

Technical and Business Considerations of Cobalt Hydrometallurgy*

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Approximately 55,000 tonnes of cobalt are produced annually worldwide, which represents an estimated \$1–3 billion in annual sales depending on cobalt price changes. Cobalt is a common impurity in both non-ferrous mineral sulfide and oxide processing. In this paper some business and technical considerations are presented to facilitate the decision-making process required to produce either an intermediate or a finished cobalt product via a hydrometallurgical route. Methods currently available and practiced for the recovery of cobalt are considered, as are process requirements up- and down-stream associated with each chosen method are discussed. In particular, some environmental, energy, or other sustainable development implications of each process are mentioned. An outlook on the future of the cobalt industry and anticipated future trends is included.

COBALT – THE DEVIL IN DISGUISE?

“Whether or not the Devil and his hellish crew gave their name to cobelt, or kobelt, nevertheless, cobelt is a poisonous and injurious metal even if it contains silver.” These are the words of Johann Mathesius in 1562, long before cobalt was identified as an element. He was referring to health troubles caused by the processing of mixed cobalt-arsenic-silver sulfide minerals then mined in Schneeberg, in the Hartz Mountains of Saxony, Germany. The old German kobelt, derived from the Greek kobali (mime), translated means goblin or gnome, whom the miners believed lived in those mountains. In hindsight we now know that exposure to volatile arsenic species made during roasting contributed to those health issues. In

addition, the presence of copper and nickel sulfide minerals in the ore further puzzled and frustrated the alchemists of those days in their efforts to extract metal, specifically silver and copper.¹

Curiously enough, cobalt is a relatively common element in nature, and the Earth’s crust contains ~0.002%, which ranks it no. 33 in abundance.² It is an essential element for all animal life and is the central constituent of vitamin B₁₂, which catalyses the regeneration of red blood cells. The metabolism of

vitamin B₁₂ and the daily ingestion of cobalt-containing foodstuffs provide the most significant source of cobalt in the human body, as discovered in 1948. An adult human body contains around 3 mg of cobalt, and poor absorption of vitamin B₁₂ or diet deficiency can lead to anemia. On the other hand, the ingestion of relatively high levels of cobalt may pose health risks to humans. Cobalt salts (1–2 ppm) were added to beer as a foam stabilizer in the 1960s, and heart disease with subsequent death was reported among heavy beer drinkers.³

Cobalt is clearly a part of our everyday lives. From its devilish origin and requisite presence in our bodies to its present use in batteries and jet engines, cobalt is ubiquitously present in the 21st century society. Yet cobalt has historically proven to be a difficult metal to recover from its ores and continues to pose unique process challenges. This article aims to present key factors which drive process decisions related to cobalt recovery from hydrometallurgical solutions. See the sidebar on page 44 for a history of cobalt and its uses.

COBALT SUPPLY AND ITS MINERALOGY

Economic concentrations of the element cobalt are the exception, so that supply is ruled by its by-product output from mines for the recovery of other elements. The cobalt content of these ores is low, less than 0.5% and often less than 0.1%. At the turn of the century, the small high-grade cobalt mines of New Caledonia supplied most of the world output (oxide ore). In 1906, the cobalt-silver sulfide mines of Ontario took over world leadership in cobalt supply and became the only important producer of the element for the next

How would you...

...describe the overall significance of this paper?

It provides an historical perspective on the cobalt markets and the hydrometallurgical technologies in use to extract it from both primary and secondary raw material resources each with inherent mineralogical challenges.

...describe this work to a materials science and engineering professional with no experience in your technical specialty?

The article describes the reagents, processing techniques, and engineering design considerations available in aqueous solution chemistry to recover cobalt metal or its intermediates. It also makes a connection between the application and uses of cobalt in view of these highly specialized processing methods.

...describe this work to a layperson?

This article outlines the diverse applications of cobalt in our society at present and in the future (e.g., batteries). The road to producing cobalt metal is long and complex and depends on the hard work of many people like engineers, scientists, politicians, and economists.

HISTORY OF COBALT AND ITS USES

The supply and demand of a metal is always closely linked to its industrial applications, and cobalt is no exception. Commercially, cobalt has been used to color pottery and glass since at least 2000 B.C. For example, when primary cobalt ores were roasted to eliminate most of the sulfur and arsenic, they yielded a mixture of crude cobalt oxide and sand, called zaffre. Fusion of the latter with potassium carbonate produced smalt, basically potash silica glass colored blue with cobalt. For centuries the alchemists believed the color, which had extensively been used in Egyptian, Persian, and Chinese pottery, was due to arsenic or bismuth, but in 1735 a great Swedish scientist Georg Brandt (1694–1768) showed that the effect was derived from cobalt metal. Around 1780, Bergman and others further studied the properties of cobalt and established its elemental character. In his time Brandt was more famous than his presently better known student, Axel Cronstedt (1722–1765), the discoverer of nickel. The close association in the discovery of the two elements is not surprising. They are invariably closely associated in nature.⁴

Although electroplating of cobalt was performed for the first time in 1842, coloring from oxides and silicates remained its main use well up to the 20th century, and even in 1916 the global cobalt output was only 554 tonnes, of which 400 tonnes was in the form of oxide.² However, the development of the Stellite® cobalt chrome

alloys (1907) and cobalt-chrome-tungsten alloys (1913) by Elwood Haynes would eventually initiate a great leap forward in the use of cobalt. Very slowly, but steadily, other industrial applications of cobalt were developed as cobalt supply increased. Applications such as steel-to-enamel bonds, cutting tools (1923; tungsten carbide patented), hydrogenation (1953; commercial catalyst applications), and paint drying emerged.² In the first 50 years of the 20th century, cobalt consumption steadily expanded, primarily as an indispensable component of permanent magnet materials (1936; AlNiCo magnet production) and of numerous heat-resisting and high strength alloys.

By 1939, yearly world output had reached 4,500 MT, of which 75% came from Africa.⁴ Cobalt prices were high, but stable and ranged from \$1.75–2.50/lb for four decades (1925–1965).⁵ For clarification, since the early 1930s cobalt was primarily found and mined in Katanga, Zaire (Democratic Republic of Congo) and Rhokana, Zambia as a valuable by-product from copper production. These unique copper deposits and their colonial rulers determined the growth potential of the cobalt market. However, during World War II two events occurred that would ultimately change the supply mechanism of cobalt forever. First, the Caron ammoniacal leach process was applied to nickel oxide ores at Nicaro in Cuba, and second, the recovery of cobalt originating from sulfide nickel ores was initiated at Clydach in Wales (Mond Process⁶). Most importantly, these pioneering industrial achievements pointed to nickel ores as a vast new source of cobalt albeit as a by-product. In 1959 new technology in the form of pressure acid leaching (Moa Bay) unlocked another cobalt recovery route from nickel oxide or laterite ores. Around the same time pressure hydrometallurgy for cobalt in ammoniacal solutions using hydrogen reduction was developed by Sherritt–Gordon.⁶ The transformation was completed in the late 1960s by the commercial implementation of solvent extraction for nickel/cobalt separation, which is amongst others applied at Xstrata Nickelverk AS.^{7,8} Consequently, the past 50 years has seen a cobalt supply shift where nowadays (2007) ~48% comes from the nickel industry and its unique processes, ~37% from the copper industry (and other), and only 15% from primary cobalt producers.⁹

Due to its ability to impart strength and corrosion resistance at high temperatures, cobalt is favored in alloys used in high temperature applications (e.g., gas turbines, jet engines, and high-speed tools). Cobalt is a ferromagnetic material, and it retains its magnetism up to 1,121°C, the highest Curie temperature known. Hence, cobalt became vital in the magnet industry, as a catalyst in the petroleum

industry and in the medical field, in prosthetics, and radiology. These developments increased annual cobalt production to 20,000 MT in the early 1970s when its uses were characterized as shown in Figure A.

The use of cobalt in electronics has grown enormously during the last 10–15 years, in both magnetic recording and especially in the battery sector. Cobalt is an important component in nickel-cadmium, nickel-metal hydride, and lithium-ion rechargeable batteries, and in 2007 the manufacture of batteries represented about 25% of the total cobalt consumption, which equaled ~54,000 MT.⁹ This shift in cobalt use is shown in Figure B. As a result of both economic growth in China and constrained availability of raw materials from Central Africa the cobalt price spiked at just over \$50/lb in April 2008. This steady demand growth for cobalt in new applications, which has been quantified in Figure C, brings us back to having a closer look at the metallurgical supply side.

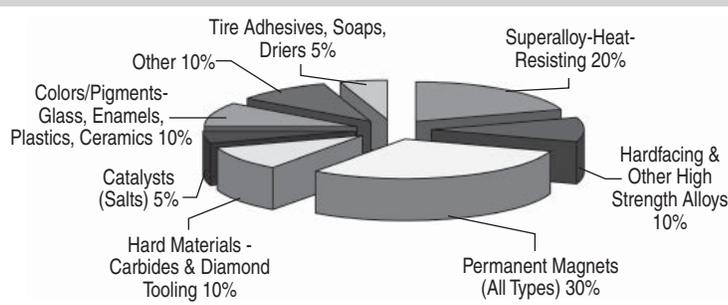


Figure A. Cobalt uses in 1970.⁴

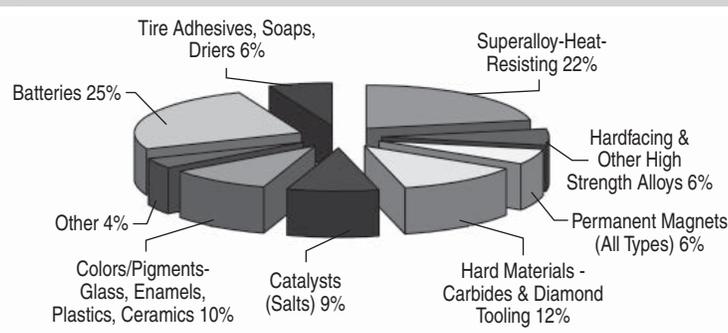


Figure B. Cobalt uses in 2007.⁹

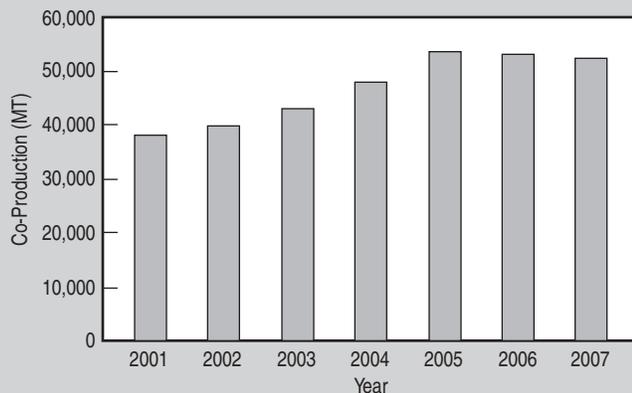


Figure C. Cobalt production trend in recent years.⁹

Table I. Economically Important Cobalt-Bearing Minerals

Mineral Group; Name	Formulae	Co (%)
Sulfides		
Linnaeite	(Co,Cu,Ni,Fe) ₃ S ₄	≤~45%
Carrollite	CuCo ₂ S ₄	≤~35%
Pentlandite	(Fe,Ni,Co) ₉ S ₈	≤~2%
Cobaltiferous Pyrite	(Fe,Co)S ₂	≤~5%
Arsenides		
Skutterudite	(Co, Ni, Fe)As ₃	≤~20%
Cobaltite	(Co,Fe)AsS	≤~30%
Oxides		
Heterogenite	Co ₂ O ₃ ·H ₂ O	≤~60%
Asbolite	(Co,Ni)O·2MnO ₂ ·4H ₂ O	≤~25%

20 years. Nonetheless, their maximum production rate scarcely exceeded 1,000 tonnes per year. In 1926, domination of the cobalt market shifted to Africa due to the large cobalt by-product output from the Congo's copper mines (Union Minière de Haut Katanga). In 1934 Zambia became a significant cobalt producer, again as a by-product of copper (Rhokana Corporation). A year later, Morocco became a supplier of the element from its small but high-grade cobalt deposits. African market dominance was maintained well into the 1990s and cobalt price volatility was linked to political events in the region.

After World War II the nickel industry entered the cobalt market and it generated ever growing quantities of cobalt from both its nickel sulfide and to a lesser extent laterite oxide ores. One of the drivers behind this turnaround was the development of nuclear power reactors, where only stainless steel based on pure nickel was tolerated, since cobalt would have been converted to the cobalt-60 isotope, a hard gamma ray emitter with a half-life of over five years.³ Another driver was that high-purity cobalt was needed for the newly developed high-performance aircraft jet engines. To meet both these quality and market requirements, the main nickel producers decided to modify their refining processes so that both nickel and cobalt could be extracted into pure metals. Due to the highly competitive nature of the nickel industry hydrometallurgical cobalt recovery methods in the sulfate, chloride and ammonia systems emerged.

Cobalt-bearing deposits in the cop-

per belt of Central Africa typically have a Cu/Co ratio of 7–50 (there are both sulfide and oxide reserves), while nickel sulfides such as those found in Sudbury, Ontario and Western Australia have a Ni/Co ratio of 20–50. Laterite ores, on the other hand, have a Ni/Co ratio of 10–30, and they are generally considered to be the growth engine of the nickel industry, which at 1.4 million tonnes of nickel (2007) is a much larger market than cobalt. In addition, there is a vast untapped wealth of cobalt in deep sea manganese nodules provided economically viable mining technology can be developed. The main minerals encountered for metallurgical process development are listed in Table I.

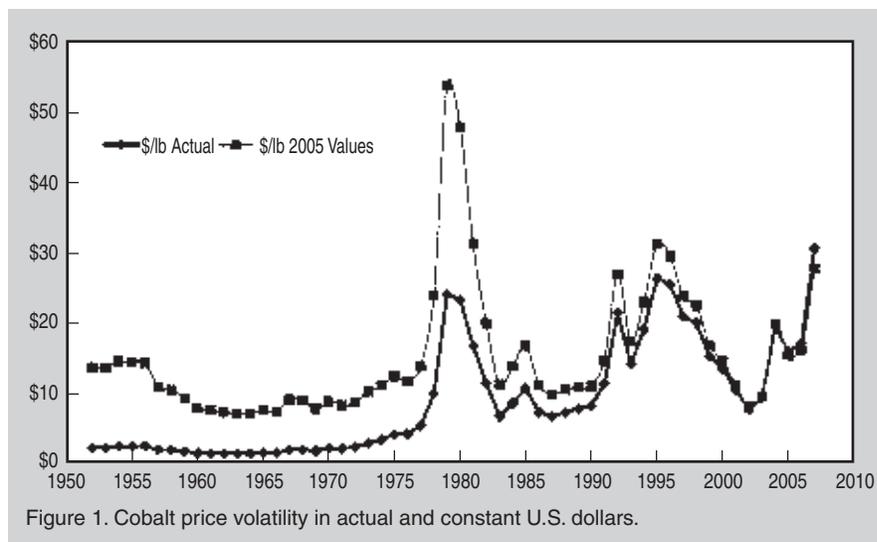
So-called primary cobalt ores mainly consist of arsenide minerals and they are found in Morocco, Russia, the United States, and Canada. Often silver is an important by-product which drives the process economics. Despite their high cobalt grade the metallurgical effort to manage the arsenic content in these minerals has restricted their continued commercial use and success. The stability of arsenic-bearing tailings deposited into surface or underground structures represents an essential economic driver for these cobalt-silver projects.

The copper-cobalt sulfide and oxide ores found in the Central African Copper Belt, which is shared between Zambia and the Democratic Republic of Congo, constitute by far the largest cobalt reserve in the world, approximately 50% of the known ~7 million tonnes of world cobalt reserve. Lin-

naeite and carrollite are the primary minerals. Heterogenite reserves are not insignificant. At present China and its entrepreneurs play an active role in shipping ore, concentrates and metal from Central Africa into Chinese manufacturing facilities for producing cobalt chemicals, batteries, and other valued-added products. Naturally, Zambia and the DRC attempt to maximize cobalt value creation inside their country, which combined with their political and economic climate can lead to supply interruptions and corresponding cobalt price volatility. The latter has been exemplified in Figure 1 where the major spikes 1978–1982 and 1992–1997 are related to Central African supply limitations. More importantly though, Central Africa has the resources to recapture its leading position in the cobalt market, which it only recently (past decade) lost to the nickel industry, provided that it can successfully execute a rich pipeline of cobalt mining projects. This is a major market supply and sustainable development uncertainty.

Over the years cobalt supply from nickel-copper-cobalt sulfide ores has steadily increased through the growth of the nickel market and its primary use in stainless steel. Ore supply is geographically spread among Canada (Vale Inco, Xstrata Nickel), Russia (Norilsk), Australia (BHP Billiton), China (Jinchuan), and South Africa (Anglo-American). The minerals pentlandite and cobaltiferous pyrite constitute the primary resource.

In the past 10–15 years nickel lat-



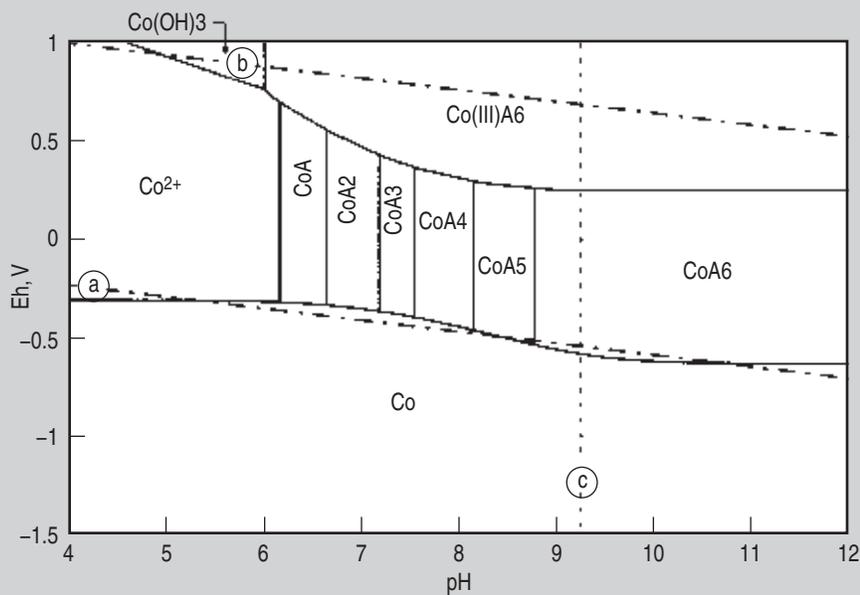


Figure 2. Pourbaix diagram for cobalt in the ammoniacal system (activities are unity).

erite ores have regained a strong process development and project interest. The primary cobalt mineral is asbolite, which is found primarily in the limonite (upper) section of the ore body. The application of the Caron process (Yabulu, Australia) and pressure acid leaching (e.g., Moa Bay, Cuba, and Murrin-Murrin, Australia) has yielded a steady stream of cobalt from such oxide ores. Both technologies are under continued scrutiny for their capital-intensive nature, operating cost profile (energy) and tailings disposal strategy. Often a mixed nickel-cobalt sulfide intermediate is created from these laterite ore bodies, which depending on ore body ownership leads to the purchase of ammoniacal refining technology (Sherritt International) or application of existing or novel chloride, ammoniacal or sulfate refining technology.

LIXIVIANT OPTIONS FOR COBALT

With the exception of laterite ores, commercial cobalt concentrates are successfully created from cobalt ROM ore. Although there are pyrometallurgical routes for recovering cobalt (e.g., the production of the so-called White Alloy [Cu-Co-Fe-Si]), this paper focuses on the hydrometallurgical aspects. Often this involves a roasting step, in which the cobalt mineralogy is changed to sulfates, oxides, or alloys prior to dissolving them in a lixiviant. It is inter-

esting to note that a sulfating roast, as practiced in the Central African Copper Belt, works for both oxide and sulfide minerals. There are three commercially proven hydrometallurgical lixivants for cobalt: ammoniacal, sulfate, and chloride solutions.

The quasi-equilibrium Pourbaix diagram for the Co-NH₃-H₂O system is shown in Figure 2, while the generic Pourbaix diagram for the Co-H₂O system is shown in Figure 3. The latter is meant to represent the unspicied thermodynamic stability in both the chloride and sulfate systems at room temperature. These diagrams, which can be made quite complex when adding species, allow the metallurgist to deter-

mine Eh-pH regimes in which they can separate the cobalt species from other impurities while continuing to maintain cobalt in solution. In sulfate and chloride systems cobalt is soluble in acidic solutions only (Figure 3). A clear difference gained by the use of ammonia lies in the ability to retain cobalt in solution as an ammine complex at mildly alkaline pH—in practice usually around pH 9. In contrast cobalt is precipitated at the same pH in non-ammoniacal sulfate and chloride solutions (Figure 2). The use of ammonia results in less corrosion of plant infrastructure and cheaper construction materials. Furthermore, since ammonia can be driven out of solution by steam and collected for re-use it is in theory a fully recyclable reagent. However, ammonia hydrometallurgy is associated with high energy and thus higher operating costs as a result of recycling ammonia. The need for reagent recycle is also practiced and mandatory in chloride solutions through electrowinning (chlorine) or pyrohydrolysis (HCl).

The flow sheet options for cobalt dissolution from its mineral are varied. In the nickel laterite industry, high pressure acid leaching followed by neutralization and iron removal by pH adjustment is standard practice. Mixed sulfide precipitation is one option of primary concentration. In the Cu-Co industry a roast-leach-electrowin from concentrates is used followed by copper stripping through cementation or electrowinning.⁶⁻⁸ pH adjustment can then successfully remove other impurities prior to cobalt recovery.

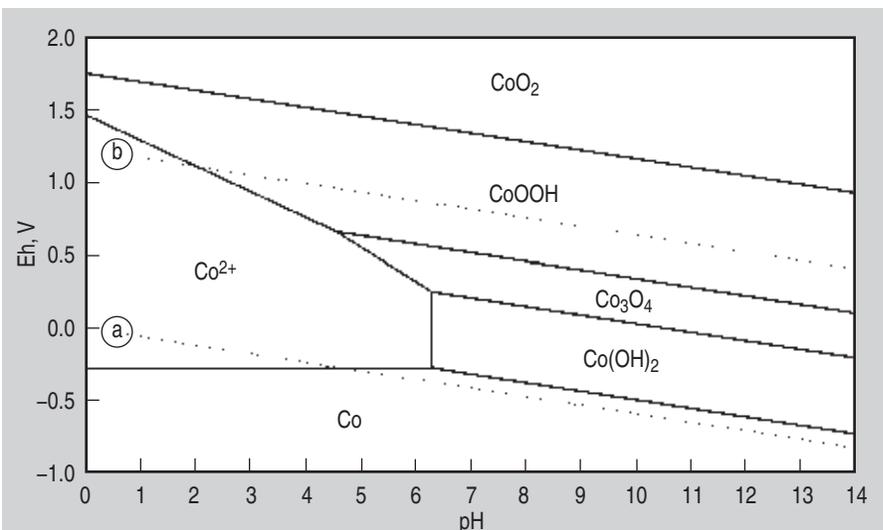


Figure 3. Co-H₂O Pourbaix diagram at 25°C (activities are unity).

MnS	-12.55
FeS	-17.31
NiS	-20.55
CoS	-21.64
ZnS	-24.05
PbS	-27.03
CuS	-35.05

PURIFICATION AND RECOVERY OF COBALT-BEARING SOLUTIONS

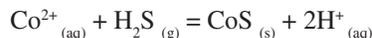
Precipitation Methods

Most of the world's cobalt supply has at some stage of its processing been precipitated as an intermediate product in sulfide or hydroxide form prior to being refined into its elemental state. In some cases precipitation is also used to recover the metal as a finished product. A good example of both is seen in Sherritt's processing of the Cuban laterites at Moa Bay. In this process the limonitic laterite is leached in a high-pressure acid leach and a mixed Ni/Co sulfide product is precipitated at Moa Bay. This intermediate product is then shipped to Sherritt's Fort Saskatchewan (Alberta, Canada) refinery where it is further processed to finally recover cobalt through hydrogen reduction.^{10,11} Where cobalt is recovered from copper mining operations such as in Africa it is usually precipitated as a hydroxide after copper recovery. This hydroxide is then re-dissolved to concentrate the cobalt prior to electrowinning.

Sul de Precipitation

Sulfide precipitation is practiced as a means of primary concentration from laterite process streams at both Moa Bay, Cuba, and Murrin Murrin, Australia.^{12,13} It has also been selected as the bulk concentration process for the new Coral Bay project in the Philippines.¹⁴ Sulfide precipitation is known to be highly selective and relatively low cost (>99% recovery). It has the significant advantage of producing fast settling, easily filterable, and washable precipitates. However, these nickel operations have a high Ni:Co ratio and both met-

als are usually precipitated together as a mixed sulfide. The overall precipitation reaction for cobalt can be expressed as:



This reaction is highly dependent on the equilibrium established between the gas phase H_2S and its solute which is itself a weak dibasic acid. A thorough presentation of the thermodynamic situation is presented in the work of Simons.¹⁵ For the purposes of establishing the degree of selectivity which is achievable by sulfide precipitation, the K_{sp} of some common sulfides at 25 C are presented in Table II.¹⁵ Clearly copper and some zinc, for example, can be preferentially precipitated from solution prior to bulk cobalt and nickel concentration, as practiced at Murrin Murrin and Moa Bay.^{13,15} While the precipitation of nickel or cobalt sulfides is thermodynamically favorable in weakly acidic solutions, such as those generated by typical high-pressure acid leach processes after neutralization and iron removal, it is not kinetically favored. In fact Simons has noted that "nothing happens" at pH 3.0, 70 C, 100 psig H_2S . Experience has shown that if temperature is increased to 120 C then 95–97% of the nickel and cobalt precipitates instantaneously via "self-nucleation." Similar effects can be obtained at lower temperatures by catalyzing the reaction through seed recycling which offers the added benefit of generating coarser particles for good settling and washing characteristics. To avoid scale formation in precipitation tanks, it has been reported that lower temperatures (~80 C) and fine particle seed recycle result in optimal conditions.¹⁴

The principle cost item in sulfide precipitation is the H_2S . If H_2S is made from molten sulfur and hydrogen then costs will be dependent on the price of sulfur and the hydrocarbon used for producing hydrogen through a reforming process.¹⁵ Efficiency for H_2S use can be in excess of 99%.¹² Clearly there remains a health and safety concern as H_2S is highly toxic. However, there are many industrial applications of this reagent which implies that safe handling methods are well established.

Hydroxide Precipitation

Hydroxide precipitation is practiced

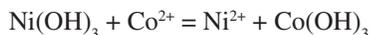
as a means of concentration at the Central African Cu-Co operations. Lime is typically used to precipitate the hydroxide through pH adjustment. The hydroxide slurry is then thickened and re-dissolved in spent electrolyte (sulfate) originating from the cobalt tank house. For successful concentration of cobalt in hydroxide form metals like iron, aluminum, and copper must first be removed. This is normally done through pH adjustment in the case of iron and aluminum while copper can then be partially removed by electro-winning. Any remaining copper can then be completely stripped through a combination of cementation and chemical precipitation (with lime for example). The hydroxide order of solubility is presented in Table III to underline the possibility of selective precipitation. Clearly ferric hydroxides, which generally have poor filtration characteristics, are extremely insoluble and rejection of iron is quantitative and fast under mildly oxidizing conditions at moderate pH. Cobalt hydroxide is rejected last under pH increase which allows for efficient separation of metals such as zinc and lead.

At the BHP/QNI Yabulu refinery cobalt is recovered as a oxy-hydroxide cake through steam stripping of a cobalt ammine solution which drives off the ammonia responsible for maintaining the cobalt as a solute (Figure 2). This product is suitable for the production of many organic and inorganic cobalt chemicals.¹⁶

Hydroxy-oxides of cobalt can also be separated from nickel-bearing solutions through redox precipitation. This method is based on the fact that nickel is much more difficult to oxidize than cobalt. Strong oxidants such as chlorine, air under pressure or ammonium

Fe(OH) ₃	-38.55
Pb(OH) ₂	-19.84
Zn(OH) ₂	-16.52
Fe(OH) ₂	-16.31
Ni(OH) ₂	-15.26
Cu(OH) ₂	-14.70
Co(OH) ₂	-14.23
Mn(OH) ₂	-12.70

persulfate are required to this end.¹⁷ An example of the use of chlorine is found at the Vale Inco refinery in Port Colborne, Ontario, which receives a nickel-cobalt carbonate from its Sudbury operations. This carbonate is leached in sulfuric acid and cobaltic hydroxide is then selectively precipitated by chlorine oxidation under controlled pH of 2.5–3.¹⁸ Outokumpu Oy developed a cobalt hydroxide precipitation process based on the electrolytic production of Ni(OH)₃ and its subsequent reduction in the presence of cobaltous ions:



However, this process did result in a precipitate which actually contained more nickel than cobalt. Filtering characteristics of the obtained cobaltic cake are reported to be acceptable.¹⁷

Hydrogen Reduction

Hydrogen reduction is currently used by Sherritt as its principal method of refined cobalt production.^{11,19} It is also used at Murrin Murrin.²⁰ Hydrogen reduction for nickel and cobalt is not self-nucleating and therefore a catalyst is required. At Sherritt's operations the batch reduction process is initiated from an ammoniacal cobaltous ammine solution by the addition of Na₂S and NaCN catalyst.¹¹ The combined use of organic catalysts, such as thioacetamide and nucleation promoters

such as gum Arabic and dextrin, have also been reported to be effective for increasing the rate of reduction.²¹ The cobalt particles which are produced grow by agglomeration and usually several densification stages are undertaken before the powder is discharged for further processing. As in the case of nickel reduction, cobalt tends to plate on the reduction autoclave wall. This requires periodic removal through leaching. Historically this has been done in ammoniacal sulfate solution with air under pressure but recent plant practice has involved the use of nitric acid. The cobalt and nickel powders obtained via hydrogen reduction typically contain too much sulfur for metallurgical use which means that they require further processing.^{11,19} The reduction of cobalt by hydrogen gas is reportedly more energy efficient and more productive than electrowinning.^{19,20}

Solvent Extraction

Solvent extraction (SX) has been in commercial use for the separation of cobalt from nickel at the Xstrata Nikkelverk refinery in Norway since 1968.^{22–24} Since then SX has gradually become more and more popular in cobalt processing, and it is now represented in the majority of refinery flow sheets involving cobalt, either in chloride, sulfate, or ammoniacal media.

Solvent extraction is an alternative to

the classical solution purification methods based on precipitation. In Central Africa, metal impurities in the copper tank house bleed streams for cobalt recovery can be removed by SX instead of electrolytic de-copperization, sequential hydrolytic precipitation, sulfide precipitation, or cementation.²⁵ The subsequent precipitation and partial re-dissolution of cobalt hydrate can also be replaced by SX, as practiced at the Kasese cobalt refinery in Uganda.²⁶

In the hydrometallurgical processing of nickel laterites, mixed nickel-cobalt hydroxide or sulfide precipitates are usually produced as intermediates, which then undergo further upgrading to high-purity nickel and cobalt products. These processes can be simplified by applying direct solvent extraction on the laterite leach solutions, thereby eliminating the need for a solid intermediate. Direct SX was in operation at the Bulong plant in Western Australia,²⁷ and it is a key part of the flow sheet for the Goro refinery currently under construction in New Caledonia.²⁸

It is in the area of cobalt/nickel separation that SX has become most widely used, first in chloride solutions and later also in sulfate and ammoniacal solutions. Due to its highly improved selectivity, SX has demonstrated itself as being an attractive alternative to the conventional oxidative precipitation of cobaltic hydroxide. Another important application of SX technology in the cobalt industry is the conversion from sulfate to chloride media.^{28–30}

In addition to the favorable selectivity, resulting in improved metal recovery and higher product purity, implementation of SX as a substitute for precipitation technology also means elimination of solids handling and use of hazardous chemicals like H₂S. However, several potential operational challenges must be evaluated carefully (e.g., the use of flammable organic liquids, degradation and poisoning of the extractant or diluent, third phase formation, organic/aqueous phase separation problems, and organic losses.)³¹ The latter, in the form of volatilized, entrained, and dissolved organic material, will increase operating costs and may also be harmful to the environment and downstream processes.

Industrial solvent extraction involv-

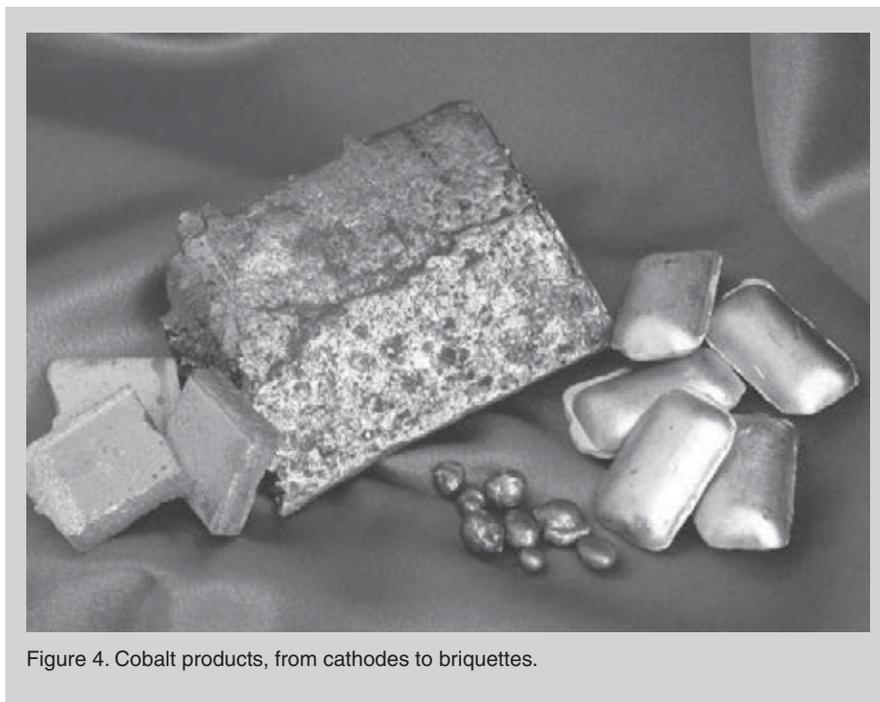


Figure 4. Cobalt products, from cathodes to briquettes.

ing cobalt is usually carried out in conventional mixer-settlers due to its simple design and easy start/stop procedures. Pulse columns, having a smaller footprint and reduced organic inventory, may be preferred if an inert atmosphere with a lower exposed surface area is essential in order to suppress organic degradation (Goro). Centrifugal extractors were applied by Nippon Mining.³⁵ Equipment in use for separation of entrained and dissolved organics from SX raffinates includes after-settlers, air flotation columns, dual media filters, and activated carbon filters.

A range of different organic extractants are employed in industrial cobalt processing. The main classes, pros and cons, plus examples of commercial ap-

plications are outlined in the sidebar.

Electrowinning

Production of electrowon cobalt cathodes came on stream at the Shituru plant, DRC in the mid 1940s.³⁸ Since that time electrowinning (EW) technology has been a predominant route for the recovery of cobalt, and an appreciable amount of the world cobalt production is marketed in the form of cathodes. An example of various cobalt products including sheared cathodes is presented in Figure 4.

Industrial EW of cobalt is performed in either chloride or sulfate aqueous media, of which the latter has been the most widely used. Since cobalt is less noble than hydrogen, the cathodic de-

position of cobalt is accompanied by simultaneous hydrogen evolution. However, when operating in solutions of low acidity, cobalt current efficiencies close to 100% can still be achieved. In sulfate media the main anode reaction is water splitting into oxygen and acid, but if chloride ions are present, chlorine evolution is kinetically favored. From thermodynamics, a certain amount of energy must be supplied for the electrode reactions to proceed. However, when the electrolytic process is supposed to take place at higher rates, like in commercial EW, additional energy is needed due to electrode overpotentials and voltage drop in solution and contacts, which increase with increasing current density.

ORGANIC EXTRACTANTS USED IN COBALT PROCESSING

Tertiary amines are used to separate cobalt from nickel in chloride media. Cobalt is extracted as anionic chloro complexes, necessitating high chloride concentrations ($>200 \text{ g/L}^{31}$), whereas nickel does not form such complexes and is not extracted. Cobalt is stripped from the organic phase by contact with low chloride aqueous solutions or water. This cobalt/nickel separation is very selective with a separation factor $>10,000$ at optimum chloride concentration.¹⁷ Aromatic diluents with low flash points must be used in order to avoid third phase formation, restricting operational temperature.²³

TBP—(*organophosphorous ester*) is applied at the Sandouville refinery in France for the extraction of iron from a strong nickel-cobalt chloride solution.³² Iron must be present as the ferric FeCl_3 complex to be extracted, and it is stripped with water.

D2EHPA—(*organophosphoric acid*), a relatively cheap and stable reagent, is utilized by several cobalt producers to separate metal impurities from cobalt sulfate solutions; zinc in particular but also manganese and calcium.³³ The latter may create problems in the stripping stage due to gypsum precipitation. Like the other phosphoric acid based SX reagents, extraction and stripping take place by cation exchange, controlled by the acidity of the aqueous phase. pH in the loading stage may be controlled by addition of base or by prior conversion of the extractant to its salt, while stripping is carried out using stronger acid. Despite its relatively low cobalt/nickel separation factor ($\sim 10^{34}$), *D2EHPA* has also been used in several plants for separating cobalt from nickel in sulfate media. The Rustenburg refinery in South Africa still operates a cobalt/nickel separation step using this reagent before crystallization of their cobalt sulfate product.³³

PC-88A—(*organophosphonic acid*), marketed as P507 in China,³⁴ replaced *D2EHPA* in 1978 as the extractant of choice in the cobalt/nickel separation process from sulfate solution operated by Nippon Mining in Japan,³⁵ due to its superior separation factor ($\sim 300^{34}$). Cobalt is extracted from nickel sulfate solution using P507 by Jinchuan in China, and conversion into a cobalt chloride solution is achieved by hydrochloric acid stripping.³⁰

Cyanex 272—(*organophosphinic acid*) became available in the early 1980s, and is currently the most widely used extractant for cobalt/nickel separation—approximately half of the Western world cobalt production passes through a SX step utilizing this reagent.²⁷

Its popularity is explained by its unique properties; a very high selectivity so that high nickel/low cobalt sulfate solutions can be treated efficiently (typical cobalt/nickel separation factor $\sim 7,000^{34}$), limited co-extraction of calcium and magnesium, and stripping of co-extracted iron is relatively easy. Aliphatic diluents are used, and diluent oxidation is controlled by adding an antioxidant. At the Murrin Murrin operation in Western Australia, *Cyanex 272* is utilized in two consecutive SX processes, where zinc is removed in the first step followed by the standard cobalt/nickel separation in the second step.²⁷ By using the same extractant in both processes, the risk of detrimental cross contamination is thus avoided.

Cyanex 301—(*organodithiophosphinic acid*), the sulfur analogue of *Cyanex 272*, shows a high selectivity for nickel and cobalt over manganese, calcium and magnesium.²⁸ Furthermore, the extraction of nickel and cobalt can be carried out at low pH without the need of base, and organic losses are low. Vale Inco has therefore included the use of this novel extractant in their Goro laterite project for the direct bulk extraction of nickel and cobalt from high pressure acid leach solution. Some challenges related to the industrial application of *Cyanex 301* have been reported, like instability toward oxidants (chromium) and copper poisoning.

Versatic—(*carboxylic acid*), a highly branched aliphatic monocarboxylic acid, is a cationic extractant used for bulk extraction of nickel and/or cobalt. Nickel and cobalt are co-extracted into *Versatic* from a sulfate solution at the Niihama plant in Japan.²⁹ Stripping using hydrochloric acid is then applied in order to make a strong chloride solution amenable for effective cobalt/nickel separation by a tertiary amine in a second SX step. *Versatic* was also utilized in a nickel SX-EW circuit at Bulong.²⁷ High solubility in the aqueous phase is a challenge for this reagent.³¹

LIX 84I—(*ketoxime*) is a chelating reagent able to selectively extract nickel from cobalt in ammoniacal media.³⁶ Cobalt must be present as the cobaltic pentammine complex to be rejected from the organic phase. On the other hand, any divalent cobalt is extracted, and a sophisticated treatment involving a reductive strip followed by regeneration of the organic phase is needed for cobalt removal. In order to improve the purity of the nickel product, ammoniacal solvent extraction was implemented at the Yabulu plant in Queensland, Australia in 1989. A similar process was also in operation at the Cawse refinery in Western Australia.³⁷

Electrowinning of cobalt from chloride solutions has several advantages over sulfate, like higher electrolyte conductivity, lower electrolyte viscosity, higher activity of the cobalt ion, and lower anodic and cathodic overpotentials. Higher solubility also makes it possible to operate with more concentrated solutions, and electrolyte pH within the cells is also more stable due to limited anodic acid formation. Furthermore, electro-active and inert dimensionally stable anodes (DSA), made of titanium coated with noble metal oxides, are available for chlorine evolution, in contrast to lead anodes currently in use in sulfate media. Lead anodes show high overpotentials for oxygen evolution, and lead contamination of the cobalt cathodes will deteriorate product quality. In chloride systems there is also less co-deposition of nickel, and the cobalt metal deposited is more ductile,³⁹ making production of starting sheets and shearing of cathodes possible.

However, there are some disadvantages related to chloride solutions, like the more advanced cell designs needed for safe handling of toxic chlorine liberated at the anodes, the fact that chloride solutions are more corrosive than sulfate solutions, and the higher internal stresses in electrolytic cobalt produced in chloride media.⁴⁰ Chlorine may also react with organics in solution or construction materials, forming harmful chlorinated organic compounds. Another issue is that manganese cannot be tolerated in chloride systems, since its presence in the electrolyte may lead to anodic deposition

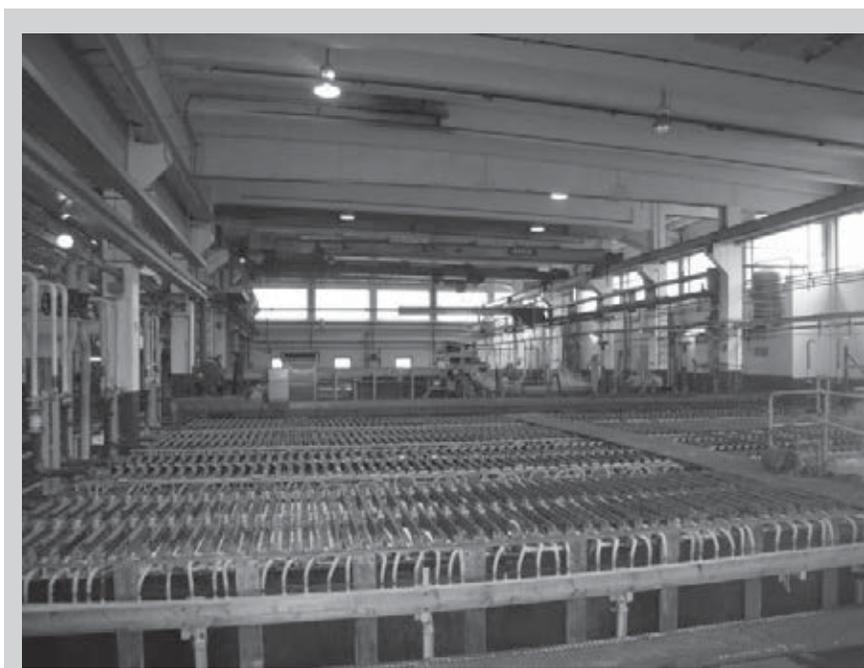


Figure 5. Cobalt electrowinning cell house at Xstrata Nikkelverk AS.

of manganese dioxide, which is detrimental to DSA noble metal coatings, it tends to increase the anode potential, and the main anode reaction is shifted from chlorine evolution to oxygen evolution.⁴¹ The latter may be critical for plants where other process steps rely on the use of chlorine from the tank house, as an oxidizing agent in, for example, leaching and precipitation.

Commercial cobalt EW is carried out in rectangular open cells made of wood, lined concrete, plastic or polymer concrete, with alternate anode and cathode vertical plate electrodes. The electrodes are electrically connected in parallel within each cell, while the cells are arranged in series. Cells for

chloride media are usually divided by encapsulating the anodes in individual bags of permeable synthetic cloth to collect the chlorine by suction. In sulfate solutions permanent stainless steel cathodes are mostly used, while in chloride solutions cobalt starting sheets are produced on titanium blanks. Lead alloyed with antimony (6%) is the predominant anode material in sulfate solutions, whereas DSA-type anodes are used exclusively in chloride media. EW operating data for selected cobalt refineries are listed in Table IV. Cobalt electrowinning as practiced at Xstrata Nikkelverk is depicted in Figure 5. See the sidebar on page 52 for operational challenges in industrial EW of cobalt.

Shituru Sulfate ⁴²	12	30–40	—	6.2–6.4	50–60	260–335	4 or 5	55–60	5.3
Luilu Sulfate ^{38,43}	—	45	6	—	70	350–400	4	80	5–6
Chambishi Sulfate ⁴⁴	30	30–40	4	1.9	70–75	280–400	4 or 5	65–70	6.5
Kasese Sulfate ²⁶	36	50	5	—	70	250	5	—	—
Nippon Mining Sulfate ³⁵	—	100	—	—	60	200	—	—	—
Port Colborne Sulfate ⁴⁵	36	45	7	3.7	50	200	5	93	3.6
Niihama Chloride ²⁹	38	55–65	—	1.2–1.5	55–60	233	8	90	3.1
Jinchuan Chloride ³⁰	11	65–80	35–60	2	55–60	300–350	4	94	3.4
Pomblière Chloride ⁴⁶	—	—	—	—	60	350	—	90	—
Nikkelverk Chloride	48	53	5	1	60	220	7	90	3.7

TECHNICAL & BUSINESS SELECTION CRITERIA

When assessing whether to participate in the ~55,000 tonne cobalt market, the following selection criteria may come in handy.

Choose your cobalt product purity and its form carefully. The complexity of cobalt processing represents a major capital cost hurdle to new participants. Low value products are shipping ore, concentrates (mainly sulfide), White Alloy and impure sulfide and hydroxide intermediates, which are commonly priced on the contained cobalt content minus a refining/processing fee. Nonetheless, the intermediate route is an attractive route to get started in the business and build-up cash reserves. Subsequently, there are two platforms to operate on: cobalt metal (either 99.3% or 99.8% purity) or value-added cobalt products. The latter includes cobalt hydroxide, battery grade oxide, and extra fine powders, which can allow you to collect 125–175% of the cobalt price, but your market is more restricted.

Determine the experience, technical know-how, and business aptitude within the company that owns the ore body and controls its development. Companies tend to choose similar technologies to what they are familiar with.

Assess the location of the ore body and the intended site for a cobalt refinery:

- Is there access to skilled labor for complex process technology? The cost of labor will determine the level of automation (capital expense) in the plant
- What is the availability of reagents and clean process water including its composition?
- A coastal location allows for easy delivery of spare parts, reagents, dispatch of the cobalt product and disposal of any tailings or effluent streams. These can all be an important part of process selection.
- Determine the access to and the cost of energy (i.e., hydro-electric power versus hydrocarbon-based electricity for electrowinning, steam stripping or hydrogen reduction). For example, if you have easy access to hydrogen and the plant is surrounded by farms, you

may choose hydrogen reduction and produce ammonium sulfate fertilizer as a by-product (Sherritt). It is a business decision to enter both the cobalt and the fertilizer market.

- Consider site topography. If available floor space is limited or expensive to create, you may choose H₂ reduction which is more compact than conventional tank house technology for electrowinning.
- Health, safety, environmental, and community issues related to the stature of the company and the jurisdiction of the country in which the ore body is found and the company is operating are important decision factors.

Select the plant size/capacity of your project in relation to the overall cobalt market, your ability to raise capital, and the overall mineral reserves in the ground (payback period). In short, know your competitors and their strengths and weaknesses. For example, if you oversupply the market with an unwanted 5,000 tpy of cobalt then your operating costs ought to be in the lower first quartile of the cost curve to build a sustainable business.

Naturally the ore body itself plays a key role in the economic evaluation. In the case of nickel ores the cobalt content usually represents less than 10% of the overall revenue, while the Central African copper mines rely on 25–35% of their revenue from cobalt. In the case of cobalt slag or tailings treatment more than 50%, if not >80%, of the revenue comes from cobalt. Another business anomaly is that the silver values in primary cobalt ores can easily exceed the cobalt value. Of course cobalt grade and tonnage and the chosen mining method (surface versus underground) are key economic variables as well. From a technical point of view the mineralogy will drive the process selection options, since the minerals and their impurities determine the operating costs of the process.

Practice process risk management. Producing an intermediate product (mixed sulfide, mixed hydroxide, white alloy, etc.) is less risky than refining all the way to pure metal. Also, using innovative process technologies to get to refined metal adds to the start-up risk

through ramp-up time and lowers the net present value profile of a project.

OUTLOOK FOR COBALT

In view of cobalt's now recognized valuable properties, it is not surprising that it is one of the most useful of the ferro-alloy metals. The outlook for cobalt use is dynamic as exemplified by continued production growth and new applications such as batteries. Due to their strong ties to nickel processing, laterite ores hold one of the wild cards for cobalt production and its pricing in the future. Cobalt by-product output from those nickel oxide ores can easily exceed that of sulfide ores based on the fact that nickel reserves are driven by oxide ores (70%), while sulfide reserves lag against a background of continued stainless steel growth. Another key wild card constitutes the dominant cobalt reserves still present in Central Africa and awaiting commercialization. One could argue that imminent oversupply is unavoidable. However, a corresponding and sustainable lower cobalt price could also bring about new or expanded applications for cobalt, which in itself can instigate substitution by cobalt under those circumstances. Cobalt remains to be a valuable by-product in many businesses.

Identified growth markets for cobalt are rechargeable batteries (hybrid vehicles), catalysts, and to a lesser extent superalloys (new commercial aircraft jet engines, defense procurement, and demand for gas turbines in electricity production). Apparent demand has shifted to both China and Japan as a shift of manufacturing capability that produces and uses cobalt (~20,000 MT cobalt in China) has moved away from the United States and Europe. Not surprisingly, the cobalt price is linked to the world economy through its specific infrastructure-related uses. The market for batteries, mainly applied in mobile phones, has now outgrown the traditional market for superalloys. In the next 5–7 years we can expect to reach a 60,000 to 70,000 tonne cobalt market with a traditional mix of products such as 99.8% cathode, 99.3% cathode, 99.8% powder/briquette, and large quantities of specialty products and chemicals—a key growth sector.

OPERATIONAL CHALLENGES

Industrial electrowinning (EW) of cobalt is associated with several operational challenges.

Internal stress in cobalt electrodeposits causes peeling of metal from the blanks, warping of starting sheets, ripping of anode bags, and electrical short circuits. Stress is controlled by operating at favorable condition, (i.e., high cobalt concentration, high temperature, and high pH) in order to reduce inclusion of hydrogen in the metal, which generates stress.⁴⁰ Removal of “stress promoters” like organics and active sulfide ions by passing the advance electrolyte through activated carbon is common practice. Organic contamination from upstream solvent extraction process steps may also intensify surface pitting from hydrogen bubbles sitting on the cathode surface.

Proper deposit adhesion to the cathode blanks is essential to avoid premature stripping. Blanks are therefore pre-treated by pickling or sandblasting. Dipping of stainless steel blanks in a gelatine solution used as a releasing agent for the cobalt deposit has also been reported.³⁸ At Shituru, less corrosion-resistant mild steel blanks are employed to obtain sufficient deposit adhesion at the lower electrolyte temperature used.³⁸ Most African cobalt producers do not use edge strips to allow the metal to grow around the cathode blank, but this makes stripping more difficult.⁴⁷ Thicker blanks, which tend to warp less, can also be employed. Vale Inco has solved the problems related to internal stress by producing cobalt rounds instead of sheets, by use of stainless steel mandrel sheets with areas of diameter 1 inch not masked by a dielectric heat-cured epoxy paint applied by silk screening.⁴⁵

Nodular metal growth causes inclusion of impurities in the cobalt product, ripping of anode bags, and short circuits. Formation of nodules and dendrites is controlled by operating with even current distribution and limited current density. Too-high electrolyte pH may result in the precipitation of cobalt hydrates at the cathode surface, accelerating nodular growth. Electrolyte polishing for removal of solid particles, known to promote nodular growth, is applied in most refineries. The Shituru plant is based on in-pulp electrolysis, where the electrolyte contains 40–70 g/L of solid cobalt hydrates/gypsum kept in suspension by air sparging.⁴² Severe dendritic growth occurs, and the cathodes must be lifted frequently to break electric shorts. It should be noted that unlike in copper, addition agents are normally not applied in cobalt electrowinning.

Cobalt is a relatively non-noble metal, and extensive solution purification is required for high-purity cobalt to be produced by EW. A bleed stream from the tank house is also important for controlling the build-up of inert salts in the electrolyte. Cathode impurities may originate from feed materials or the reagents used, however, the main source of lead when operating in sulfate media is the lead anodes. To reduce lead contamination, the use of cobalt alloy anodes (Co 82%, Si 14%, Mn 4%) has been reported by some African cobalt producers.^{43,44} In Table A, impurity levels in electrolytic cobalt produced by various cobalt refiners are presented. Large differences in metal purity exist, and the cathodes produced at Shituru and Chambishi are melted for improving product quality. Annealing of cobalt at ~850 C is practiced by several producers to remove hydrogen.

Anodic deposition of cobaltic hydroxide causes masking of DSA noble metal electrocatalysts, aggressive corrosion of the catalytic coating, clogging of anode bags and piping, and chlorine in the tank house atmosphere when operating in chloride electrolytes.³ This type of anode scaling is controlled by operating at low electrolyte pH and by regular cleaning of anodes. When using lead anodes in sulfate media, anodic deposition of some cobaltic hydroxide may be advantageous, since the deposited layer then acts as a collector for lead corrosion particles. Cobalt also shows a depolarizing effect on the oxygen evolution reaction on lead. In sulfate based systems, unwanted formation of larger amounts of cobaltic hydroxide is avoided by the presence of manganese ions in the electrolyte.⁴⁸

According to Table IV, specific energy consumption in cobalt EW tank houses varies between 3.1 and 6.5 kWh per kg of cobalt pro-

There are risks. For example, batteries have seen increasing quantities of cobalt. In the 1980s Ni-Cd batteries contained 1–5% cobalt, the nickel-metal hydrate (1.2 V) batteries can contain up to 15% cobalt. In 2005 the lithium-ion (3.7 V) batteries emerged, which can contain up to 60% cobalt in the cathode. However, substitution of LiCoO₂ by manganese and nickel in these lithium-ion batteries is possible with reportedly limited performance loss. Depending upon the life cycle and technology development in the battery business, catalysts and electronics, recycling of these components represents another interesting parameter in the supply and demand cycle of cobalt. Several companies have already positioned themselves to take advantage of this recycling or custom feed opportunity, which is consistent with sustainable development goals. From a process technology point of

view it means that traditional primary base metal producers may have to, for example, address lithium, vanadium and molybdenum removal. The latter two elements may also constitute an economic driver for recovery, as exemplified by the spent catalyst recycling business where nickel and cobalt can be a by-product.

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duced. The specific energy consumption can be lowered by increasing cobalt current efficiency and reducing cell voltage. Increased current efficiency can be obtained by:

- Reducing the extent of hydrogen evolution. High cobalt concentration, high pH, and high temperature are beneficial. Negative influence of the acid generated at the anodes may be counteracted by operating with short electrolyte residence time in the cells (high electrolyte circulation, small cells, cross flow²⁶), divided cells,⁴⁵ or in-pulp electrolysis, where cobalt hydrates are neutralizing the acid as it is produced. The cobalt concentration is then kept constant as well. Co-deposition of certain impurities with low hydrogen overpotentials may also accelerate hydrogen evolution.
- Minimizing cathodic decomposition of anodically formed oxygen or chlorine (divided cells).
- Avoiding short-circuiting (electrode alignment, avoid deposit peeling, cell inspection, reduced pulling cycles, etc.).

Apart from reducing the current density, lower cell voltage can be obtained by increasing electrolyte conductivity (higher concentration of inert salts, higher electrolyte temperature); reducing the voltage drop across the separator by improving its properties, if divided cells are applied; reducing electrode spacing; removing accumulated slimes from anodes and cleaning electrode contacts; introducing DSA-type anodes in sulfate media; converting to another anode reaction taking place at lower potential.⁴⁹

Aerosol and acid mist formation, caused by gas bubbles bursting at the electrolyte surface, can have a negative effect on tank house operators' health. The levels of aerosol and acid mist are controlled by covering the cells with plastic beads or foam,⁴⁵ tank house ventilation or surrounding the anodes with bags operated under vacuum. As opposed to copper and zinc, cobalt EW tank houses are relatively small with limited automation and extensive manual handling—manual stripping of sharp and stressed cobalt electrodeposits is a potential safety hazard. In addition, cell currents may be high, and proper electrical insulation and grounding are essential.

Shituru ⁴²	1406	72	439	101	354	12664	281	486	—	1076	1444
Luilu ³⁸	454	17	36	3	2	25*	—	59	—	10	12
Chambishi ⁴⁴	5000–7000	12–30	8–40	20–50	2–10	1–25	8–13	<100	25–100	—	6–20
Nippon Mining ³⁵	200	20	50	1	—	1	—	—	—	—	—
Port Colborne ⁴⁵	950	1	5	5	—	<10	0.1	20	60	<10	10
Niihama ²⁹	400	15	50	<1	<1	30	—	—	—	<10	10
Jinchuan ³⁰	20	10	20	3	—	10	—	40	—	10	10
Pomblière ⁴⁶	1000	15	400	—	1–10	5	1	—	—	1–10	1–10
Nikkelverk	200	3	10	1	—	1	—	15	40	<5	2

* Zn + Cd

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