COBALT PROCESSING DEVELOPMENTS

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ABSTRACT

Since the early years of cobalt production, and particularly during the last century, the major source of cobalt has changed whilst the world's cobalt usage has increased steadily. Cobalt is produced mostly as a by-product of other major metal extraction processes – mainly copper and nickel – and in recent decades the nickel industry has been the major source of cobalt. Now however the Democratic Republic of Congo (DRC) copper-cobalt production is coming to the fore once again after a 20-year period of decline.

This paper highlights the technological developments that have made the increased production possible, particularly trends over the last 10 - 20 years, discusses cobalt product selection for new projects and reviews the status of several technologies available for cobalt production flowsheets. Electrowinning is currently of particular interest because of the large number of new cobalt projects, many in the DRC, all seeking to maximise their revenue by making cobalt metal.

It is concluded that, despite the many developments, there is no entirely satisfactory or obvious flowsheet for cobalt recovery. The choice of process steps is often driven mostly by the project owner's requirements in terms of cobalt product and grade, and is constrained by other factors such as environmental compliance, logistics and risk.

INTRODUCTION

There is only 20 ppm cobalt in the earth's crust but cobalt is an important element for humankind, in fact essential as the central component of vitamin B12 which catalyses the regeneration of red blood cells. However the world requires only a small amount of cobalt compared to major metals such as copper, nickel, iron and zinc; which is fortuitous since in nature cobalt occurs in relatively minor quantities in association with ores of other metals – predominantly copper, nickel and silver/arsenic. Hence cobalt is seldom mined solely in its own right and its recovery is usually viewed as a by-product.

Cobalt was originally mined together with silver and arsenic in Saxony and Bohemia in the 15th century but its use then was only in the oxide form as a colorant ("cobalt blue"). Swedish chemist Georg Brandt first isolated metallic cobalt in 1735 and it was subsequently established as an element in 1780 by Torbern Bergman. Only after that were industrial uses other than coloring developed and in fact until circa 1914 cobalt was really only available or used as the oxide. Since then, as Figure 1 illustrates, there has been a steady increase in demand for cobalt as new uses have been developed. At the same time, the major source of feed material has changed and the metallurgical processes for cobalt recovery have been developed, adapted and improved over these years to satisfy the increasing demand.

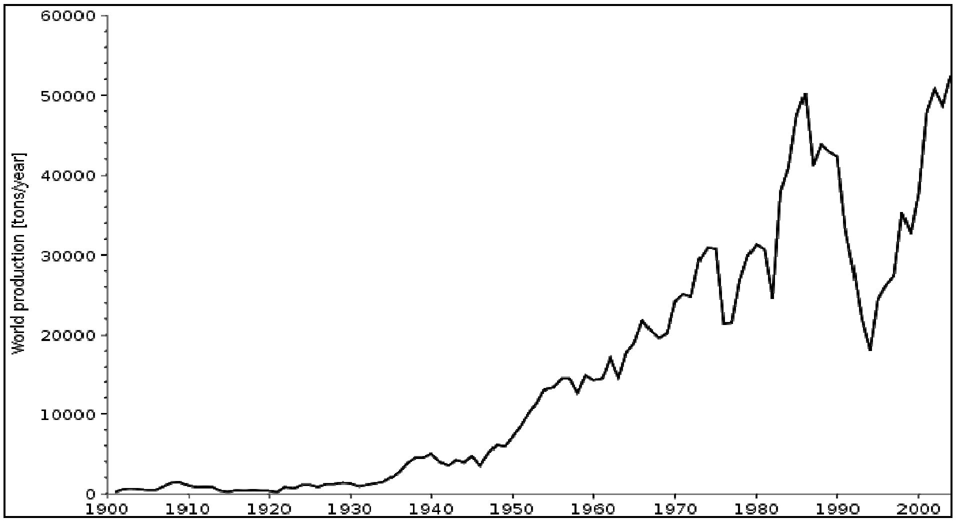

Figure 1 - World Cobalt Production from Year 1900 (from Wikipedia)

This aim of this paper is to highlight the technological developments that have contributed to the increase in world cobalt production, especially the more recent and topical ones.

1. Sources of Cobalt

2.1 Historical

By the early 19th century, cobalt deposits had been found all around the world; including Germany, Norway, Sweden, Transylvania (Rumania), France, Spain, England, Chile, Argentina and Tasmania. In the late 19th century, the oxidized cobalt mines of New Caledonia became the major source of cobalt, producing "alliage blanc", up until 1904 when the silver-cobalt-arsenic ores of Cobalt, Ontario started being exploited. Cobalt production at this time was only around 1,000 tpa. Subsequently cobalt-arsenic deposits were also mined in Bou-Azzer, Morocco from 1932 and the Blackbird district of Idaho, USA from 1952.

From around 1926, cobalt production as a by-product from the Congo's copper mines (Union Minière du Haut Katanga at the time) came to the fore with Northern Rhodesia (Zambia) joining in around 1934. The first commercial cobalt electrowinning plant was opened in 1945 at Shituru, DRC, closely followed by Rhokana, Zambia in 1952; at which point world consumption was still less than 10,000 tpa (see Figure1).

After World War II, the demand for cobalt metal increased considerably, driven by the requirement for high-purity cobalt for aircraft jet engines and gas turbines. There was also a major increase in demand for nickel for use in stainless steel, including high-grade nickel for nuclear reactor stainless steels. This was satisfied by growing output from the massive nickel sulphide deposits of Canada (Sudbury) and Russia (Norilsk); with the associated cobalt output helping to meet the increasing cobalt demand.

Nickel oxides (laterites) were first processed by hydrometallurgy in 1944 at Nicaro in Cuba (by the Caron Process) and in 1959 the first sulphuric acid pressure leach plant came on line at Moa Bay, Cuba; thereby adding nickel laterites as a significant source of by-product cobalt – a source that would grow in importance subsequently.

From the 1950's on, world cobalt production was dominated by the Congo (Zaire, now DRC) and Zambia, peaking in 1986. Thereafter this source declined dramatically but, fortunately, cobalt from emerging nickel producers increased substantially such that cobalt produced from combined nickel sources (sulphides plus laterites) became the world leader. In 2010, with cobalt supply at almost 60,000 tpa, a rough split of new cobalt arisings according to the Cobalt Development Institute (CDI) was as follows:

Nickel industry	-	50%
Copper industry & other	-	35%
Primary cobalt operations	-	15%

Approximately 51% of this cobalt was produced in metallic form and 49% in chemical form.

2.2 The Future and the DRC

The Central African copperbelt constitutes almost half of the world's cobalt reserves and now, in 2011, production from DRC copper-cobalt operations is on the increase again as political hurdles are being overcome after the 1990s decline. In the near future, major DRC producers could include the following:

- Tenke Fungurume (Freeport McMoRan) – 9,500 tpa cobalt as hydroxide
- KOL Luilu refinery (Glencore) – 8,000 tpa cobalt cathode
- Ruashi (Metorex) – 3,500 tpa as hydroxide
- Mukondo (Boss Mining) – 5,000 tpa as cathode (estimate)
- Luita (Boss mining) – 6,000 tpa as cathode
- Mutanda (Glencore) – 9,400 tpa as hydroxide
- Kolwezi Tailings Project (ex First Quantum) – 7,000 tpa as hydroxide
- Etoile (Chemaf) – 6,000 tpa as cathode (estimate)

Given a world cobalt market currently around 60,000 tpa, these figures tell us that the DRC and its copper industry should be the world's major cobalt producer for the foreseeable future. They also suggest that there will be an over-supply situation!

3. Primary Cobalt-Producing Processes

The base metal recovery processes giving rise to significant cobalt production can be summarised into four main groups as follows:

3.1 Cobalt Arsenides

A variety of processes were in operation during the 20th century to process cobalt arsenide ores/concentrates (refer to a paper by Ferron[1]). Many of these featured a roasting stage and most included pressure leach but, because of health and environmental issues, almost all have now closed down. Only the Moroccan source (CTT)[2] currently remains active although there are plans to restart soon in Canada and N. America (refer to section 4.7 below).

3.2 DRC/Zambian Copper-Cobalt Ores (Oxides & Sulphides)

Historically, most of the DRC/Zambian cobalt has been recovered from copper flotation concentrates by a Roast-Leach-Electrowin (RLE) process. This comprised roasting (for the sulphides), sulphuric acid atmospheric leach and direct copper EW; plus impurity removal and cobalt hydroxide precipitation, often followed by re-leach and cobalt EW. In recent years, apart from a few older plants, direct copper EW has been replaced by copper SX-EW in order to make LME Grade 'A' specification.

The copper flotation step is inherently inefficient for cobalt, with recoveries typically from 40% for oxides up to 80% for sulphides, so there is a substantial amount of cobalt contained in tailings dams that could be recovered – e.g. the Kolwezi Tailings Project. Similarly, because cobalt follows iron during smelting, some of the copper smelter operations have generated large slag dumps with a high cobalt content – e.g. Nkana containing 0.65% cobalt.

3.3 Nickel Sulphides

Nickel sulphide deposits have historically been processed by flotation, followed by smelting to produce a PGM-bearing nickel matte which is shipped to specialist refineries using hydrometallurgical processes to recover the nickel, copper, PGMs and cobalt. There are many such refinery processes including:

- ammonia leach, e.g. the Sherritt-Gordon process which produces LME grade nickel briquettes and cobalt by means of hydrogen reduction;
- a "modified" Sherritt-Gordon process (pressure oxidation leach), e.g. Impala BMR, South Africa.
- sulphate oxidative leach, e.g. Outokumpu;
- chlorine leach as practised at Xstrata Nikkelwerk (ex Falconbridge/ Kristiansands) where the cobalt is recovered by chloride electrowinning;
- electro-refining of nickel matte anodes (Jinchuan and Inco, Thompson);
- electro-refining of impure metal (Russia).

Environmental pressure on the matte smelting operations has lead to the development of wholly hydrometallurgical alternatives (refer to section 4.5 below) and now the scarcity of new economic nickel sulphide deposits is shifting the nickel development focus onto laterites.

3.4 Nickel Laterites (Oxides)

Nickel laterites are set to become the world's major source of nickel from 2012, as the supply of sulphides dwindles and laterite processing technology improves. Laterites were processed almost exclusively by pyrometallurgy until 1954 when Nicaro, Cuba started up, employing the Caron process; followed by Moa Bay, Cuba in 1959 employing high-pressure acid leach (HPAL). These hydrometallurgical processes have the benefit of recovering cobalt, which the pyrometallurgical processes did not do, so since circa 1974 there has been a growing trend towards hydrometallurgy for processing the higher grade laterites (normally the cobalt-containing limonites), to the benefit of world cobalt output.

The currently preferred process is HPAL combined with a variety of nickel and cobalt production processes. Examples are Bulong, Cawse and Murrin Murrin (all started in 1999), Coral Bay (2005), Ravensthorpe (2007), Goro (2010) and Ambatovy, Madagascar (2011).

4. "Recent" Technology Developments

Over the last 10 – 20 years, there have been many developments in cobalt extractive metallurgy and process engineering technology that contributed to satisfying the increasing demand for cobalt whilst the major source of supply (DRC) was in decline. These are:

4.1 "Bigger and Better" Equipment

The major technical development of a general nature enabling increased mine and process plant production over this period has been the dramatic increase in process equipment sizing. This has been driven by increasing primary metal (copper and nickel) demand and the need for competitiveness and reduced unit costs. This in turn has been facilitated by the development and availability of powerful computers and equally powerful analytical design software such as static and dynamic stress analysis, computational fluidynamic modeling (CFD), etc.. It has also been assisted by huge advances in the field of process control and Human-Machine Interfacing (HMI). A paper by Imrie[3] describes this development in detail. As an example, Figure 2 (from Imrie's paper) illustrates the magnitude of the economy of scale advance since 1980 for SAG milling (installed power per single mill).

Similar advances on the mining front have facilitated large-scale automated mining and at the same time have brought about huge improvements in mine safety.

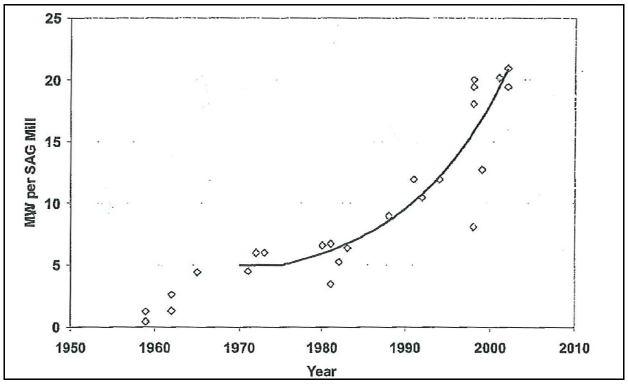

Figure 2 - Trend for SAG Mill Power (by Imrie[3])

4.2 Implementation of the Whole Ore Leach Concept

Direct whole ore leach (WOL), as opposed to the traditional but inefficient oxide ore flotation and concentrate leach, is now being applied to many copper oxide ores particularly those in the revitalized DRC. At current metal and acid prices, the much improved metal recoveries more than off-set the cost of the additional acid needed in the leach. It should however be noted that WOL requires a plentiful supply of cheap sulphuric acid, which has fortunately been the case thanks to the large amount of cheap elemental sulphur available as a by-product of the Middle East and Canadian oil industries.

The WOL process features in 4 of the 8 current DRC projects noted in section 2 above, responsible for some 28,000 tpa potential new cobalt capacity (i.e. half of current world demand).

4.3 Improvements to Nickel Laterite High Pressure Acid Leach (HPAL)

The traditional Caron process employs a reducing roast followed by ammoniacal leach; e.g. Yabula, Australia which produces cobalt as an oxy-hydroxide cake using steam stripping. There are several Caron installations worldwide, but the process is less popular nowadays due to high energy requirements and low recoveries. Over the years, improvements to autoclave design detail and ancillary equipment have progressively facilitated the treatment of laterites by HPAL in preference to the Caron process or pyrometallurgical processes – as demonstrated in the recent Australian projects, albeit with varying degrees of success.

However, the difficulties experienced with the Australian HPAL projects have stimulated a continuing search for other hydrometallurgical laterite processes (see 4.4 below). Refer to a paper by Taylor[4] for a discussion on trends in PAL plant design and laterite processing.

Note that the biggest autoclaves yet are currently being commissioned at the Ambatovy nickel laterite project, Madagascar, which will be producing 5,600 tpa cobalt from 2012.

4.4 Alternative Nickel Laterite Hydrometallurgical Processes

For nickel laterites, there are a number of potentially viable alternatives to the HPAL and Caron processes currently under development. These include nitric acid leach (Direct Nickel), atmospheric sulphuric acid leach (e.g. BHP Billiton, Ravensthorpe), hydrochloric acid leach (Jaguar, Intec, ARNi) and heap leach – see 4.8 below.

A recent paper by Kyle[5] provides a review of HPAL, Caron and the alternatives. Another paper by Dalvi et al[6] gives a description of laterite processing technologies in general – past and future, including the difficulties encountered with HPAL and commentary on comparative costs of the competing technologies.

4.5 Development of Hydrometallurgical Processes for Nickel Sulphides

Driven by increasing environmental pressures on the smelters, hydrometallurgical alternative processes for nickel sulphide concentrates (as opposed to matte) were seriously developed in the 1990s. Several such processes (acid-oxidative leach) are now possible – practical examples being Vale-Inco's current Voisey's Bay project (capacity 2,450 tpa Co rounds) which employs a sulphate-chloride pressure leach; and the Activox® leach process which was to be implemented at Tati, Botswana (capacity 640 tpa Co as carbonate) until it was cancelled in 2008. Others include CESL (chlorine catalyzed pressure oxidative leach), INTEC chloride, bio-leach (e.g. BioNIC®) and Sherritt-Gordon's ammonia leach.

The hydrometallurgical route is best suited to concentrates low in PGMs, since their recovery is very challenging. Residue storage and containment is also more problematic than the pyrometallurgical route – which produces a relatively inert slag for disposal.

4.6 Solvent Extraction Developments

The first commercial SX application was at Xstrata Nikkelverk (ex Falconbridge) in Norway in 1968 for cobalt/nickel separation. Since then SX has gradually become very popular in cobalt flowsheets, particularly the use of Cyanex®272 (which first became available in the early 1980s) to separate cobalt from nickel before cobalt EW.

Many current cobalt projects are employing SX for impurity removal, even to the extent of having three or four SX sections in series – each using a different reagent. A paper by Sole et al[7] describes several southern Africa SX plants and projects, with a particular focus on cobalt. It illustrates the wide range of SX options and permutations now open to the flowsheet designer.

New Reagents:
Currently, there is much interest in the so-called "SSX" (synergistic SX) or "DSX" (synergistic direct SX) reagent combinations which have the potential to streamline nickel-cobalt processing by directly separating (extracting) cobalt and nickel from impurities without the need for intermediate precipitation and re-leach.

CSIRO, Australia have developed a range of synergistic systems for various specific applications (refer to a paper by Cheng[8]). For example, in Baja Mining's Boleo project in Mexico (capacity 2,400 tpa Co cathode from 2012), zinc and cobalt will be co-extracted together and separated from manganese by synergistic DSX (refer to a paper by Dreisinger et al[9]). In this case the organic is a Versatic10/LIX63 mixture.

Recently, some new extractants have been developed that have the ability to extract cobalt and nickel together at a relatively low pH, leaving behind the impurities manganese, magnesium and calcium. These include Cyanex®301 and 302; with a 301 circuit being employed on Vale-Inco's current Goro project which is planned to produce 5,000 tpa cobalt as carbonate (refer to papers by Mihaylov et al[10,11]).

The Bateman Pulsed Column (BPC):
The BPC is an alternative to conventional SX mixer-settlers and was first used in the metals industry at Olympic Dam, Australia in 1996 for uranium SX. The new SX reagents such as Cyanex®301 are very easily and irreversibly oxidized; however their practical use has been made possible by the totally enclosed design of the BPC which is ideal for maintaining an inert atmosphere in the reactor/contactor vessels. The Goro project is a prime example with 22 columns installed.

4.7 High-Temperature/Pressure Leach of Cobalt Arsenides

Successful high-temperature/pressure leach testwork has been done recently for several cobalt arsenide projects (refer to the paper by Ferron[1]). The key to success has been the generation of an environmentally acceptable, stable arsenic residue in the process. As a result, a minor revival in cobalt production from arsenical ores may be expected; e.g. Formation Metals Inc.[12] in Idaho (capacity 1,650 tpa cathode) and Fortune Minerals' NICO project (Mezei et al[13]) in north-west Canada, which plans to produce 1,800 tpa cathode from 2012.

4.8 Improvements to Conventional Heap Leach

Significant improvements to heap design, feed preparation, irrigation etc. have enabled projects such as European Nickel's Çaldağ Ni-Co laterite heap leach project in Turkey to be developed. This was set to produce 1,000 tpa cobalt as a mixed hydroxide precipitate (MHP), but their focus has recently shifted to Acoje, Philippines (930 tpa Co as MHP). The main driver for heap leach development has been the high capital cost of the competing smelting and PAL technologies.

Heap leach has historically been avoided in wet climates on account of the major upsets caused by major rainfall events. However, even this hurdle is now being overcome – for example Boss Mining's Luita Cu-Co heap leach/SX/EW plant in the DRC.

4.9 The Advent of Heap Bio-Leach

The advent of bio-leach technology is further opening up heap leach possibilities for sulphides, especially in colder climates such as the Talvivaara polymetallic Ni-Zn-Cu-Co sulphide deposit near Sotkama, Finland. This will produce 1,800 tpa cobalt as a mixed sulphide precipitate (MSP) from 2012 using BioNIC® technology.

4.10 Bio-Leaching of Cobaltiferous pyrites

Agitated tank bio-leach was successfully implemented at Kasese, Uganda in 1998 and is still producing 700 tpa cobalt cathode. The project is well described in a paper by Morin & d'Hugues[14]. Several other projects have considered a similar process (e.g. BacTech), since it is well suited to remote locations such as North America and Canada.

4.11 Cobalt Recovery from Copper Smelter Slag

A DC arc furnace process combined with hydrometallurgy was successfully implemented at Chambishi, Zambia in 1998 for recovery of cobalt from copper reverb slag (refer to a paper by Jones et al[15]), adding ~4,000 tpa to world cobalt production. The DC arc furnace effects a selective reduction of cobalt and leaves the bulk of the iron in the slag. The cobalt alloy product is processed further by pressure leach.

5. Cobalt Recovery Flowsheets

5.1 Generic Flowsheet

Cobalt is usually a by-product of copper and/or nickel production and the overall process flowsheet will usually feature a leach of some type followed by recovery of the copper first; impurity removal and cobalt recovery second, with nickel recovery (if any) last - as the generic flowsheet in Figure 3 illustrates:

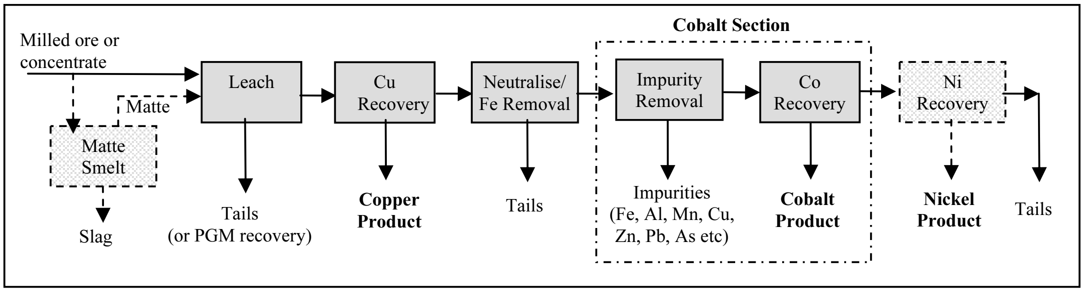

Figure 3 - Generic Copper/Cobalt/Nickel Recovery Flowsheet

The feed to the cobalt section is almost always an acidic or neutralised cobalt-bearing solution with minor quantities of copper and iron and many other impurity elements; plus (sometimes) a significant quantity of nickel.

5.2 Process Selection

The copper and nickel recovery processes are generally pre-defined, often SX/EW, but within the cobalt section the flowsheet designer must first confirm the type of cobalt product to be produced (see 5.3 below). Then he faces the challenge of providing a process that will satisfy all the other stakeholder requirements, normally:

- Safe and environmentally acceptable process
- Lowest capital cost
- Lowest operating cost
- Highest cobalt recovery efficiency
- High-quality product
- Good operability and maintainability
- Low-risk, proven technology

In recent years, some projects have run into serious difficulties (notably the Western Australia laterite projects) and the 2008 global financial crisis has resulted in a shortage of quality investment capital. Consequently, investors are now very sensitive to the technical risk factor and the trend is in favour of tried and tested processes.

5.3 Product Selection

Cobalt is produced and traded in various forms, ranging from concentrates through various intermediates to high-purity metal and salts. The stakeholders in a cobalt project must decide upon the cobalt product they want to make, before the cobalt flowsheet can be finalised. Options include:

- Cobalt sulphide, or mixed Ni-Co sulphide precipitate (MSP);
- Low-grade cobalt hydroxide;
- High-grade cobalt hydroxide, or mixed Ni-Co hydroxide (MHP);
- Cobalt carbonate;
- Cobalt oxide or oxy-hydroxide;
- Cobalt sulphate;
- Cobalt electrowon cathode – HG (99.8%) or LG (99.3%);
- Cobalt powder/briquettes, via hydrogen reduction.

Prior to the November 2008 world market crash, the cobalt price had increased considerably from around US$8 per pound in 2003 to a peak around US$50, as Figure 4 below shows. At the time, this was encouraging project owners to focus on the production of their cobalt as a high-quality product – usually hydroxide, carbonate or preferably cathode. Cathode metal always appears to be an attractive option since it not only maximises revenue but also minimises the cost of transport to the off-taker. However, cobalt cathode production is complex and capital intensive so, as a conservative approach after the 2008 financial crash, some projects elected to make an intermediate product initially, until cash becomes available to add on electrowinning later.

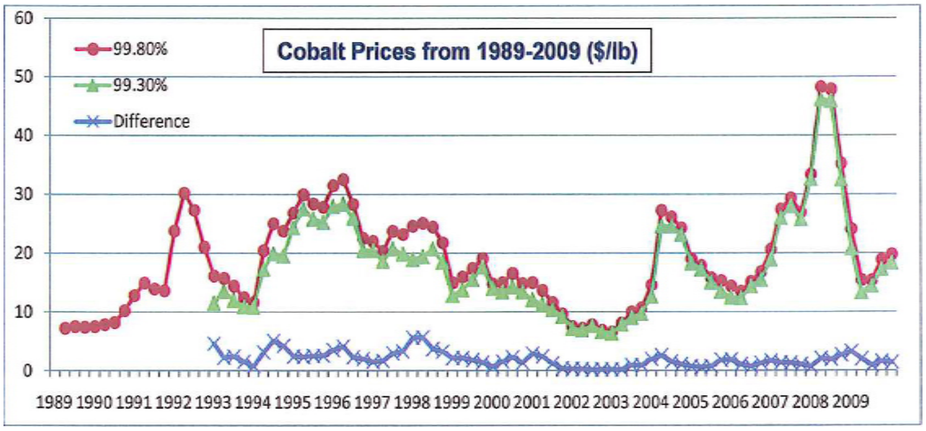

Figure 4 - Cobalt Price (1989 – 2009) (CDI, Cobalt Facts 2010)

A paper by Peek et al[16] examines business and technical considerations of cobalt production and looks at the product selection issue in some detail. Factors to be considered, apart from capital and operating costs, include availability of skilled labour, availability of reagents, site location and logistics, availability and cost of electric power, available floor space, health, safety and environmental issues, and government policy on beneficiation.

Note that more than half of the mines' cobalt production (metal and intermediates) is subsequently re-dissolved, further purified and converted to higher purity salts and other products by specialist companies, many of them in China. Such products include chloride, carbonate, hydroxide, acetate, nitrate, sulphate, oxalate, powders, oxides and active battery chemicals (e.g. $LiCoO_2$); but are not considered further in this discussion.

6. Key Cobalt Process Technologies

6.1 General

Before producing a cobalt product, impurities must be removed – the extent depending on the product specification and sales contract agreement. There are several tried and tested, fairly satisfactory, well documented impurity removal processes, such as:

- impurity precipitation with "lime" - i.e. limestone ($CaCO_3$) and/or milk of lime ($Ca(OH)_2$);
- Solvent extraction (SX) for removal of copper and zinc, and even manganese; plus cobalt-nickel separation;
- Ion exchange (IX) for removal/polishing of zinc, copper and nickel.

The following discussion focuses on some of the more topical issues.

6.2 Manganese Removal with Air/SO_2

Manganese has proved to be perhaps the most troublesome impurity in cobalt circuits, especially in the DRC where manganese is present in the copper-cobalt ores in significant quantities in the heterogenite mineral (Co,Cu,Mn,Fe)O(OH), psilomelane (mixed manganese oxides) and manganite (MnO(OH)). It is only removed to a minor extent by the traditional lime precipitation process.

The use of air/SO_2 or O_2/SO_2 mixtures to oxidise and precipitate manganese from sulphates has been extensively researched and documented by several authors including Zhang et al[17,18,19]; and the process has recently been adopted for the first time on a commercial scale, with qualified success, in the current generation of DRC copper-cobalt plants including Tenke Fungurume and Ruashi.

There are several other possible manganese removal processes (refer to a recent paper by Fisher[20]) but the air/SO_2 process possibly has the least disadvantages, especially on a large scale, although its ability to remove all the manganese is questionable.

6.3 Solvent Extraction Problems

As noted above, SX is often a preferred process for impurity removal and cobalt separation, since it can be elegant and very efficient if properly controlled.

However, a serious problem with cobalt SX, especially on larger plants, is the need for pH control in the extraction stage which necessitates the use of sodium-based neutralising agents such as NaOH and Na_2CO_3. The resulting highly soluble sodium sulphate ultimately reports to the plant aqueous effluent and tailings dam and nowadays this is deemed to be an unacceptable environmental risk requiring the (expensive) lining of the dam or (very expensive) recovery of sodium sulphate. The alternative use of ammonia (NH_4OH) gives rise to similar problems. These problems are perhaps more manageable on smaller plants.

Similarly, the inherent problems of oxidation, degradation and crud formation are manageable on small plants but less so on the larger plants. Note also that the cobalt-nickel SX reagents such as Cyanex®272 are relatively expensive and mishaps can be costly.

Cyanex®301 as used at Goro for bulk Ni/Co extraction is essentially Cyanex®272 with the active oxygen atoms replaced by sulphur atoms. As noted in section 4.6 above, care is needed since it is easily oxidised and decomposes to 272 in two stages - only the first of which is reversible. Very strict process control is also required to ensure that no ferric ion or copper are present in the feed, since these elements are irreversibly extracted and poison the reagent.

The obvious drawback of any SX process is the fire risk and the high cost of prevention measures. Furthermore, because of the fire risk, any SX plant must be located well apart from the rest of the plant – sometimes placing constraints on lay-out and floor area.

6.4 Resin-In-Pulp (RIP)

The RIP process is analogous to the CIP process used in the gold industry but, instead of activated carbon, a specially developed resin similar to an IX resin is used to load the target metal(s) from a slurry. The principles are described in a paper by Van Hege[21].

An interesting potential RIP application is to extract cobalt from a low-strength, partially purified aqueous stream and transfer it into a high-strength, high-purity solution suitable for cobalt IX/EW; thus avoiding the alternative messy, inefficient and expensive cobalt intermediate precipitation and re-leach processes. At the same time manganese and magnesium will be largely rejected.

When compared to SX, RIP has the advantage that neutralisation can be done in the pulp with lime rather than using sodium salts, so there is no adverse environmental impact. As yet there is no commercial application on cobalt, although demonstration plants have been run.

6.5 Molecular Recognition Technology (MRT)

MRT is similar to conventional ion exchange but employs specially made SuperLig® resins capable of targeting single specific molecules. The process has been in use since 1990 and has been trialed with some success on cobalt solutions for removal of Fe, Ni, Cu, Cd, Pb and Zn. A paper by Van Deventer et al[22] describes testwork on cadmium removal and one by Izatt et al[23] gives a general update on the status of MRT applied to cobalt.

MRT may in future fulfil a niche role in removing individual troublesome impurities on a project-specific basis. Unfortunately, there is not a resin with selectivity for Mn over Co (which would solve the tricky manganese removal problem) and, due to the expensive resins and cost of resin usage, the economics remain a barrier to implementation.

6.6 Precipitation of Cobalt Intermediate Product

For many cobalt projects, the chosen end product is an intermediate precipitate. There are a number of reagents possible for this precipitation, including:

- NaHS (sodium hydrosulphide) or H_2S – gives a good quality cobalt sulphide;
- $Ca(OH)_2$ – gives a low-grade (<20%) hydroxide/basic sulphate containing gypsum;
- Na_2CO_3 – gives a high-grade (35-43%) basic carbonate;
- NaOH – gives a high-grade (40-45%) hydroxide;
- Magnesia (MgO) – gives a high-grade (up to 45%) hydroxide.

All the above intermediates except sulphide would be suitable feed for a subsequent EW circuit; but note that the use of sodium reagents, although a popular choice, introduces sodium sulphate environmental problems as described above for SX.

In the nickel industry, the sulphide route is a common choice since it rejects manganese and gives a clean, readily saleable product. It is less popular in the cobalt context since the product is less saleable and, in the context of the DRC, the process is relatively complex and high-risk due to the toxic nature of H_2S and the hazards and complexities of producing and storing it.

The magnesia route, although somewhat specialised, is gaining in popularity and merits discussion. A paper by White[24] describes the development of the process applied to mixed nickel-cobalt hydroxide (MHP) production in Australian laterite projects. Considerable work has also been done in recent years to optimise the process specifically for cobalt; and some current cobalt projects are adopting the MgO process on account of the following advantages:

- Much cleaner, lower mass product than lime;
- Easy materials handling;
- The hydroxide cake is easily filtered and releached;
- Effects some manganese rejection;
- Magnesium sulphate is very soluble but, unlike sodium, magnesium can be precipitated from the end solution with lime; hence there need be no impact on the tailings dam and environment.

However, there are problems with the use of magnesia:

- Large quantity of expensive high-grade MgO required;
- It is usually imported from USA or Australia – hence logistical issues;
- The reagent is vulnerable to hydration and ageing before use;
- Associated CaO in the MgO forms gypsum in the product;
- Grades of MgO vary markedly in their effectiveness; even with the most reactive grades, not all the MgO dissolves and at least 2% reports to cobalt product.

6.7 Cobalt Electrowinning (EW)

Many current cobalt projects have elected to produce cobalt as cathode but not all appreciate how difficult it is to make quality cobalt cathode in large quantities. Apart from the extensive solution purification requirements, the fundamental practical problem is the highly stressed nature of the cobalt that plates onto the stainless steel cathode blanks. The stress increases with deposition time and other factors until the deposit suddenly exfoliates or "peels" itself off the blank, with disasterous consequences for the EW cell.

Full-sheet cathode vs "Rounds":
The traditional cobalt EW process employs full-sheet cathodes and undivided cells as for copper and zinc. Standard practice in Zambia and the DRC is to use blanks with no edge strips, so as to allow the cobalt to grow around the edges whereby it simply cannot peel off. Mintek[25] recently patented a special edge strip, used at Kasese, Uganda, that is designed to allow only a small controlled amount of plating around the edges and so reduce the manual effort required to separate the deposit from the blank.

One particular downside of this process, apart from the major manual effort required for stripping and the mechanical damage caused to the blanks (see Figure 6), is the low cobalt "bite" (ΔCo) achievable over the cell – which is only about 5-10 gpl. Beyond this, the acid formed in the cell causes too much hydrogen gas evolution at the cathode and the current efficiency decreases to unacceptable levels. A low ΔCo also means that high flowrates are required, impacting adversely on opex and capex up-stream of EW.

At Vale-Inco's Port Colborne cobalt refinery (PCCR) in Canada, to avoid the peeling problem, cobalt is plated as "rounds" - which are 1" diameter discs (see Figure 5) deposited onto stainless steel sheets (mandrels) on which a di-electric heat-cured epoxy paint has been applied following a suitable pattern using a silk screening process. The cobalt plates only on the exposed round areas of the blank and is easily stripped, enabling the process to be mechanised (see Figure 7). The process is briefly described in an old paper by Agnew et al[26].

Figure 5 – Cobalt Rounds (left) and Crushed Cobalt Cathode (right)

Figure 6 - Stripping Full-sheet Cathodes

Figure 7 - Stripping "Rounds"

Until recently, rounds technology was protected by patent so it was not normally a viable option; but there are now some projects electing to go this route, although the process and technical detail is relatively complex and still closely held by Vale-Inco. The up-side is that the process can be mechanised, in fact automated in parts, so it is potentially suitable for large capacity plants.

The stress problem is reduced in a chloride electrolyte medium and conventional starter sheets (thin cobalt plated on titanium blanks) can be used, as in many nickel and older copper EW plants. However, chloride electrowinning introduces a whole new set of problems such as corrosion and chlorine gas containment and would not normally be considered on a relatively large scale and/or in the DRC context.

<u>Divided vs Undivided Cells:</u>
Conventional EW cells are undivided (see Figure 8), whereas in a "divided" cell as used in nickel EW (see Figure 9), the anodes and cathodes are separated by semi-permeable membranes.

Figure 8 – Undivided Co Cells

Figure 9 – Divided Ni Cells

There is now a growing interest in using divided cells for cobalt because, compared to undivided cells, this should:

a) allow a much higher ΔCo across the cell by keeping the acid produced in the cell away from the cathode - i.e. in the anolyte compartment;
b) improve current efficiency by withdrawing anolyte (high in acid) from the anode side of the membrane and so reducing the competitive side-reaction of hydrogen evolution at the cathode; and
c) reduce the hydrogen content of the cobalt deposit, for the same reason.

Anode Bags vs Cathode Bags:
The dividing membranes could theoretically be either cathode bags (as in Figure 9 above) or anode bags (as in Figure 10 below). Unfortunately, cathode bags are only suitable for nickel (which seldom peels), but not for full-sheet cobalt – which will inevitably peel and destroy the bag. Hence, for cobalt, the interest is in anode bags

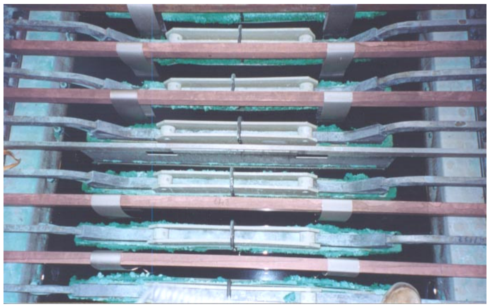

Figure 10 – Divided Ni Cell - Anode Bags

Figure 11 – Damaged Anode Bag

The advantages of using anode bags, as opposed to cathode bags, are:

- Facilitates recirculation and improved flow of catholyte; so improving control of pH in the cathode compartment with further benefits in terms of cathode quality and current efficiency;
- By sealing the anode bags and linking them to an extraction system, allows capture of the acid "mist" evolved at the anode (a mixture of oxygen and fine acid droplets), resulting in a much healthier working environment;
- Less vulnerable to damage caused by cathodes exfoliating (see Figure 11).

The PCCR "rounds" process employs anode bags to take advantage of these benefits.

However, a notable disadvantage of anode bags is that solid anode products (MnO_2, PbO_2, $PbSO_4$, Co^{3+} oxides etc.) accumulate inside the bag – necessitating their regular removal and cleaning. Also, one failed anode bag can harm the entire metal production in a cell, whereas one failed cathode bag impacts only on that single cathode.

The Way Forward:
Several projects continue to go with the traditional full-sheet & undivided cell process for its proven robustness and low risk. Some are attempting to develop their own "rounds" process and a few are contemplating the use of full-sheet cathode with anode bags, even though such technology is unproven on a large scale – the key to success is still the adherence or otherwise of the cobalt to the cathode blank.

6.8 Other Cobalt Products & Processes

Briquettes – Hydrogen Reduction
Cobalt metal (powder or briquettes) can be produced by hydrogen reduction in an autoclave. The process is well-known and is usually associated with the up-stream process (e.g. Sherritt). However, EW is normally preferred on account of lower capital and operating costs, higher metal recovery, and easier and less stringent operability and maintenance.

Cobalt Sulphate – Crystallisation
Cobalt sulphate is produced via evaporation/crystallisation and can be a high-value product if it is good grade – but the grade is entirely dependent on the extent of up-stream purification (notably manganese and magnesium removal). Gypsum contamination and scaling is also a problem. Crystallisation is a relatively complex process to operate; energy costs are major and it is maintenance intensive. The practical advantage is that no reagents are needed.

Hydroxy-oxides – Strong Oxidants
Nickel is more difficult to oxidise that cobalt and so a number of processes exist that aim to oxidise and precipitate cobalt in preference to nickel. Strong oxidants such as ozone, Caro's acid, ammonium persulphate or even chlorine can be used. Such processes are specialised and should be considered only in an environment where the safety issues can be managed. Poor Co/Ni selectivity can be a problem and SX would normally be preferred.

7. Which is the Best Cobalt Process?

The question is often asked "Which is the best process, or combination of processes, for cobalt recovery?" but the answer is seldom clear cut. Figure 12 below shows a typical flowsheet recently proposed for a DRC cobalt project. This would not be a unanimous choice, but it does illustrate the relative complexity of the cobalt recovery section.

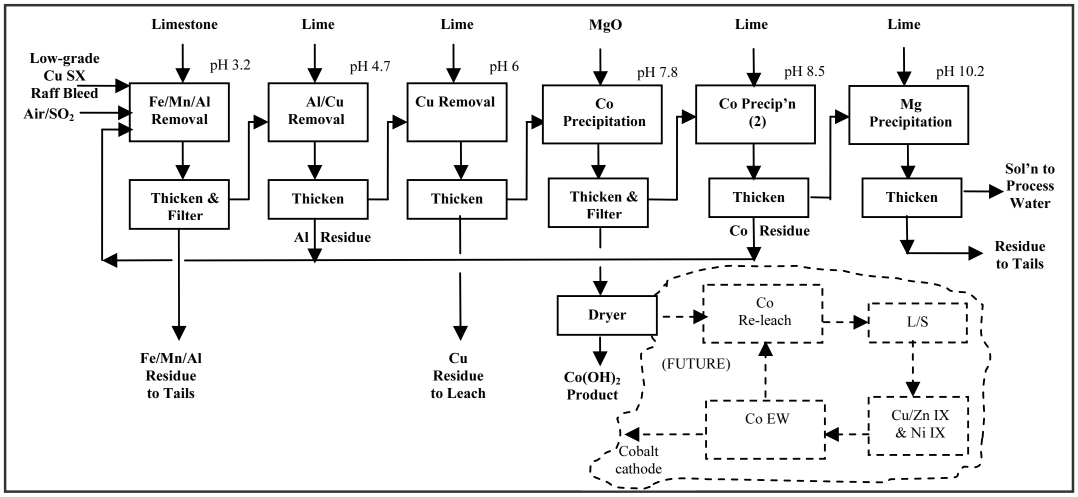

Figure 12 – Typical DRC Cobalt Flowsheet

The pro's and con's of many of the processes discussed in section 6 above are noted in a recent paper by Swartz et al[27] which attempts to quantify their relative merits in terms of costs, risks and benefits applicable in the DRC context. Not surprisingly, there is no preferred process; however, the complexity and risk involved in cobalt EW metal production are emphasized and the initial production of a cobalt hydroxide intermediate is recommended. This author would concur with their conclusions in the DRC and elsewhere.

8. Conclusions

1) In the last 10 – 20 years there have been many significant technical developments in the processing of copper-cobalt and nickel-cobalt ores. Together, these developments have helped to satisfy a steadily increasing world demand for cobalt.
2) The DRC copper-cobalt industry now looks set to be the world's major source of cobalt well into the future.
3) Whole Ore Leach technology is a major factor in the DRC's revival.
4) There is a wide range of cobalt recovery processes available, although each has pro's and con's:
    - There have been major developments in the field of SX and it is a popular process. However, there are significant problems to be considered.
    - Cobalt product selection is an important issue in new projects. Because of the relatively high value of cathode metal, many projects are planning to install electrowinning facilities, although some are conservatively electing to produce only an intermediate precipitate initially.
    - Cobalt electrowinning is fraught with practical difficulties. Technological advances such as anode bags with full-sheet cathode will be watched with interest!

5) There is no clear cut choice of cobalt process(es) that should be used and each case must be considered on its merits. Environmental, safety and logistical issues have to be considered and risk is a serious constraint.

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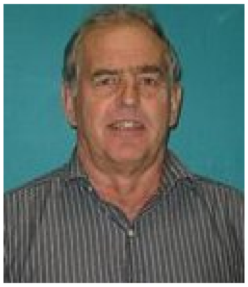

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    - Impala BMR Expansion
    - Kasese Cobalt Project, Uganda
    - KOV copper-cobalt project, DRC
    - Cooke Uranium
    - El Boleo Cu-Co Project, Mexico