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Cobalt Metal: Overview of Deposits, Reserves, Processing, and Recycling

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Abstract: Cobalt, like other critical elements, is gaining in importance today. The great technological advances and the deep knowledge of the physical and chemical properties of this element have allowed to enhance its applications in various fields, such as: catalysts, paints, alloys for the mechanical and aerospace industries, as well as the medical sector and in recent times, its use within the rechargeable battery industry. The main exploitable deposits are in the Democratic Republic of the Congo, which have economic potential due to a strong influence on their mineralization processes. However, the growing demand for cobalt and the search for less dependence on African deposits leads to targeting other regions, so it is necessary to carry out exhaustive exploration to find out the potential of its reserves for a subsequent benefit of the mineral. Generally, cobalt comes as a by-product of the extraction of other metallic minerals, mainly from Cu-Co, Ni-Co, Ni-Cu-Co deposits. From the above, a first review is carried out on the differences that exist in the geochemical, mineralogical and forecast properties that exist within the different deposits that harbor cobalt. As a second review topic, it delves into efficient processing for cobalt recovery, which is generally carried out by flotation, acid leaching, in addition to its recovery from secondary sources, such as batteries and metallurgical waste. However, generally speaking there is still a vast lack of fundamental knowledge about the processability of cobalt. Said processing has been affected from the point of view of mineralogy, that is, understanding and knowing the cobalt-bearing minerals, as well as gangue mineralogy, these aspects exercise significant control during their processing and selection of the most appropriate route. suitable for cobalt extraction (leaching and/or flotation). In this context, the document concludes with a vision of the challenges that the mining industry must implement to enter circular economy models, mainly in the creation of sustainable processes from secondary sources.

Keywords: cobalt; critical elements; beneficiation

1. Introduction

Over the last century, the diversification of cobalt applications has led to an increase in its production with some ups and downs due to political instability and fluctuations in the international market price. In 2019, over 140 kt Co was produced from primary sources worldwide, with ~70% (100 kt Co) produced by the Democratic Republic of the Congo (DRC). Cobalt production in the DRC has been a dominant proportion of the world supply for several decades [1]. Schmidt et al. estimated that nearly 100% of cobalt chemicals such as (i) oxides, (ii) hydroxides, (iii) carbonates, and (iv) sulfates are produced from Cu-Co ores accommodated in eroded stratiform sediments located in the Democratic Republic of the Congo (DRC). Metallic cobalt is produced from nickel sulfide ores (49%), copper sulfide ores (32%), and nickel laterites (limonites, 19%) [2].

The purification of cobalt metal is currently dominated by China (~67%), followed by Finland (~11%), and Canada (~5%). This means more than two-thirds of refined cobalt is produced in countries where cobalt is not extracted [3,4]. Less than 10% of global cobalt production [1]is refined in the country of origin, implying that cobalt production is often based on imported materials. About 69% of the cobalt used in manufactured products is sent to landfills and 22% of discarded cobalt is collected from scrap markets and the remainder degrades for other scrap markets. The importance of cobalt is due that its excellent performance combinate with lithium and other metals for energy storage and conversion, which has been classified as a critical metal, especially for energy demand [5].

Cobalt is generally considered complementary and its extraction is associated with the extraction of raw materials such as copper (~55%), nickel (~35%), and arsenic [6,7]. A small part of cobalt metal is from the Bou Azzer mine (Morocco) [8], the cobalt mine in Ontario (Canada), the Black Bird district in Idaho (EE.UU) [7]., and the Mount Cobalt mine (Australia) [9].

The purpose of this document is to present a geochemical, geological, and mineralogical review of the major cobalt-bearing deposits, including a market, resource, and reserve analysis. The main producers of cobalt and its processing are mentioned. In addition, the circular economy is addressed through the recovery of cobalt through the recycling of secondary sources, such as batteries and metallurgical waste.

2. Cobalt Demand

In 2016, a greater demand for cobalt was registered in 98.000 tons (three times more than in 2000 [10]. Globally during 2021, cobalt metal demand grows by about 22%, due in huge proportion to electromobility and storage of chemical energy [11]. In 2021, due to the accelerated production of electric cars, the demand for cobalt increased by about 63% for the use of lithium-ion batteries as a specific component. The use of cobalt in energy storage based on the nickel-cobalt battery is compared to 25% of $LiFePO_4$ battery demand [12-14].

3. Cobalt metal market

The main exporters of cobalt minerals and their concentrates in 2020 were (i) the Democratic Republic of the Congo (US$145M), (ii) Austria (US$6.61M), and (iii) Turkey (US$2.99M). In the same year, the main importing countries of Cobalt Minerals and Concentrates were (i) China (US 113M), (ii) Morocco (US 26.2M), and (iii) the United Arab Emirates (US 8.86M) [15]. On the other way, the principal companies that produced cobalt chemicals estimated that 42% of the cobalt consumed was used in the fabrication of super-alloys, and the production of gas turbines; about 9% in cemented carbides; about 16% in other metallic applications, and 33% in chemical applications, estimated in $340 million of cobalt consumption [16].

4. Cobalt use

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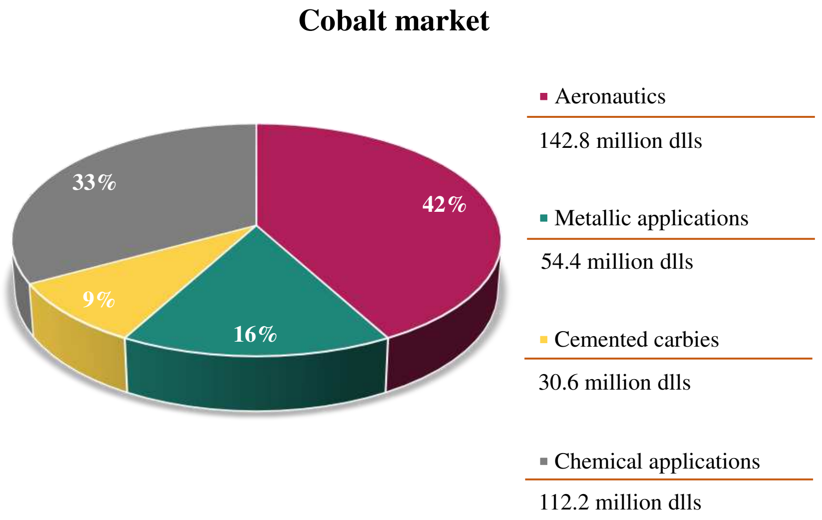
[1]

The use of cobalt is due to its excellent properties such as (i) ferromagnetism, (ii) hardness, (iii) resistance to corrosion, and wear, (iv) high melting point, (v) multivalence, and (vi) interesting electrical conductivity [17].The first use of cobalt metal and cobalt minerals were for the pigmentation of (i) ceramics, (ii) glass, (iii) paints, and (iv) jewelry.At the moment, many chemical industries consume significant amounts of cobalt for the production of paints and inks, additionally, this industry also extends to the manufacture of (i) dryers, (ii) tires, and (iii) catalysts [18]. According to the USGS, cobalt is used mostly for superalloys used for the manufacture of engine parts, on the other hand, cobalt magnetic alloys are used in the manufacture of wear-resistant materials such as (i) cemented carbides, (ii) diamond tools, (iii) alloys and (iv) magnets [19]. Darton Commodities Ltd. in 2020 mentioned that cobalt superalloys are also used as materials in aerospace and marine equipment and the medical sector used for (i) prosthetics, (ii) vitamin B12, (iii) tumor detection, (iv) cancer radiotherapy, and (v) sterilization. Finally, in the energy sector is used small rechargeable batteries, where 50% of the cobalt production is used in the manufacture of batteries for (i) laptops, (ii) smartphones, and (iii) tablets, as well as electric vehicles such as (iv) electric bicycles, (v) cars (electric and hybrid) and for the development of renewable energies technologies, represented in Figure 1 [20].



340 million dollars generated by the productions of cobalt in 2021 in the USA

Figure 1. Cobalt market and its different applications.

Figure 2 provides a comparison of global cobalt production in 2020 versus 2021. The main reason for the increase in the production in existing operations lies in the fact that there is a greater supply of raw materials, however, the new production and restarts in said suspended operations also contribute to this supply. According to Kovacheva-Ninova et al. The DRC (Khinshasa), remains the world's leading source of mined cobalt, supplying approximately 70% of world production. Most cobalt is extracted as a by-product of copper or nickel mineral processing, except for production in Morocco. China is the world's largest producer of refined cobalt, the major part of which is produced from refined cobalt imported from the Congo. In this way, China is crowned as the world's main consumer of cobalt metal, with more than 80% of this consumption used in the rechargeable battery industry [17].

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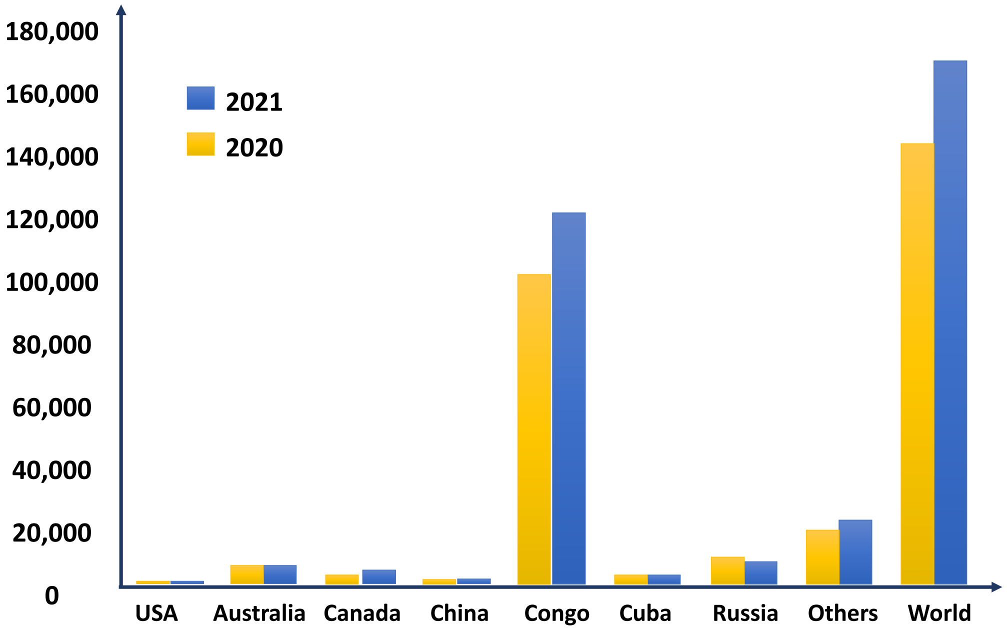


Figure 2. World cobalt production in 2020 and 2021.

5. Cobalt geochemistry

Cobalt is a brittle, silvery, shiny grayish transition metal. It is surrounded on the periodic table by iron and nickel, which show similar physical properties. In nature, cobalt is found only in the form of radioactive isotopes such as Co^{59}, but the most common is Co^{60}. The ionic radius for Co^{2+} and Co^{3+} are 0.72 Å and 0.63 Å, respectively. On heating, it is first oxidized to Co_3O_4 and then, above 900 °C, to CoO [21].

The ion Co^{2+} is stable in an acidic solution in the absence of complexing agents, but is readily oxidized to Co^{3+} in an alkaline solution or, in any solution, in the presence of complexing agents; Co^{3+} has a high affinity for complex formation. According to Donaldson et al. under oxidizing conditions, cobalt shows a strong tendency to concentrate with manganese oxides [22]. During the weathering of mafic and ultramafic rocks, manganese and cobalt oxides tend to accumulate in the upper levels of a deposit, while nickel moves downward with magnesia and silica to form laterites [22,23]. Cobalt is a common element in the Earth's crust, averaging close to 17.3 ppm [24]. which ranks it as the No.33 element in terms of crustal abundance [21]. Cobalt is found in relatively high concentrations in mafic and ultramafic igneous rocks as shown in Table 1. The Ni/Co ratio decreases from ultramafic to acidic rocks because nickel enters the lattice of early crystallizing magnesium silicates more easily than cobalt. On the other hand, the Cu/Co ratio increases globally from ultramafic to acid rocks (Donaldson & Beyersmann, 2005)[22]. In sedimentary rocks, cobalt is mainly distributed in the clayey fraction and appears to follow Fe and Mn (Carr & Turekian, 1961)[25], varying amounts of cobalt depending on the rock type, i.e. a mean cobalt content of 19, 0.3, and 0.1 ppm for shales, sandstone, and carbonates respectively [26].

Table 1. World average concentrations of cobalt in some igneous, sedimentary, and metamorphic rocks.

Rock type	*Co content (ppm)*	*Ni/Co ratio*	*Cu/Co ratio*	*Reference*
Igneous rocks Ultramafic	**200**	**10**	**0.1**	[27]
Dunita	108.6	21.5	0.2	[28]
Pyroxenite	55.2	8.1	5.1	[28]
Serpentinite	115.1	18.2	0.7	[28]

Mafic	45	3.6	2.2	[27]
Gabbro	51	2.6	-	[22]
Basalt	41	2.5	-	[22]
Diabase	47	1.6	2.3	[27]
Intermediate igneous rocks	10	5.5	3.5	[27]
Felsic	5	1.6	4	[27]
Granite	47	0.4	5.4	[27]
Shales	19	3.6	2.4	[27]
Sandstone	0.3	6.7	1	[27]
Carbonates	0.1	200	1	[27]
Metamorphic rocks	40	-	-	[25]
Quartzite	0.3	-	-	[25]

Pure Cobalt does not exist in nature, but cobalt is present as an essential component in some 66 minerals, as recorded in the RRUFF database of the International Mineralogy Association (IMA) and as a minor or trace component of several hundred others, particularly those containing nickel, iron, and manganese [29]. Cobalt can sometimes be found in cheap concentrations in olivine, spinel, and chlorite in lateritic and hydrothermal deposits [7].

By comparison, nickel and copper are essential elements in more than 160 and 710 minerals, respectively [29]. This relative scarcity of cobalt-only minerals is explained by their chalcophile and siderophile properties, which is a consequence of the fact that cobalt's charge and ionic radius are very similar to those of the more common mineral-forming elements, such as iron, nickel, and manganese, therefore, it is easier to incorporate as a minor element in abundant rock-forming minerals than to isolate it in its species [30,4].

6. Mineralogical properties of cobalt.

6.1. Cobalt mineral.

The most common primary cobalt ores currently extracted are cobalt sulfides (carrollite, cattierite, linnaeite) which represent the main source of cobalt in the Democratic Republic of the Congo, sulfarsenides (cobaltite) found in Zambia, Canada, and the United States, arsenides (skutterudite, enamelite) found in copper-cobalt ores in Ontario, Canada, and Morocco, and arsenates (erythrite) found primarily in the Bou Azzer deposit in Morocco. Primary cobalt ores less often mined include cobalt selenides like the trogtalite that was found at the Musonoi mine (Kolwezi, DRC) in association with various palladium selenides [31,32].

Secondary cobalt minerals result primarily from the alteration of primary cobalt-bearing phases by oxidative weathering, hydration, or other forms of alteration [30]. The most common cobalt oxide is heterogenite, a hydrated metal oxide that has a variable copper-cobalt composition. Heterogenite, which contains cobalt in the oxidizing states of Co^{2+} and Co^{3+}, is responsible for the majority of cobalt in weathered Cu-Co SSH deposits [33,34].

Another common cobalt oxide mineral is asbolane, a hydrated cobalt-manganese nickel ore that is the source of most cobalt in laterite deposits in New Caledonia [35]. In the laterite deposits of New Caledonia [35] supergene zones of the CAC sulfide deposits [34] and ferromanganese crusts of the Magellan Seamount Cluster [36]. Lithophorite is an oxide of manganese consisting of sheets of bonded MnO_6 octahedrons alternating with sheets of $(Li, Al)(OH)_6$ octahedrons with a crystallographic structure very similar to that of the asbolane with which it is often associated tightly [35].

Llorca & Monchoux et al. concluded that asbolane and lithophorite may be final members of a continuous series [35]. Despite its name, which suggests that lithium is an essential component of lithophorite, its composition can vary and non-lithium varieties can contain significant concentrations of Cobalt [37]. Cobalt-rich lithophorite is considered an important host for cobalt in Western

Australian laterites [38], while cobalt-rich lithophorite has been reported from New Caledonian laterites [39], as well as in the weathered Cu-Co SSH deposits of the CAC [34]. Cobalt carbonates (sphaerocobaltite, kolwezite) can occur in a primary phase crystallized from carbonate-rich solutions and in an alteration phase derived from primary cobalt minerals [30].

The Cobalt carbonates are found mainly in the supergene zones of Cu-Co sulfide ore deposits, especially in CAC [31,32]. where they have been misclassified as cobalt-rich dolomite. Hydrous carbonate kolwezite is a typical secondary cobalt ore in Cu-Co SSH deposits in the DRC, especially Musonoï Principal, Kamoto, Mupine, and Mashamba West mines . In addition to the production of cobalt from the aforementioned cobalt ores, cobalt can be extracted from other ores in which cobalt has been substituted, including arsenopyrite, pyrrhotite, pyrite, pentlandite in magmatic Ni sulfides, oxides (limonite, goethite), clays (nontronite) in Ni laterites, and carbonates (malachite, dolomite) in Cu-Co SSH deposits [22,40].

7. Geology and cobalt resources

7.1. Cobalt geology and type of mineral deposit

The Cobalt mineralization is typically found in Cu-Co sulfide or oxide minerals, Ni-Cu magmatic sulfide minerals, or Ni-Co laterites. Although the level of detail reported in the literature varies, cobalt is known to be present in many types of deposits. Slack et al. defined 8 main types of terrestrial deposits. This review primarily discusses the 3 main types of deposits from which cobalt is commercially mined on a large scale: Cu-Co deposits hosted in stratiform sediments, Ni-Co laterites, and Ni-Cu-Co sulphide magmatic deposits [40].

7.2. Cu-Co deposits hosted in stratiform sediments

Cobalt amounts of this type (SSH) are mainly confined to the adjacent regions of the DRC and Zambia in the Central African Copper Belt (CAC), which hosts the highest concentrations of copper and cobalt in the world. Cobalt is present in the siliciclastic and carbonated sedimentary rocks as well as in the mafic volcanic and plutonic rocks of the supracrustal sedimentary succession of Katagan, which are placed in a continental fault [45].

In Zambia, copper-cobalt deposits are hosted in para-native siliciclastic rocks. In the DRC, the main lithological units are dolomitic limestones and dolomite-rich shales, with deposits and host rocks forming thrust sheets within the Lufilian arc [46,47]. In general, there are three zones: a zone of weathered oxides that extends to a depth of between 70 and 150 m, followed by a zone of mixed oxides and sulphides, and a zone of sulphides that extends to depths greater than 250 m [48]. The weathering process is mainly observed in the DRC, where the effect of meteoric fluids has produced cobalt enrichment in the upper part of the weathered zone [4].

The most abundant oxidized cobalt mineral is heterogenite [4], whereas, at depth, cobalt is mainly present in the sulphide mineral carrolite [49]. The thickness of ore bodies varies from a few to several tens of meters, with variable cobalt content. Lateral zoning of metals in orebodies means that high cobalt and copper values do not necessarily coincide [50].

7.3. Ni-Co laterite deposits

The second most important class of deposits consists of middle to recent tertiary laterites, these are formed by deep tropical weathering of bedrock, during which certain elements are removed and others are enriched by supergenic processes [7]. Although these deposits primarily contain large amounts of nickel, substantial amounts of cobalt may be present [51]. There are three types of nickel-cobalt laterite deposits: (a) hydrated silicate deposits with an upper layer of oxide laterite, below which hydrated magnesium-nickel silicates occur on the lower saprolite, (b) nickel-cobalt laterite deposits clay silicate, where smectitic clays have developed on the middle or upper saprolite, and (c) limonite deposits, where altered bedrock is covered by iron oxyhydroxides, the type of laterite deposit that forms depend on the climatic conditions [52]. Cobalt is concentrated when primary sulfide and silicate minerals undergo chemical and physical changes associated with atmospheric leaching. Where laterites have developed on a substratum of mafic or ultramafic igneous rocks, nickel and sometimes cobalt are often concentrated in the weathered zone [41].

If the rocks are ultramafic, the concentration of Ni and Co may be as much as ten times greater than the original bedrock. Generally, the thickest layers of laterite with the highest concentrations of nickel, iron, and cobalt tend to occur where the bedrock is characterized by narrowly spaced joints. This geological feature promotes maximum groundwater circulation and fluid-rock interaction over time. High-grade laterites show topographic control and tend to occur below a hill or at the edge of a plateau or terrace, due to fluctuations in groundwater tables and surface erosion [53]. Stability in the geological conditions and a higher level of chemical weathering than physical erosion shall be required for the development of large nickel-cobalt laterite deposits [4].

7.4. Ni-Cu-Co sulphide magmatic deposits

Magmatic deposits are concentrations of nickel, copper, and minor platinum group metals (PGMs) and cobalt produced by high-temperature magmatic processes [54]. Of great importance for cobalt are mafic or ultramafic intrusions [41] and ultramafic volcanic flows, that is, komatiites [55]. Many deposits are conformal layers and lenses which occupy depressions at the base of host magmatic bodies. The deposits and their host rocks are the results of man-tle-derived mafic magmas that have assimilated sulfur from the crust [54]. The addition of sulfur from outside caused an immiscible sulphide to form, which was denser than the silicate melt, at the bottom of the magma chamber or the magma conduit [53,55].

The elongated lenticular masses and sulphide matrix breccia veins appear to be minerals that have undergone subsequent tectonic deformation and remobilization [7]. In general, nickel is the main economic product in magmatic deposits. Copper may be present as a co- or by-product, with cobalt as a minor by-product, and with platinum group elements in some deposits as by-products or even as a major product [7,41,56]. The main typical sulfide minerals that may be present in these deposits are pentlandite, chalcopyrite, and pyrrhotite. The cobalt grade generally varies between 0.04% to 0.08% [4].

7.5. Cobalt mineral resources and ore reserves

Table 2 summarizes the total reserves and mineral resources (measured + indicated + inferred) by deposit type based on data from a cobalt report published by the US Geological Survey [40]. This assessment of land resources, updated with the latest resource estimates from the relevant mining companies, is not complete, as many deposits are known to contain cobalt go unreported, but it does provide a good estimate of mineral resources and mineral reserves of current cobalt. It states that about 95% of the world's cobalt resources are contained in:

a) Cu-Co deposits hosted in sediments or stratified shale (~58%), found mainly in the DRC [40].

b) Ni-Co lateritic deposits (~29%) located in Australia, New Caledonia, and Cuba [40].

c) Magmatic deposits of Ni-Cu-PGE-Co (~9%) found in Australia, Canada, Russia, Finland, and the United States. Based on the current resource estimates based on a geological endowment, if significant seabed resources had been included in this evaluation, they would represent about 80 % of total cobalt reserves [40].

According to Table 2, the resource is approximately 154 Mt Co around the world, of which 121 Mt Co is derived from seabed resources. Total recoverable cobalt tonnage, calculated using an assumed cobalt recovery by deposit type, ranges from 15.9 Mt Co [42] to 34 Mt Co (Sverdrup et al., 2017) [44]. This difference is explained by the assumptions used in the two studies: the highest value was obtained assuming that technologies will be developed to convert oceanic cobalt deposits into resources [44], while the lowest value was based only on the extraction of cobalt from terrestrial resources. A summary of the main mineral deposits containing cobalt, including historic and active deposits, or some advanced exploration projects, is provided in Table 2.

Table 2. Total mineral reserves and resources from a selection of major cobalt-bearing mineral deposits, active mines, or exploration projects [20,40,42,43]. .

Operation name	*Type of deposit*	*Country*	*Tonnage (Mt)*	*Co grade (%)*	*Co (kt)*
BOSS Mining	SSH	DRC	75	0.2	150
Comide	SSH	DRC	53	0.2	106
Etoile	SSH	DRC	21	0.4	88
KCCd	SSH	DRC	574	0.51	2908
Musonoi	SSH	DRC	32	0.9	289
Mutanda	SSH	DRC	918	0.39	3584
Mutoshi	SSH	DRC			300
Ruashi	SSH	DRC	33	0.3	100
Tenke Fungurume	SSH	DRC	1015	0.29	2919
Sotkamo	SSH	Finland	1525	0.02	290
Boleo	SSH	Mexico	424	0.05	221
Bornite	SSH	USA	182	0.02	35
Iron Creek	SSH	USA	4	0.24	12
Konkola (KCM)	SSH	Zambia	12	0.34	42
Mopani	SSH	Zambia	361	0.08	289
Nova-Bollinger	Magmatic	Australia	24	0.07	16
Fortaleza de Minas	Magmatic	Brazil	10	0.2	21
Santa Rita	Magmatic	Brazil	159	0.02	24
Raglan	Magmatic	Canada	46	0.07	31
Sudbury (Glencore)	Magmatic	Canada	69	0.04	28
Sudbury (Vale)	Magmatic	Canada	61	0.03	19
Thompson	Magmatic	Canada	39	0.09	35
Voisey's Bay	Magmatic	Canada	55	0.09	49
Jinchuan	Magmatic	China	515	0.02	98
Kevitsa	Magmatic	Finland	286	0.01	30
Sakatti	Magmatic	Finland	44	0.05	20
Noril'sk area	Magmatic	Rusia	1309	0.06	785
Nkomati	Magmatic	South Africa	302	0.02	60
Kabanga	Magmatic	Tanzania	58	0.2	116
Eagle	Magmatic	USA	4	0.067	4
Murrin-Murrin	Laterite	Australia	332	0.08	261
Musgrave	Laterite	Australia	25	0.07	151
Owendale	Laterite	Australia	16	0.12	20
Ravensthorpe	Laterite	Australia	535	0.03	149
Sunrise	Laterite	Australia	101	0.12	129
Barro Alto	Laterite	Brazil	86	-	-

Jacaré	Laterite	Brazil	185	0.19	352
Niquelandia	Laterite	Brazil	56	0.06	34
Vermelho	Laterite	Brazil	148	0.05	74
Musongati	Laterite	Burundi	150	0.09	135
Nkamouna	Laterite	Cameroon	391	0.22	860
Cerro Matoso	Laterite	Colombia	95	0.1	95
Moa Bay	Laterite	Cuba	89	0.12	110
Cyclops Ni-Co	Laterite	Indonesia	37	0.11	41
Sorowako	Laterite	Indonesia	116	-	-
Ambatovy-Analamay	Laterite	Madagascar	251	0.08	201
Goro	Laterite	New Caledonia	323	0.11	355
Ramu	Laterite	Papua New Guinea	175	0.1	175
Agata	Laterite	Philippines	45	0.05	23
Berong	Laterite	Philippines	18	0.08	15
Mindoro	Laterite	Philippines	315	0.06	189
Rio Tuba (Coral Bay)	Laterite	Philippines	57	0.012	69
Taganito/Adlay	Laterite	Philippines	123	0.012	146
Çaldag	Laterite	Turkey	37	0.05	119
Olympic Dam	Hydro & volc	Australia	605	0.02	121
NICO	Hydro & volc	Canada	64	0.012	74
Kylylahti	Hydro & volc	Finland	8	0.012	10
Rompas-Rajapalot	Hydro & volc	Finland	4	0.04	2
Bou Azzer (district)	Hydro & volc	Morocco	45	1.5	686
Blackbird (district)	Hydro & volc	USA	16	0.74	124
Idaho Cobalt Operation	Hydro & volc	USA	5	0.55	31

DRC, Democratic Republic of the Congo

USA, United State of America

7.6. Secondary Cobalt Resources

Recent changes in cobalt prices have been worrying due to the availability of long-term supply, with only 10% of cobalt being produced as a primary product, plus cobalt mining supply is a near monopoly as the DRC accounts for 70% of the world's cobalt extraction [20]. According to Huang et al. [57] cobalt is a key element, and new sources of raw material from the recycling of spent metallurgist waste and cobalt compounds must be considered as demand for its products continues to grow rapidly. In addition, some batteries can be used to obtain valuable metals such as Ni, Mn, Cu, rare earth, and Co. This includes extraction and recovery, the battery that is most used for these kinds of processes are Li ion batteries, Cd-Ni metal Hydrema or NiMnMHn Batteries [58]. Table 3 shows case studies that some researchers have developed for the recovery of cobalt from different types of waste.

Table 3. Case studies for the recovery of cobalt from waste.

Type of waste	*Leaching reagents*	*Extractant*	*Conditions*	*Co species extracted*	*Extraction*	*Reference*
Lithium ion battery(LIB)	**Glycine (0.5 M), Absorbic Acid (0.02)**	-	**80° C, 360 min**	**Co (II)**	**95%**	[59]
Cathode materials for lithium ion batteries	Choline Chloride Citric Acid DES	LIX 984 / Aliquat 336	40° C, 60 min	Co (II)	81%	[60]
Used Lithium Ion Batteries For Mobile Phones	Sulfuric acid and hydrogen peroxide	Cyanex 272 dissolved in kerosene	75° C, 90 min	Co	97-99%	[61]
Lithium ion battery(LIB)	-	Di-(2-ethylhexyl) phosphoric acid (D2EHPA)	80° C, 360 min	Co	90%	[62]
Nickel-metal hydride (NiMH) batteries	NaOH y Na_2SO_4	Cynaex 272	70° C, 60 min	Co	98%	[63]
Used Ni-Cd Batteries	H_2SO_4	Adogen® 464	80° C, 360 min	$Co(OH)_2$	100%	[64]
Used NiMH Batteries	-	Cyanex 301 Solvent 70 (Statoil)	23°C, 10 min	Co	79.60%	[65]
Used NiMH Batteries	Di-2-ethylheixl phosphoric acid (D2EHPA)	-	50° C, 15 min	Co (II)	3,7 g/L	[66]

Every day, there are more companies recycling thousands of tons of battery waste every year, where the process used majority is pyrometallurgical to recover critical metals such as Co and Ni, from its metal alloys [67]. The most important companies are expressed in Table 4.

Table 4. Main recycling companies for exhausted batteries.

Company	*Location*
Umicore	Belgium
Xstrata Nickel	Canada
Accurec	Germany
Inmetco	USA
S.N.A.M	France
Sony-Sumitomo	Japan

USA, United State of America

8. Cobalt processing

8.1. Recovery of cobalt from nickel-cobalt ores

Moats & Davenport et al. [68] discuss that Ni and Co are commonly found together as oxides (laterites) or sulfide minerals, considering that their processing is complex mainly due to Co presence [68]. Derived from the above, each type of mineral is processed differently, according to Morcali et al. [69] the interest in Ni laterite deposits, which are produced by weathering and generally formed of serpentinites, has increased because of the scarcity of nickel sulfide minerals [69]. These minerals change their composition according to the depth of where they are found [70]. In the case of saprolite, it is found to be deeper and has a lower Fe content and a higher Mg content; it is produced by pyrometallurgical means to produce ferronickel [68]. On the other hand, limonite is found at a lower depth, has high Fe and low Mg content, and is usually processed by hydrometallurgical means [68]. The extraction of Ni and Co from limonitic laterites through the pressure acid leaching process has increased relevance in recent years, for this reason, Georgiou & Papangelakis et al. carried out a mineralogical analysis using transmission electron microscopy (TEM) of the laterite [71]. Limonite was obtained from pressure leaching with sulfuric acid, finding that the dominant phase in limonite is goethite and that Co was associated with the Mn phase that was rich in Ni, concluding that both Co and Ni were highly leachable in the Mg structures to which they were associated [71].

Based on the above, Ribeiro et al. [72] carried out a study to determine the influence of Ni-bearing minerals in three different laterite samples, during their extraction treatment through a sulfation-roasting-leaching process, to do this they used various characterization techniques such as diffraction of X-rays (DRX), scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and chemical analysis by atomic absorption spectroscopy (AAS). These researchers observed that quartz and hematite are present in the main phases in all the samples. They were able to detect that sulphuric acid was reacting mostly with serpentines and oxides in the analyses carried out after sulfation [72]. The results indicated that the best recovery of Ni and Co metals is when the content of Mg is lower obtaining 93 and 91.9 % respectively. Finally, another factor associated with low recovery rates was the existence of amorphous silicate associated with Ni [72].

As previously mentioned, Ni-Co lateritic ores are commonly processed by the hydrometallurgical route, according to Kursunoglu et al. [73]. The principal process is currently (i) high-pressure acid leaching (HPAL), (ii) atmospheric acid leaching (AL), and (iii) heap leaching (HL) are applied, they mention that each process has its advantages and disadvantages. The HPAL method provides high Ni and Co recovery and consumes little acid solutions (generally sulfuric acid), the AL method requires less capital as it consumes less energy than the HPAL process, and has similar recoveries. The HL method is the most economical mineral processing, but it provides a lower recovery of Ni and Co than the other processes mentioned. These researchers applied the AHP (Analytic Hierarchy Process) technique in the mentioned leaching methods to determine the most appropriate method to leach Ni and Co, where the software results showed that the HL method was the most appropriate for lateritic ore [73].

For laterite leaching processes, the use of organic acids has recently been studied such as sulfuric acid (H_2SO_4, 1 mol/L), combined ascorbic acid ($C_6H_8O_6$, 4 g/L), obtained a solid-liquid ratio of about 1/10 to leach a Ni-Co laterite during 4 hours operation, achieving the extraction of 99% Co and 98% Ni, respectively [74]. These researchers mentioned that possibly the high dissolution rates were achieved because $C_6H_8O_6$ may play a role as a goethite dissolved, liberating Ni [74].

Some lateritic minerals with high content of goethite (FeO(OH)) may become resistant and costly to process, moreover, their refractoriness can be attributed to the fact that laterites are minerally fragile and therefore a mixture of limonite ($FeO(OH)\cdot nH_2O$) and saprolite ($Al_2(OH)_4$) (Li et al., 2013)[75]. Li et al. studied the effect of thermal pretreatment to increase the percentage of Ni and Co recovered by slow-leaching limonite mineral to evaluate the effect of roasting on the recovery of Ni and Co. The previous result has attributed the heat treatment that releases the Ni from the crystalline structure of the iron oxide during the dehydroxylation of the goethite (FeO(OH). Finally, they concluded that a high extraction yield of Ni and Co is obtained by mixing roasted and unroasted minerals decreasing the cost of the mineral process [75].

Morcali et al. [69] have proposed treating a mixture of limonitic and saprolitic laterite minerals, which have a certain refractoriness, through a smelting process using borax as a flux, to separate the

Ni and Co from the mineral and produce a Ni matte with a lower melting point. When they used 12.7% borax, they recovered 65 and 74% of Ni and Co respectively, however, when they added 5g of sulfur and 0.8g of coke in addition to borax, the recoveries improved to 98 and 95% respectively. Moreover, an alternative is to extract them and separate the Ni from the Co, when coexist in the sulfate media, however, some elements present in the solution, such as magnesium can interfere with the refining process. For this reason, some researchers required the ideal conditions to precipitate Ni and Co, and they used a suspension of magnesium oxide (nMgO: [nNi + nCo]) = 2.0, hydrolysis time of 2 hours, hydrolysis temperature of 60 °C, stirring speed of 350 rpm, and pH of 8.98, with these parameters they managed to obtain Ni and Co precipitations of 98.1 and 99.1 % respectively, and Mg of 0.2 %, which can be recycled [76].

In addition, the electrodialysis process has been studied to recover Co ions from an acid solution generated from laterite leaching evaluated this technique in a solution containing Co^{2+}, Mn^{2+}, Mg^{2+}, Cr^{3+}, and $SO_4^{=}$ ions, where these ions generate competition between it in the solution, however, a Co recovery was of more than 98% [77].

The treatment of Ni laterites was previously mentioned; however, the Co can also be found in Ni sulfides. Ni sulfide deposits are found typically as massive or disseminated sulfides, where most of the nickel is present in the mineral pentlandite, which is composed of approximately 36% Ni, 30% Fe, 33% S, and 1 % Co, respectively [48].

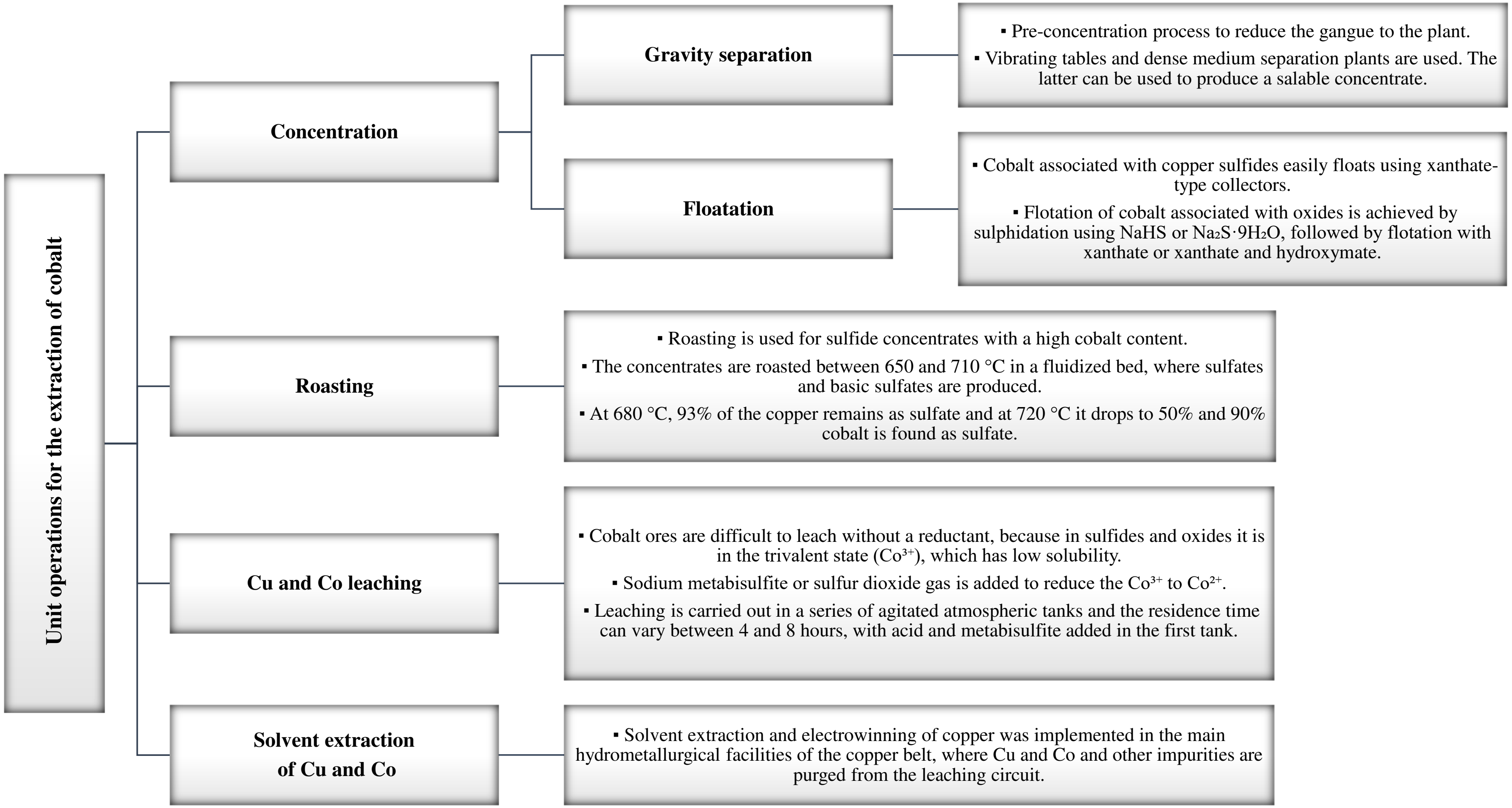
Another process that has been tested for Ni laterites was the one studied by Ilyas et al, which consists of roasting the mineral by applying a thermal reduction using coal and Na_2SO_4 as an additive, and subsequent ammonia leaching process. The following conditions are optimal conditions for the roasting process: 10% by weight of coal, 9% by weight of Na_2SO_4 for a time of 120 minutes at 800 °C, this is because, for the ammoniacal leaching process of the roasted ore, they determined that the best concentration of the $NH_4OH–(NH_4)_2CO_3$ solution was 150 g/L of total NH_3, however, they observed that this process is possibly influenced by the concentration of carbonates for the extraction of Ni and Co, where is, 90 and 67% recovery respectively [78].

In the sulfides treatment, the first step is the crushing process and then the flotation process. The smelting-leaching-electrorefining route is followed [57,68]. As a result of the above, other minerals containing nickel and cobalt are released from pentiteland when crushing it, in addition to pyrrhotite, chalcopyrite, and gangue. In the case of foam flotation, this is implemented in two stages; First, the froth flotation material is processing for to separate Ni, Co, and Cu from pyrrhotite and gangue. Subsequently, the Ni-Co concentrate is melted to obtain a matte with a high Ni-Co and low Fe content. This process can be implemented in a flash or electric furnace [48]. Immediately, the molten material is leached by heap leaching, with NH_3 solutions, in sulfate or chloride mediums [48]. Other studies, give up very good results, where the use of glycine in alkaline leaching at pH 10 generate a low-grade Ni sulfide mineral and high acid consumption, these researchers managed to obtain a solution of 83.5% Ni and 76.3% Co after 672 hours of leaching. Finally, the refining of nickel and cobalt can be carried out by some techniques such as solvent extraction, electrowinning, or hydrogen reduction [79].

8.2. Recovery of cobalt from copper-cobalt ores

Another source from which cobalt is extracted is Cu-Co ores. According to Crundwell et al. the African copper belt located in the DRC is the largest Cu province in the world. In 2018, 60% of the Co produced contained ore of copper, whereas approximately 5000 million tons correspond to 3.3% which generates 185 million tons of Cu and Co as a by-product. On the other hand, 60% of refinery production is carried out in China. In the RDC, the processing of Cu and Co is in two ways: (i) the hydrometallurgical process, where copper cathodes and partially purified cobalt hydroxide ($Co(OH)_2$) are obtained, and (ii) the metal refinery, where the $Co(OH)_2$ is dissolved and produces a cobalt cathode through electrochemical techniques [48].

Crundwell et al. mention that in the copper industry, valuable minerals are divided into two types: sulfides, main ones are chalcopyrite ($CuFeS_2$) and covellite (CuS) and oxides, mainly carbonates and hydroxides such as malachite ($Cu(OH)_2 \cdot CuCO_3$) and heterogenite (CoO(OH)). As far as Zambia is concerned, minerals are often more sulfurous and also composed of oxides within the DRC. For sulfurous minerals, it is possible to recover these by floatation and oxide mineral extraction via leaching as well as solvent extraction. A diagram of unit extraction operations for Co is shown in Figure 3 [48].



Gravity separation

- Pre-concentration process to reduce the gangue to the plant.
- Vibrating tables and dense medium separation plants are used. The latter can be used to produce a salable concentrate.

Floatation

- Cobalt associated with copper sulfides easily floats using xanthate-type collectors.
- Flotation of cobalt associated with oxides is achieved by sulphidation using NaHS or $Na_2S \cdot 9H_2O$, followed by flotation with xanthate or xanthate and hydroxymate.

Roasting

- Roasting is used for sulfide concentrates with a high cobalt content.
- The concentrates are roasted between 650 and 710 °C in a fluidized bed, where sulfates and basic sulfates are produced.
- At 680 °C, 93% of the copper remains as sulfate and at 720 °C it drops to 50% and 90% cobalt is found as sulfate.

Cu and Co leaching

- Cobalt ores are difficult to leach without a reductant, because in sulfides and oxides it is in the trivalent state (Co^{3+}), which has low solubility.
- Sodium metabisulfite or sulfur dioxide gas is added to reduce the Co^{3+} to Co^{2+}.
- Leaching is carried out in a series of agitated atmospheric tanks and the residence time can vary between 4 and 8 hours, with acid and metabisulfite added in the first tank.

Solvent extraction of Cu and Co

- Solvent extraction and electrowinning of copper was implemented in the main hydrometallurgical facilities of the copper belt, where Cu and Co and other impurities are purged from the leaching circuit.

Figure 3. Unit operations for Co extraction (Adapted from (Crundwell et al. [80]).

According to Ntakamutshi et al. [81] during the leaching of Cu-Co ores, the Co is found as Co^{3+} by the addition of sodium metabisulfite ($Na_2S_2O_5$) to reduce Co^{3+} to Co^{2+}, respectively. The $Na_2S_2O_5$ is the most recommended reducing agent used in the process, However, it can hurt Cu recovery and cause concerns about the environment if it is present in very high quantities in the leach solution. This occurs because, during the leaching process, the $Na_2S_2O_5$ reacts with H_2SO_4 to form SO_2 which reduces the Co^{3+} to Co^{2+}. Nevertheless, in the leach liquor, it is largely carried away and causes problems such as those described above [81].

In the case of oxide minerals, the leaching process with sulfuric acid has been studied. Clotilde Apua & Madiba studied the kinetics of the Cu and Co dissolution of an oxide composed mainly of malachite, which contained 10.07% Cu and 0.71% Co. They found the following optimal leaching conditions: a 0.77 M H_2SO_4 solution, pH=1, t= 60 min, and T= 70 °C, respectively. Their experimental data were adjusted to a controlled mixed mechanism and they determined that the reaction order was the Gompertz kinetic model [82].

As for the intermediate product of the metallurgical processing of Cu ores and Co oxide such as CoO, Co_2O_3, and Co_3O_4 present in the Cu-Co alloy Zhang et al. implemented a selective dissolution process, where mixed particles of the Cu-Co alloy with Mg as impurities were kept in a temperature range of 700 °C to 900 °C for 0.5 to 2 h, obtaining an Mg-Cu alloy. Then, the application of a vacuum distillation process improves to obtain Cu metal with 80% purity, recovering the Mg for recycling, therefore these researchers propose this method as an alternative for the treatment of Cu-Co alloys [83]. According to Dehaine et al. [18] the progressive depletion of the mineralization of Cu-Co oxide minerals, sulfide ore has begun to be extracted in deep areas. However, these minerals are composed of sulfides and oxides that are extremely hard to treat during the flotation process. The method currently used to treat this type of mineral are (i) sulfide flotation, and (ii) flotation of oxides using controlled potential sulphidation [18].

This method, however, is inefficient because the gangue composed mainly of dolomite and magnesite constitutes a large proportion of the mineral, and these compounds are inhibitory to flotation. In this sense, Dehaine et al. proposed an interesting treatment for this type of mineral such as (i) sulfur flotation at neutral pH, and (ii) acid reverse flotation (pH 4.5 to 5). The reverse flotation was implemented using a mixture of phosphoric acid (H_3PO_4) and sulfuric acid in a 4:1 ratio, and the global recoveries of Cu-Co are between 93.5% and 85.1% respectively [18].

Another method that has been studied for the treatment of Cu-Co ores was presented by Zhang et al. The process considered a roasted of the mineral with ammonium chloride (NH_4Cl) at 300 °C, with NH_4Cl and mineral ratio of 1:2 for 3 hours. The intermediate component that was formed is $Co(NH_3)_6CuCl_5$. The roasted material was leached at pH 7 (adjusted with NH_3) to later precipitate the Cu and Co by adding ammonium bicarbonate (NH_4HCO_3) at 60 °C for 40 minutes recovering 90% of Cu and 95% of Co, respectively [84].

8.3. Recovery of cobalt arsenides from Morocco

One more source for the recovery of Co is from arsenides deposits since there are minerals such as safflorite ($CoAs_2$), and skutterudite ($CoAs_3$). But there is little of that mineral, and currently, only the Bou Azzer mine in Morocco produces cobalt as its main product [85]. Gienberg et al. implemented a bioleaching and Leptospirillum ferriphilum (DSM14647) supplemented with citric acid ($HOC(CH_2CO_2H)_2$), using a mineral that contains (i) loellingite, (ii) safflorite, and (iii) skutterudite [85].

A plasma mass spectrometer (ICP-MS) found the presence of a nickel-(sulfur)-arsenide, visualizing that Ni and Co had a different behavior before leaching, where the recoveries of Co is about 35% and grow up to 92% using $HOC(CH_2CO_2H)_2$ [86]. Johnson et al. [86] verify if the oxidative bioleaching could be implemented using acidophilic microorganisms in an acid medium using arsene, and arsenide sulfide ores as $CoAs_3$. Two different minerals from Iron Mask (Canada) are the deposits of Ag-Co with carbonate (CO_2^{-3})structures, and Bou Azzer (Morocco) where the deposits have Co-Ni- Fe with sulfoarsenides, gold sulfides occluded in quartz carbonates, the Co contained in the Fe

Mask ore was leached faster compared to the mineral from Bou Azzer, however, they were able to recover cobalt despite having a lower concentration in the ore [86].

Table 5 shows some of the cobalt industrial processes developed by various companies around the world.

Table 5. Industrial processes of cobalt.

Company	*Total production, t*	*Location*	*Project type*	*Reserves, Mt*	*Grade, Co*	*Products*	*Reference*
Kamoto	23,900	Lualaba, DRC	Subterranean mine	26,6	0,54 %	Copper and cobalt	[87,88]
Tenke Fungurume	15,440	Lualaba, DRC	Open sky	176,8	0,30 %	Cu cathode and Co hydroxide	[87,89]
Metalkol RTR	10,500	Haut-Katanga, DRC	Tailings	-	-	Co hydroxide and metallic Co	[87],90]
Etoile	7,000	Katanga, DRC	Open sky	648,046	0,35 %	Copper and cobalt ore	[87,91,92,93]
Luiswishi	5,390	Katanga, DRC	Open sky	12,4	0,95 %	-	[87]
Ruashi	5,090	DRC	Open sky	5,5	0,2 %	Co hydroxide	[94]
Lubumbashi Slag Hill	4,000	DRC	-	-	-	Co alloy and Zn oxide powder	[87]
Mutoshi	4,000	DRC	Surface mining	-	-	-	[95]
Cuba's Moa Bay	3,370	Cuba	Open sky	-	-	-	[87]
Papua New Guinea's Ramu	2,940	New Guinea	Open sky	-	0.09 %	Co and Ni metal concentrate	[96]
Murrin Murrin Mine	2,900	Australia	Open sky	145	0,085%	Cobalt and nickel	[97,98]
Ambatovy	2,860	Madagascar	Open sky	152.1	-	Co concentrates	[99]
Polar Division	2,700	Russia	-	-	-	-	[87]
The Phillipines Taganito	2,550	Philippines	Open sky	-	-	Mixed nickel-cobalt sulfide	[99]
Morocco's Bou-Azzer	2,420	Morocco	-	-	-	-	[87]

t, ton
DRC, Democratic Republic of the Congo
Mt, Millions of tons

9. Cobalt recycling

At present, the major mining industries have a challenge adjusting to the circular economy, mainly in creating sustainable processes that combat the change climate caused . The literature has been developed and discussed the concept (i) life cycle, closed-loop models, (iii) remanufacturing, (iv) product reuse, and (v) waste management although none have in-depth discussions [100, 101].

Secondary sources that contain Co include (i) catalysts waste, (ii) magnets, (iii) superalloys, (iv) carbides, (v) rechargeable batteries, and (vi) other waste metallurgical by-products [102]. The recovery of Co from catalyst materials is by a hydrometallurgical process. Hydrometallurgical routes often require a pretreatment process such as (i) calcination, (ii) pre-oxidation, (iii) roasting, or (iv) washing before dissolution [103]. Pretreatment will significantly increase the rate of catalyst leaching since coke and other particles that can reduce contact between acid and reactive components in catalysts have been reabsorbed. Among various acids, H_2SO_4 is the most efficient leaching agent as reported by Hamza et al [104].

Critical metals such as Cu, Ni, and Co are extracted from e-waste and inorganic solutions [105]. HNO_3 in low concentrations and at room temperature is used to oxidize Cu contained in electronic waste, but this methodology has important limitations. It is not possible to process the resulting solution directly by electrical means, and it must therefore be essentially converted into CuS/CuS_2 via additional processes [106].

The high production of electronic equipment has increased the manufacture of lithium batteries. The pretreatment of Co, Cu, Ni, and Li was obtained in an acid solution; due to the similarities in the chemical properties between Co and Ni, is a challenge. The Cl^- ion has a positive and significant effect in the extraction of Co using methyltrioctylammonium chloride (MTOAC, $C_{25}H_{54}NCl$), where the extraction results of purity are close to 98% and 97.7%, respectively [58,107].

5. Conclusions

Cobalt is generally accompanied by other metallic minerals and its extraction is associated with other primary materials such as copper, nickel and arsenic. Its processing and refining is due to its excellent properties such as its ferromagnetism, hardness, resistance to corrosion and wear, high melting point, conductivity and interesting electrical properties. Within the energy sector, it has gained great importance and is used in the manufacture of batteries, laptops, smartphones, tablets and electric vehicles such as electric bicycles, cars (electric and hybrid) and for the development of renewable energy technologies. . Geologically, it is common to find it in areas of weathering in mafic and ultramafic rocks, where manganese and cobalt oxides mineralize in the upper levels of a deposit, while nickel tends to mineralize in areas where there is a higher concentration of magnesium and silica to form laterites. Sometimes cobalt can be found in low concentrations in olivines, spinels and chlorite, also in lateritic and hydrothermal deposits. Secondary cobalt minerals result primarily from the alteration of primary cobalt-bearing phases by oxidative weathering, hydration, or other forms of alteration. The most common cobalt oxide is heterogenite, a hydrated metal oxide that has a variable copper-cobalt composition. Heterogenite, which contains cobalt in the oxidizing states is responsible for most of the cobalt in weathered Cu-Co deposits, whereas, at depth, cobalt is mainly present in the sulphide ore carrolite. As mentioned above, Ni-Co lateritic ores are commonly processed by the hydrometallurgical route. The main process currently is high pressure acid leaching, atmospheric acid leaching and heap leaching, they mention that each process has its advantages and disadvantages. For sulphide minerals, it is possible to recover them by flotation and extraction of oxide minerals by leaching and solvent extraction. However, from the point of view of the expectations of an increase in the supply of cobalt for the coming years, there are latent risks, derived both from the high degree of concentration of production in the DRC and from the political instability of the country, existing the probability of a conflict breaking out that paralyzes part of the exploration and exploitation, therefore, the part of processing and benefit could be affected. Derived from the above, it is important to look for alternative sources for the recovery and extraction of cobalt, such as batteries and metallurgical waste, since today it is important to promote the circular economy.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, X.X. and Y.Y.; methodology, X.X.; software, X.X.; validation, X.X., Y.Y. and Z.Z.; formal analysis, X.X.; investigation, X.X.; resources, X.X.; data curation, X.X.; writing—original draft preparation, X.X.; writing—review and editing, X.X.; visualization, X.X.; supervision, X.X.; project administration, X.X.; funding acquisition, Y.Y. All authors have

read and agreed to the published version of the manuscript." Please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

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