexyl)phosphoric acid (D2EHPA). $Co(OH)_2$ is subsequently precipitated stepwise, first at pH 6.5 using impure cobalt materials obtained from external regional sources and then at pH 7.8–8.2 using lime, which separates cobalt from the remaining manganese and magnesium impurities: these exit in the waste liquor (although the separation from manganese is incomplete). The $Co(OH)_2$ precipitate is redissolved at pH 6.4 in acidic spent electrolyte from Co EW. Nickel is removed from a bleed of this 25 g/L Co electrolyte by IX using Dow's hydroxypropyl picolylamine (HPPA) resin[29-31]. The purified cobalt advance electrolyte then passes to the tank house for cobalt recovery by EW.
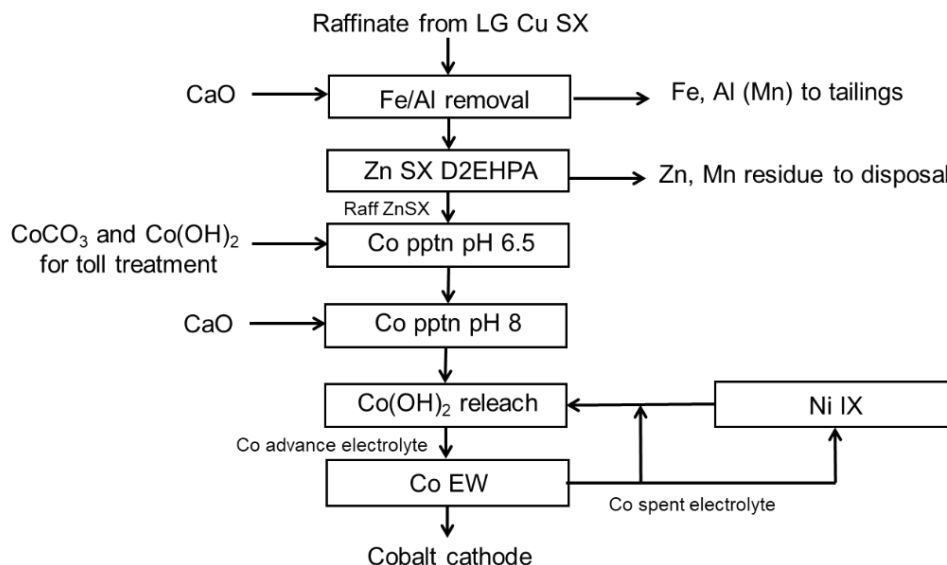

Figure 11: Simplified flowsheet of Chambishi Metals cobalt recovery process

Organophosphorus-acid extractants are most widely employed for purification of cobalt streams, particularly on laterite operations and in refineries. SX has, to date, been largely avoided in Africa because of its perceived sophistication required in terms of operational control and the need for pH control. Zinc (and residual copper) can be readily removed using D2EHPA with no loss of cobalt (see Figure 12(a))[32,33] and without the need for pH control, so this is the preferred reagent when Zn levels exceed about 0.5 mg/L.

In contrast, Cyanex 272 can be used to extract cobalt from Ca, Mg, and Ni, and thereby purify the cobalt stream; however, pH control is typically required because of the higher pH range in which this reagent operates (Figure 12(b)). Sodium or ammonium hydroxide can be used, usually in a preneutralisation mode that makes pH control easier and does not require inter-stage neutralisation. These reagents do not introduce any solids to the circuit, but produce a sodium- or ammonium-containing barren stream that needs to be treated before it is discarded.

(a)

(b)
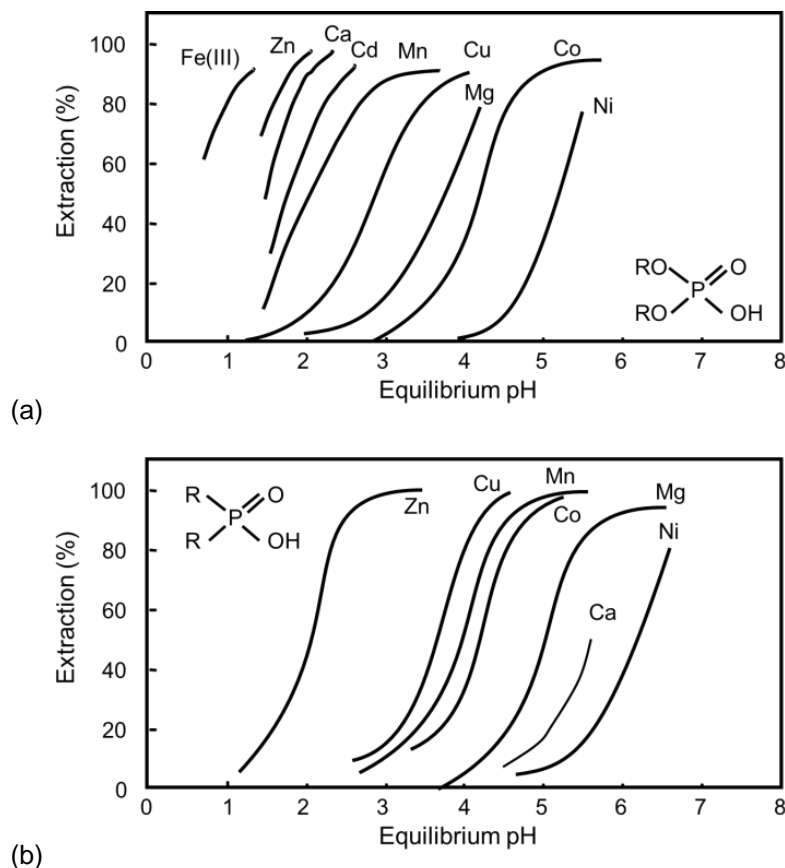
Figure 12: Order of selectivity of base metal extraction for (a) organophosphoric (D2EHPA) and (b) organophosphonic (Cyanex 272) acid extractants[32]

In general, however, IX is a more suitable technology to achieve the high-purity specifications of cobalt electrolytes, does not require the use of flammable and toxic solvents, and is easily automated and controlled. Swartz et al.[34] assessed various flowsheet options for the processing of Copperbelt ores and recommended achieving the required purity of cobalt electrolytes by simultaneous removal of Cu and Zn by IX using aminophosphonic-acid functionality, which has an order of selectivity of:

Pb > Cu > Zn ~ Al > Mg > Ca > Cd > Ni > Co > Sr > Ba > Na.
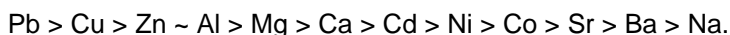
These resins were successfully piloted for the Kakanda flowsheet (now Boss Mining) for the removal of trace Cu (~70 mg/L) and Zn (~2 mg/L) from 50 g/L Co electrolyte using fixed-bed lead–lag columns[35,36] and for Kolwezi Mine Tailings (now RTR)[37]. IX has also been successfully proven at pilot scale for purification of a 20 g/L Co electrolyte at Kamoto Copper's Luilu plant[38,39]: using a lead–lag fixed-bed configuration, Cu was first removed using an iminodiacetic-acid resin (TP 207), which has an order of selectivity of:

Cu >> Ni > Zn ~ Co ~ Cd > Fe(II) > Mn > Ca,
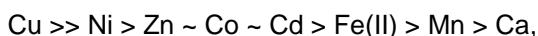
followed by Zn using an aminophosphonic-acid resin (TP 260). A cobalt electrolyte containing <1 mg/L Cu and Zn was consistently produced. Dowex M4195 bispicolylamine resin (or its more modern HPPA versions)[29] can be similarly used for the removal of trace nickel.

Resins impregnated with D2EHPA (such as Lewatit VP OC 1026) and Cyanex 272 (TP 272) have also been successfully used for the purification of cobalt- (and nickel-) containing streams[40,41] or are in development for the production of battery-grade sulphate products. The use of molecular recognition technology, which can be considered a sister technology, has been proposed for Cd removal from cobalt electrolytes[42], although this impurity is not prevalent in DRC ores.

Several sites also contain measurable amounts of uranium. (Uranium used in the first atomic bomb was mined at Shinkolobwe near Likasi,[43] which is in the central Copperbelt region (Figure 6).) Its removal from sulphate liquors by IX using strong- or weak-base anion-exchange resins is well-known technology. The first application of uranium removal from a cobalt stream using Clean TeQ continuous IX resin-in-pulp technology will be commissioned later this year[44].

SX and IX applications, once regarded with some trepidation, are now under active consideration for Copperbelt cobalt flowsheets, particularly when higher-purity products are targeted. It is likely that these unit operations will feature commercially in Africa in the near future.

Cobalt Recovery as Cobalt Sulphate

Cobalt sulphate heptahydrate ($CoSO_4 \cdot 7H_2O$), containing approximately 21% Co, is prepared commercially by high-speed evaporation of water from concentrated cobalt sulphate solution in a crystalliser. On further heating to ~250°C, the product can lose its waters of crystallisation, becoming anhydrous cobalt sulphate. Cobalt sulphate is highly soluble in water and generally more stable than the other crystalline cobalt products and, for these reasons, is widely used as a source of cobalt(II) for the manufacture of cobalt chemicals, as well as for the electroplating industries and as an additive in animal feedstock.

Evaporative crystallisation of cobalt sulphate is successfully used at Rustenburg Base Metal Refiners (RBMR), South Africa[14]. The crystallisation process is non-selective, so a much higher purity of electrolyte is required: specifically, cations such as Mn, Mg, and Na need to be removed. At RBMR, cobalt is removed from a nickel leach stream by precipitation with nickelic hydroxide, $Ni(OH)_3$, and the filter cake is re-dissolved using formalin as a reductant for Co(III). After further steps of purification, the cobalt is extracted from nickel using D2EHPA[33] in an SX step to produce a pure cobalt sulphate solution from which high-purity $CoSO_4 \cdot 7H_2O$ is crystallised. Sodium levels are controlled by crystallising highly pure sodium sulphate that is sold as domestic detergent filler. Contamination by calcium and magnesium are avoided by using deionised water as make-up to the refinery; this also prevents chloride ingress to the circuit. Other soluble species present with cobalt in solution report to the crystal product, roughly in proportion to their relative concentrations in the feed solution.

The economics of a crystallisation process become more favourable as the saturation level in solution of the crystallising species is approached: 65 g/L Co for a cobalt sulphate solution. Crystallising from dilute solutions negatively impacts operating cost because energy requirements increase and the need for multiple crystallisation units significantly increases capital cost. While upgrading a dilute cobalt solution to more favourable concentrations for feeding a crystalliser is easily achieved using SX, the stringent specifications imposed on the crystalliser feed solution to produce premium-grade cobalt sulphate require further extensive purification. All contaminant metal species need to be removed to low levels, including magnesium, manganese, and sodium—in contrast to the requirement for cobalt EW. Greater sophistication of purification processing is required for high-purity cobalt sulphate production than is needed to produce a pure electrolyte suitable for cobalt EW.

Achieving the specification for manganese is possible using several sequential separation steps. The bulk of the manganese can be precipitated with a suitable oxidant, such as air/SO_2, that ensures Mn(II) oxidation to Mn(IV) and precipitation of insoluble MnO_2[22-24]. D2EHPA (see Figure 12(a)) is also able to achieve selective extraction of manganese over cobalt, thus providing further scope for reducing its concentration to acceptably low levels. Low levels of Mn may also be more suitably targeted using the D2EHPA-impregnated resin, VP OC 1026.

Achieving the magnesium specification is problematic. For D2EHPA, the order of metal extraction for cobalt and magnesium is reversed and magnesium extracts ahead of cobalt, but the separation is too poor (see Figure 12(a)) to effect any significant removal of magnesium without compromising

cobalt losses. Although Cyanex 272 demonstrates selectivity for cobalt over magnesium (see Figure 12(b)), the separation is not good enough to completely prevent magnesium extraction, even with the inclusion of a scrubbing step on the loaded organic phase.

Using the magnesium-rejection capability of a precipitation step in combination with an SX step using a phosphinic-acid extractant may prove successful in satisfying the specification demands on magnesium concentration in the feed to the crystalliser. The flowsheet shown in Figure 13 has features of the Tenke Fungurume and Ruashi II flowsheets up to production of a $Co(OH)_2$ intermediate; this precipitate can be further treated to generate a pure solution for feeding a crystalliser. Precipitating cobalt with MgO at pH 8 rejects in excess of 90% of the soluble magnesium. After redissolution in sulfuric acid, the solution is treated in an SX circuit that uses D2EHPA to remove copper, manganese, zinc, and iron. The raffinate advances to a second SX circuit where Cyanex 272 is used to upgrade the cobalt into a purified stream suitable for crystallisation of cobalt sulphate heptahydrate. IX is included as a polishing step for removal of residual copper and zinc. The use of three different extractants (including that of Cu SX) on a single plant is, however, potentially problematic, owing to loss of selectivity that would be caused by any cross-contamination. Highly clarified solutions are also required as feed to SX to avoid the formation of crud and the associated product contamination that arises from solids' egress to these systems. Despite many such flowsheets being proposed over the years[28,45-47], no commercial implementation has yet taken place.

An alternative to all of the above is to use metal production to effectively remove manganese and magnesium, as discussed in the following section. The metal can be atomised and redissolved in chemically pure (CP) sulphuric acid to generate CP-grade cobalt sulphate.
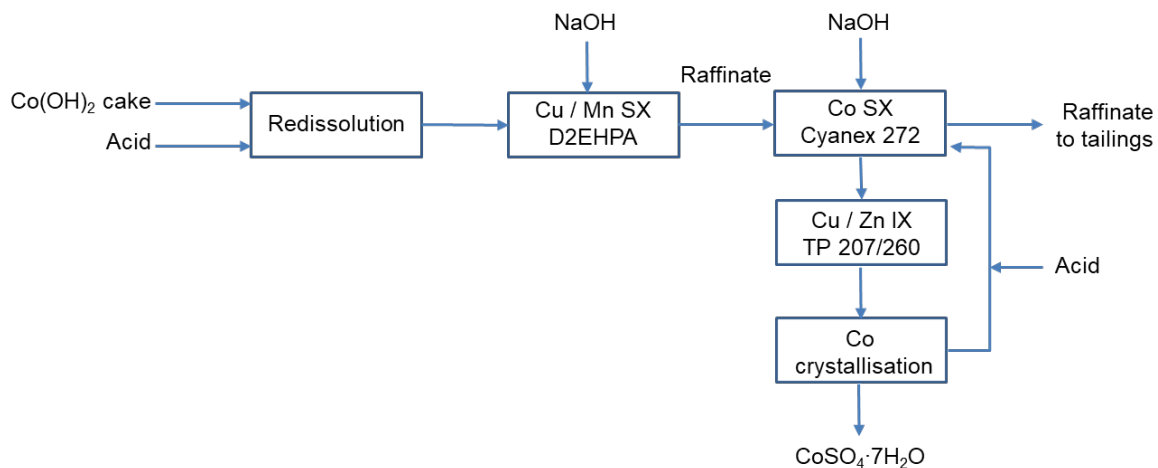
Figure 13: Schematic cobalt recovery flowsheet to produce high-purity CoSO₄·7H₂O

Electrowinning of Cobalt Cathode

Cobalt cathode is produced by electrowinning in undivided cells or using a membrane (divided cell). Cobalt in solution is reduced to metal at the cathode, but hydrogen evolution is thermodynamically favoured, which is why a divided cell may be preferred. The overpotential for hydrogen evolution is, however, such that use of a high Co concentration in the electrolyte, high temperature (~60°C), and high current density can reduce the tendency for this reaction to occur.

$$Co^{2+} + 2e^- \rightarrow Co \qquad\qquad E^0 = -0.28 \text{ V}; \qquad [4a]$$
$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad E^0 = 0.00 \text{ V}. \qquad [4b]$$

Water is oxidised at the anode to produce oxygen and acid:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad\qquad E^0 = -1.23 \text{ V}. \qquad [5]$$
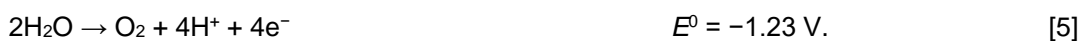
The overall cell reaction in a sulphate medium can therefore be written as follows:

$$2CoSO_4 + 2H_2O \rightarrow 2Co + O_2 + 2H_2SO_4 \qquad\qquad E^0 = -1.51 \text{ V}. \qquad [6]$$

This reaction is thermodynamically unfavourable, so cobalt EW requires precise control of operating parameters to produce high-quality cathode[48].

The economic feasibility of cobalt EW increases as the cost of energy decreases. The power consumption is estimated to be 3.5 kWh/kg Co, based on the following process conditions:

Current density:	300 A/m^2
Cell voltage:	3.5 V
Cathodic current efficiency:	70%
Rectifier efficiency:	90%

The cost of electricity in DRC is currently about USD 0.06/kWh, but backup generators, using diesel as fuel, are often employed due to grid stability issues, so the average energy cost may be up to USD 0.16/kWh.

Cobalt cathode produced to the required specification is the most marketable and saleable cobalt product. Cobalt metal is traded according to two specifications: premium (99.83%) and standard grade (99.73%). Table 2 compares the required composition of an advance electrolyte to a typical cobalt EW process to achieve a cathode purity of 99.7% Co with that for the production of high-purity cobalt chemicals[45].

Table 2: Specification of cobalt advance electrolyte to produce standard-grade metal and high-purity chemicals compared with a typical feed composition to cobalt circuit[45]

Element	Typical feed to Co circuit (mg/L)	Advance electrolyte (mg/L)	High-purity chemicals (mg/L)
Co	6000	60 000	60 000
Mn	1400	2000	10
Al	700	1500	2
Mg	1500	< 10 000	10
Ni	100	60	< 25
Fe	1200	< 3	2
Cu	150	< 2	2
Zn	50	< 3	2

Metal impurities such as copper, iron, and zinc have high upgrading ratios in EW and therefore have to be removed first. The EW process is fairly forgiving with regard to the levels of elements such as magnesium and manganese and complete removal of these species is not necessary, although an electrolyte bleed is required to avoid their uncontrolled build-up. High magnesium concentrations increase electrolyte viscosity. Manganese dioxide is formed at the anode and represents a mode of manganese removal from the overall process. Excessive MnO_2 production is, however, problematic; furthermore, high concentrations of permanganate that may occur in cobalt EW can cause oxidation of the organic phase in an associated SX circuit. A high concentration of sodium (up to ~20 g/L) improves the conductivity of the electrolyte.

Many flowsheet options exist for cobalt metal production, but the complexity of the purification circuit is well demonstrated by a preferred modern flowsheet, shown schematically in Figure 14. Cobalt hydroxide cake, quantitatively free of iron, is redissolved in anolyte from EW. Residual copper and zinc are removed to levels below 1 mg/L using TP 260 IX resin; alternatively, because the aminophosphonic-acid resins have relatively low loading capacity, Cu may be first removed using an iminodiacetic-acid resin and then the pH adjusted and Zn removed with TP 260[38]. As necessary, nickel is removed to levels below 20 mg/L using Dow's HPPA resin. The electrolyte is then sufficiently pure to ensure the production of premium-grade metal. It is important to note that manganese and magnesium will not plate during cobalt EW and therefore the EW is itself a purification step.
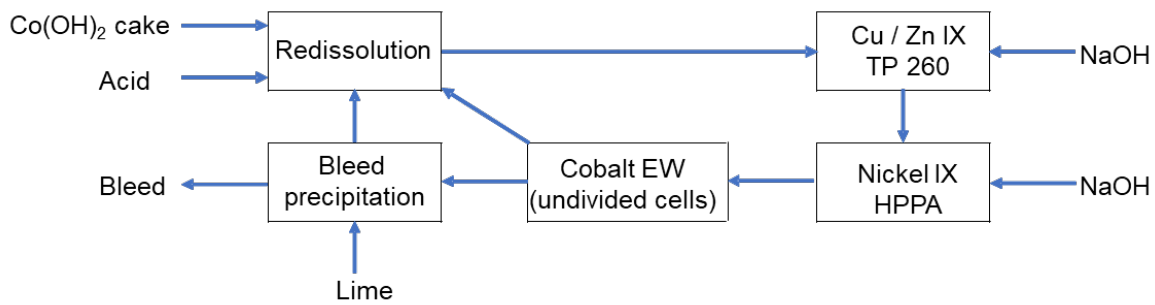
Figure 14: Preferred modern flowsheet for producing cobalt metal

COBALT PRODUCT OPTIONS

Market Value and Specifications for Cobalt Products

Cobalt chemicals that adhere to stringent chemical and physical specifications can attain significant premiums over the prevailing metal price. An example is given in Figure 15, showing the recent variation in price between cobalt metal and cobalt sulphate[49]. The premiums are generally variable and contract-dependent. Indications from cobalt sulphate producers are that a premium of up to 160% of LME metal price is possible for heptahydrate sulphate crystals.

Premiums are only realised for products that adhere to the specifications: under-specification products forfeit heavy penalties, depending on the specific contained impurities. Chemical specifications for high-purity cobalt salts and cathode are summarised in Table 3. Chemicals are generally graded according to their performance characteristics, which are directly related to their combination of both chemical and physical characteristics. Cobalt sulphate, for example, in addition to chemical purity, is usually further graded according to the free-flow ability of the material and homogeneity of the particle size.
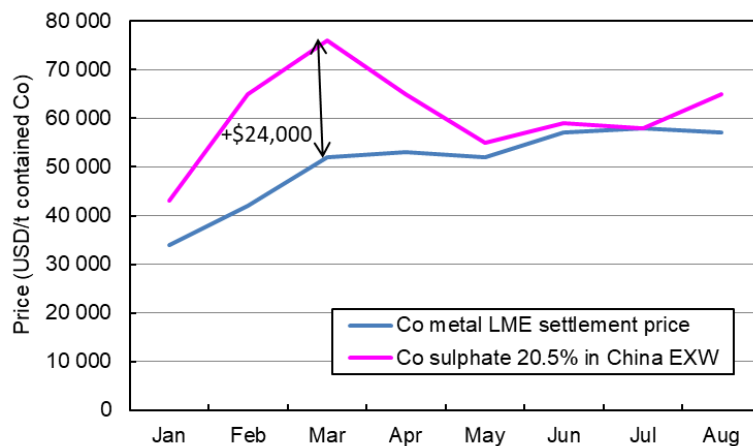
Figure 15: Fluctuation in price between cobalt metal (LME settlement) and Benchmark Minerals cobalt sulphate, 20.5%, in 2017[49]

It is important to note that most production of battery-grade chemicals presently takes place in China, where the refineries are geared towards treating feed materials such as $Co(OH)_2$ with the current suite and levels of impurities. Unless a very high-purity cobalt product can be cost-effectively and consistently produced, there is no benefit to further upgrading at a mine site: there is no advantage to producing an intermediate-grade product because the buyer will generally not be willing to pay more to treat such a product through the same refining process as lower-grade materials.

Table 3: Chemical specifications for cobalt salts and metal

Chemical		Co (%)	Ni (g/t)	Fe (g/t)	Cu (g/t)	Cd (g/t)	Zn (g/t)	Mn (g/t)	Mg (g/t)	Na (g/t)	Pb (g/t)	Hg (g/t)	SiO$_2$ (g/t)	Ca (g/t)
Co sulphate	Spec 1[a]	>21	<50	<20	<10	<50	<10	<25	<200	<50	<10	<20	<30	<20
	Spec 2[a]	>21	<100	<50	<20	<50	<10	<50	<500	<50	--	<20	<100	<50
	Spec 3[b]	>21	<200	<80	<50	<50	<50	<200	–	<50	<30	<20	--	--
	Battery	20.6	<80	<10	<10	<10	<10	<10	<10	<10	<10	--	--	<10
Co carbonate[b]	Battery/animal	46–47	<450	<35	<7	<50	--	<5	--	<50	<50	<5	--	--
	Any	46–47	<1200	<50	<50	--	<10	<200	--	<500	<20	--	--	--
	Monohydrate	52	<650	<50	<50	--	<150	<25	--	<2000	<20	--	--	--
Co hydroxide[b]		62	<300	<75	<10	--	--	<25	--	<250	<50	--	--	--
Co cathode	LME Premium Grade	99.83	<1000	<50	<30	<50	<50	<20	<10	--	<30	--	<10	--
	LME Standard Grade	99.73	<1500	<100	<50	<50	<100	<50	<30	--	<60	--	<20	--

a – Specification of Anglo American Platinum Rustenburg Base Metal Refinery CoSO$_4$.7H$_2$O crystals
b – Specifications obtained from reference[(50)]

Transport of Cobalt Products

The cobalt content of the products shown in Table 3 gives an indication of the cost per unit of cobalt for their transport. Cobalt metal, with the highest cobalt content, carries the lowest transport cost per unit cobalt of all the product options considered. Theoretically, a cobalt sulphate product would contain 21% cobalt as a pure salt and much lower for an impure salt, implying that in excess of 80% of the product transported has no value. The higher cobalt content of cobalt hydroxide makes it more cost effective to transport than the carbonate; however, slow oxidation of the hydroxide to the oxide occurs in air, giving a product that can be poorly soluble in the customary weak acids used in further processing. Adding an antioxidant to the hydroxide prevents the product from oxidising without affecting its chemical performance characteristics[50].

Typical moisture content for hydroxide and carbonate filter cakes is around 50%, but can range up to ~80%. DRC legislation requires that no more than 25% by mass of moisture can be transported across its borders without penalties: any moisture in excess of this value is subject to severe taxation. Several DRC operations have therefore undertaken considerable capital expenditure in recent years by installing driers that can reduce the water content of their export products. Those that are unable to afford driers are limited to selling on their impure products to a local refinery for further processing (or submit to punitive taxation).

ECONOMIC TRADE-OFF STUDY

The two most-widely accepted products available from DRC operations are $Co(OH)_2$ and electrowon cobalt cathode. An economic assessment of the two products and associated process routes was undertaken. The main operating costs for making metal are as follows:

- Power for electrowinning;
- Lime for hydroxide precipitation;
- Make-up acid for hydroxide cake redissolution.

For the hydroxide, the major operating costs are as follows:

- Magnesia for precipitation;
- Lime for precipitation;
- Diesel for drying the hydroxide from 55% moisture to 5% moisture.

The cost of transport to market has to be borne for both products. Table 4 summarises these costs.

Table 4. Comparison of operating costs for production of cobalt as metal and as hydroxide

| Item	Consumption (t/t Co)	Unit	Unit cost (USD)	Annual cost (USD)	
				Co metal	$Co(OH)_2$
Contained Co		t		10 000	10 000
Mass of product		t		10 000	26 316
Power	3500	kWh/t	0.16	5,600,000	—
Acid	0.375	t	400.00	1,500,000	—
Magnesia	0.75	t	1400.00	—	10,500,000
Lime	1	t	400.00	4,000,000	4,000,000
Diesel	365	L	1.20	—	4,380,000
Transport		t	400.00	4,000,000	10,526,300
Total				15,100,000	29,406,300

Owning to the high cost of magnesia and the higher transportation costs associated with shipping cobalt as $Co(OH)_2$, it is significantly cheaper to make metal. There is also additional revenue associated with the sale of pure metal as opposed to impure cobalt hydroxide. In this context, the metal, like the hydroxide, should be considered as an intermediate for the manufacture of cobalt products, such as battery precursors. The metal should be preferably produced as atomised powder to maximise this potential. Generally, the hydroxide is sold for about 70% of the contained metal value. If the metal was sold into the same markets, it should realise a value between 70% and 100% of the contained metal value. Every extra 10% realised would equate to USD 90 million annually for the scenario of Table 4.

SUMMARY AND CONCLUSIONS

Most of the existing cobalt production facilities in the African Copperbelt (primarily located in the DRC) started out with ambitious project designs to produce a high-value cobalt end product such as electrowon metal. Most later opted for a phased approach, concentrating first on developing copper production capacity and producing a cobalt intermediate product (usually $Co(OH)_2$ produced by MgO precipitation) suitable for sale or stockpiling, with a view to future implementation of plans towards upgraded cobalt products. To some extent, the choice of flowsheet was influenced by the hard line initially taken by government on legislation regarding export of concentrates and intermediate products. Another factor that has undoubtedly influenced the development of cobalt-recovery circuits is the issue of environmentally acceptable containment of sodium-bearing solutions that are generated in flowsheets employing SX upgrading steps: the tailings return solution can build up to 5–10 g/L Na. These concentrations require lining of tailings disposal dams to prevent seepage into the environment. The alternative of removing sodium by crystallising sodium sulphate is not considered a viable option, due mainly to its limited market in Sub-Saharan Africa.

Development projects, currently being investigated by all operations in DRC and Zambia that possess resources but are not currently producing cobalt, are, however, today considering more ambitious flowsheets and higher-purity products. This necessitates the incorporation of multiple SX and/or, preferably, IX steps to achieve the required purity of the electrolyte prior to the final product-recovery step. Flowsheet refinements that minimise soluble losses to tailings and filter cakes and that recover soluble cobalt (and copper) from aqueous waste streams will also receive increasing attention.

As an important caveat to the current excitement and expectations of the exploding lithium-ion battery market and associated cobalt demands, Figure 16 shows an insightful graphic from Benchmark Minerals Intelligence[51]. This clearly demonstrates the vast gap between the industries of mining and metal production compared with the production of battery-grade chemicals. It is crucially important that primary cobalt producers understand the complexity of this value chain and their well-defined role within it, to avoid implementing costly and technically sophisticated flowsheets that may ultimately not be able to deliver the desired benefits in terms of product purity and price.
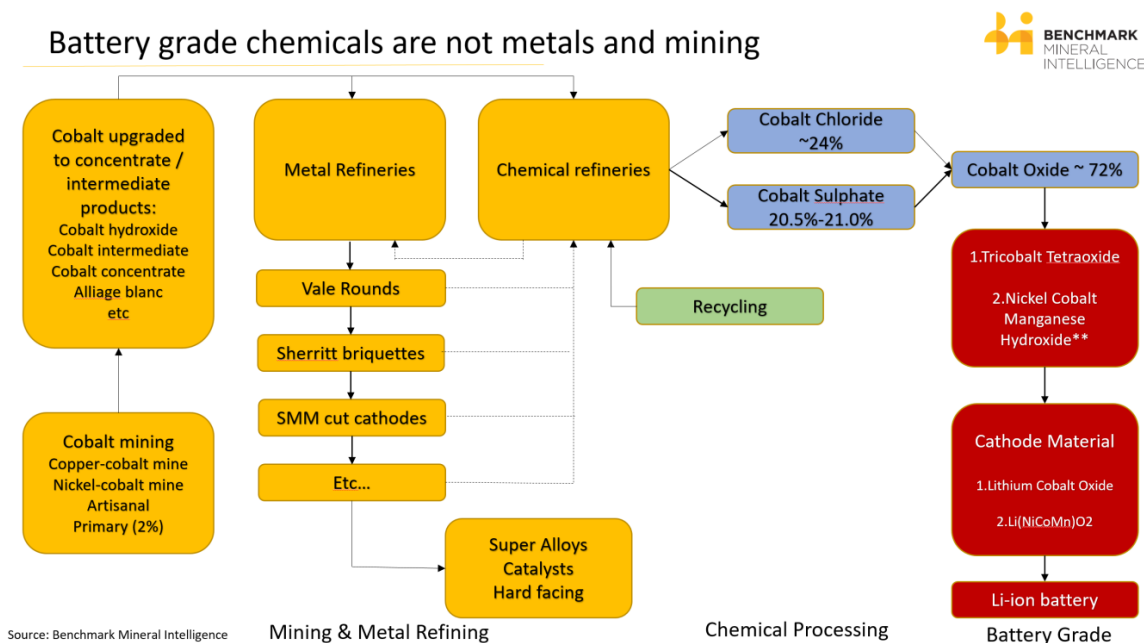
Figure 16: Battery-grade chemicals are not metals and mining[51]

Nevertheless, there is no doubt that the African Copperbelt can become the incubator of many novel and innovative flowsheets within the next five to ten years, and that cobalt—rather than copper—will become the main value product of many DRC operations, driving both the mining philosophy and focus of capital expenditure. However, given the difficult political and operating environment of the DRC and the intensifying focus of major global end-users, such as Apple[52] and Daimler[53], to procure ethically sourced materials (not using child labour and providing artisanal miners with

acceptable rewards[54,55], alternative sources of primary cobalt and LiB recycling are receiving increasing consideration, as are alternative battery formulations that do not require this strategic metal. It will require concerted, collaborative, and dedicated efforts by both mining operators and legislators to ensure that this short window of opportunity is not missed and that the enormous potential of this country with regard to cobalt is not bypassed in favour of inferior, but more reliable, sources.

REFERENCES

1. Barton, B., Schütte, P. (2016). Electric vehicle law and policy: a comparative analysis. *Journal of Energy & Natural Resources Law*, 35 (2), 147–170.

2. Wikipedia (2018). List of countries banning fossil fuel vehicles. Available at: https://en.wikipedia.org/wiki/List_of_countries_banning_fossil_fuel_vehicles

3. Hart, D., Sarkissian, A. (2016). *Deployment of grid-scale batteries in the United States.* Schar School of Policy and Government George Mason University, Fairfax, Virginia, pp. 1–31. Available at: https://energy.gov/sites/prod/files/2017/01/f34/Deployment%20of%20Grid-Scale%20Batteries%20in%20the%20United%20States.pdf

4. Xu, J., Thomas, H., Francis, R., Lum, K., Wang, J., Liang, B. (2008). A review of processes and technologies for the recycling of lithium-ion secondary batteries. *Journal of Power Sources*, 177 (2), 512–527.

5. Buchmann, I. (2017). BU-205: Types of lithium-ion–battery. Battery University. Available at: http://batteryuniversity.com/learn/article/types_of_lithium_ion

6. Saxman, D. (2017). Advanced materials for advanced batteries and fuel cells: Technologies and global markets. BCC Research, MA, pp. 1–665. Available at: http://www.bccresearch.com

7. Randell, P. (2016). Waste lithium-ion battery projections. *Lithium-ion Forums: Recycling, Transport and Warehousing*, Randell Environmental Consulting, Woodend, Victoria, pp. 1–18. Available at: http://www.environment.gov.au/system/files/resources/dd827a0f-f9fa-4024-b1e0-5b11c2c43748/files/waste-lithium-battery-projections.pdf

8. Statistica (2018). Mine production of cobalt in DR Congo from 2008 to 2017 (in metric tons). Available at: https://www.statista.com/statistics/339834/mine-production-of-cobalt-in-dr-congo/.

9. Shedd, K., McCullough, E., Bleiwas, D. (2017). Global trends affecting the supply security of cobalt. *Mining Engineering*, 69 (12), 37–42.

10. Cobalt Investing News (2018). Top cobalt production by country. Available at: https://investingnews.com/daily/resource-investing/critical-metals-investing/cobalt-investing/top-cobalt-producing-countries-congo-china-canada-russia-australia/

11. Smith, L. (2017). Cobalt controversies: delving into the how, what and why. Available at: https://www.coreconsultantsgroup.com/cobalt-controversies/

12. Infomine (2018). Historical cobalt prices and price chart. Available at: http://www.infomine.com/investment/metal-prices/cobalt/all/

13. Radley, B. (2017). The DRC is revisiting its mining code. Why reform is long overdue. *The Conversation*, 28 June. Available at: http://theconversation.com/the-drc-is-revisiting-its-mining-code-why-reform-is-long-overdue-79937

14. Crundwell, F., Moats, M., Ramachandran, V., Robinson, T.G., Davenport, W.G. (2011). *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals.* Elsevier, Amsterdam.

15. Schlesinger, M., King, M., Sole, K.C., Davenport, W. (2011). *Extractive Metallurgy of Copper,* 5th edn. Elsevier, Amsterdam.

16. Sole, K.C., Tinkler O.S. (2016). Copper solvent extraction: status, operating practices and challenges in the African Copper Belt. *Journal of the Southern African Institute of Mining and Metallurgy*, 116 (6), 553–560.

17. Burks, S.F. (1996). Cobalt in Africa: New developments. *Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum*, ALTA Metallurgical Services, Melbourne, Australia.

18. Mwema, M.D., Mpoyo, M., Kafumbila, K. (2002). Use of sulphur dioxide as reducing agent in cobalt leaching at Shituru hydrometallurgical plant. *Journal of the South African Institute of Mining and Metallurgy*, 102 (1), 1–4.

19. Ferron, C.J. (2008). Sulfur dioxide: a versatile reagent for the processing of cobaltic oxide minerals. *JOM*, (10), 50–54.

20. Nisbett, A., Baxter, K., Marte, K., Urbani, M. (2009). Flowsheet considerations for copper-cobalt projects. *Proceedings Base Metals Conference 2009*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 139–152.

21. Monhemius, J. (1977). Precipitation diagrams for metal hydroxides, sulfides, arsenates and phosphates. *Transactions of the Institution of Mining & Metallurgy C*, 86, C202–C206.

22. Mulaudzi, N., Mahlangu, T. (2009). Oxidative precipitation of Mn(II) from cobalt leach solutions using dilute SO_2/air mixtures. *Proceedings Hydrometallurgy Conference 2009*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 341–355.

23. van Rooyen, J., Archer, S., Fox, M. (2007). Manganese removal from cobalt solutions with dilute sulphur dioxide gas mixtures. *Proceedings Fourth Southern African Conference on Base Metals*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 365–376.

24. Schulze-Messing, J., Alexander, D.C., Sole, K.C., Steyl, J.D.T., Nicol, M.J., Gaylard, P. (2007). An empirical rate equation for the removal of manganese from solution using a gas mixture of sulfur dioxide and oxygen. *Hydrometallurgy*, 86 (1–2), 37–43.

25. Kotze, M.H. (2012). MgO recycle in a Co precipitation flow sheet/MgO: Regeneration of magnesium hydroxide. RSA Patent 2012/07829, DRC Patent 4129/2012/EXT, Australia Patent 2012101564, ARIPO Patent AP/P2012/006652.

26. Mokoena, S.F., Pawlik, C. (2016). Demonstration of magnesium hydroxide recycle technology using an elutriation technique. *Sustainable Hydrometallurgical Extraction of Metals. Hydrometallurgy Conference 2016,* Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 285−296.

27. Voigt, P., Hourn, M. (2017). A new method for the precipitation of nickel and cobalt. *Proceedings COM 2017 World Gold & Nickel Cobalt*, Canadian Institute of Mining and Metallurgy, Montreal.

28. Roux, L.M., Minnaar, E., Cilliers, P.J., Bellino, M., Dye, R. (2007). Comparison of solvent extraction and selective precipitation for the purification of cobalt electrolytes at Luilu refinery, DRC. *Proceedings Fourth Southern African Conference on Base Metals*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 343–364.

29. Sole, K.C., Mooiman, M.B., Hardwick, E. (2017). Ion exchange in hydrometallurgical processing: An overview and selected applications. *Separation and Purification Reviews*, 47 (2), 159–178.

30. Pavlides, A.G., Wyethe, J. (2000). Ion exchange column design for separation of nickel traces from cobalt electrolyte. *Proceedings ALTA SX/IX-1*, ALTA Metallurgical Services, Melbourne.

31. Kotze, M.H. (2012). The major roles of ion exchange in hydrometallurgy. *Proceedings International Conference on Ion Exchange 2012*, Society of Chemical Industry, London, pp. 53–54, (2012).

32. Sole, K.C., Cole, P.M. (2002). Purification of nickel by solvent extraction. *Ion Exchange and Solvent Extraction. A Series of Advances*, Vol. 15, Y. Marcus, A.K. SenGupta (eds.), Marcel Dekker, New York, pp. 143–195.

33. Flett, D.S. (2004). Cobalt-nickel separation in hydrometallurgy: a review. *Chemistry for Sustainable Development*, 12, 81–91.

34. Swartz, B., Donegan, S., Amos, S. (2009) Processing considerations for cobalt recovery from Congolese Copperbelt ore. *Proceedings Hydrometallurgy 2009*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 385–400.

35. Dry, M.J., Iorio, G., Jacobs, D.F., Cole, P.M., Feather, A.M., Sole, K.C., Engelbrecht, J., Matchett, K.C., Cilliers, P.J., O'Kane, P.T., Dreisinger, D.B. (1998). Cu/Co tailings treatment project Democratic Republic of Congo. *Proceedings ALTA 1998 Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum*, ALTA Metallurgical Services, Melbourne.

36. Wyethe, J.P., Kotze, M.H. (2000). Impurity removal by fixed-bed ion exchange from cobalt electrolyte derived from the Kakanda tailings dump. *Proceedings ALTA SX/IX-1*, ALTA Metallurgical Services, Melbourne.

37. Alexander, D. (2001). Kolwezi tailings treatment project: Development of a flowsheet for the production of copper and cobalt metal. *Proceedings 4th Anglo American Metallurgical Symposium*, Anglo American, Johannesburg.

38. Jurrius, Y., Sole, K.C., Hardwick, E. (2014). Removal of copper and zinc from a cobalt electrolyte by ion exchange at Kamoto Copper Company's Luilu plant. *Proceedings Hydrometallurgy 2014*, Canadian Institute of Mining, Metallurgy & Petroleum, Montreal, Canada, Vol. 2, pp. 281−294.

39. Sole, K.C., Jurrius, Y., Hardwick, E. (2016). Purification of a cobalt electrolyte by ion exchange: Pilot-plant results and preliminary commercial design. *Proceedings International Ion Exchange Conference 2016*, Society of Chemical Industry, London, 15 pp.

40. Taute, J.J., Sole, K.C, Hardwick, E. (2013). Zinc removal from a base metal solution by ion exchange: process design to full-scale operation. *Proceedings Base Metals Conference 2013*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 179–192.

41. Taute, J.J., Sole, K.C., Hardwick, E. (2014). Removal of zinc from a base-metal solution by ion exchange at Rustenburg Base Metal Refiners. *Journal of Chemical Technology and Biotechnology*, 89, 919–926.

42. van Deventer, J., du Preez, R., Izatt, S.R. (2007). Cadmium removal from cobalt electrolyte. *Proceedings Africa's Base Metals Resurgence, Base Metals 2007*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 377–392.

43. Williams, S. (2016). The link between uranium from the Congo and Hiroshima: a story of twin tragedies. Available at: https://theconversation.com/the-link-between-uranium-from-the-congo-and-hiroshima-a-story-of-twin-tragedies-64329

44. Multotec (2018) Multotec to provide continuous ion exchange equipment to DRC customer. Available at: http://www.engineeringnews.co.za/article/multotec-to-provide-continuous-ion-exchange-equipment-to-drc-customer-2018-02-02/rep_id:4136

45. Cole P.M., Feather, A.M. (2008). Processing of African Copper Belt copper-cobalt ores: flowsheet alternatives and options. *Proceedings International Solvent Extraction Conference ISEC 2008*, Vol. I, Moyer, B.A. (ed.), Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 131–138.

46. Könighofer, T., Archer, S.J., Bradford, L. (2009). A cobalt solvent extraction investigation in Africa's Copper Belt. *Proceedings Hydrometallurgy Conference 2009*, Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 329–340.

47. Tinkler, O., Flett, D., Bourget, C. (2007). Flowsheet considerations for copper-cobalt projects in the DRC. *Proceedings ALTA 2007*, ALTA Metallurgical Services, Melbourne.

48. Louis, P.E. (2009). Cobalt electrowinning – process and technology. *Hydrometallurgy of Nickel and Cobalt*, Budac, J.J., Fraser, R., Mihaylov, I., Papangelakis, V.G., Robinson, D.J. (eds.), Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 554–569.

49. Benchmark Mineral Intelligence (2017). Price chart: Cobalt, lithium ion batteries and EVS. Available at: http://benchmarkminerals.com/price-chart-cobalt-lithium-ion-batteries-and-evs/

50. De Beer, H. (2005). *Cobalt Chemicals Market Review*. Prepared for Formation Capital Corp., March 2005.

51. Rawles, C. (2017). Benchmark cobalt world tour 2017 Keynote. Available at: benchmarkminerals.com/wp-content/uploads/.../Benchmark-World-Tour-Cobalt.pdf

52. Reisinger, D. (2018). Here's why Apple wants to buy cobalt directly from miners. *Fortune* (21 February). Available at: http://fortune.com/2018/02/21/apple-buy-cobalt-miners/

53. Sun, Y. (2018). Daimler joins China's responsible cobalt initiative. *Reuters* (25 April). Available at: https://www.reuters.com/article/us-daimler-cobalt/daimler-joins-chinas-responsible-cobalt-initiative-idUSKBN1HW1EQ

54. Brown, H. (2018). HRW, Tiffany and the ethical cost of jewellery. Available at: https://www.coreconsultantsgroup.com/jewellery-ethical-cost-hrw-tiffany/

55. Deaville, A. (2018). Cobalt supply chain: transparency, auditability and trust using blockchain technology. Available at: https://www.coreconsultantsgroup.com/cobalt-supply-chain-blockchain/