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COBALT PERSPECTIVES

Cobalt, a transition metal with particular physico-chemical properties, is a key critical element playing an important role in the global decarbonization process with particular regard to batteries, special alloys and catalysts. The present article aims at a concise update concerning main current and future uses, production, reserves, and recycling prospects.

Cobalt has been in use for millennia as a source of brilliant pigments and today its different applications greatly contribute to develop a sustainable blue planet: Co catalysts constituted around 3% of demand in 2021 with a metal value estimated around US$ 260 million [1].

Cobalt occurs in a widespread and dispersed form with an estimated content of the earth's crust around 0.002%. The metal is brittle, hard, silvery-white, corrosion resistant, and exhibits a bluish tint once polished. Physical properties depend on the purity and the allotropic form, which is close-packed hexagonal at room temperature with transition to face-centered cubic at 417 °C. It remains ferromagnetic up to 1121 °C and has a high melting point at 1493 °C. When heated, it is oxidized to the mixed Co (II, III) oxide (Co_3O_4) but Co (II) oxide (CoO) is the end-product at temperatures above 900 °C [2].

It belongs to group VIIIB of the periodic table and the electronic configuration of the atom ground state $[Ar]3d^7 4s^2$ leads to valency (Co^{2+}) by removal of the two 4s electrons: its partially filled d orbital d^7 is the reason for the outstanding catalytic activity. The $Co^{2+} \rightleftharpoons Co^{3+}$ interconversion in the spinel structure of Co_3O_4 depends on the redox conditions and is important in many applications, including the uses as catalyst [3].

Unlike other commodity metals, trading of cobalt on the London Metal Exchange (LME) began only in correspondence of the demand acceleration which occurred during the last thirty years, and since 2010 the LME started a regulated market for spot and future contracts. However, the pricing mechanism remains opaque due to market concentration and vertical integration of the supply chain [4].

The Cobalt Institute (CI) - Guildford (London), UK - established in the 1950s as a private organization, is a non-profit trade association representing the entire industry and value chain: its members are producers, users, recyclers, and traders altogether covering about 80% of the global market [5].

The present note aims at a concise update about uses, production, market, and reserves.

Uses

The productive chain of cobalt subdivides end products into "metal" and "chemicals". Metal with purity over 99.3 wt% is used for lithium-ion batteries, metallurgy, and permanent magnets; the chemicals include cobalt oxide, hydroxide, acetate and are mainly utilized for the manufacturing of batteries, catalysts, and pigments [6].

In 2022, the total cobalt demand rose to 187,000 tons, up by 21,000 tons from 2021; in 2010 it was around 70,000 tons. Batteries account for 72% of the demand and the metal properties help to increase life, stability and corrosion resistance so that cobalt containing chemistries represent a majority share. Electric (EV) and hybrid vehicles, smartphones, and portable computers depend on the energy produced by chemical reactions in rechargeable batteries. After becoming the largest end use sector for cobalt in 2021, EV gained further share rising to 40% of the total market [7]. Battery types lack standardization and cobalt contents vary between 10-30 wt% [8]: the lithium-nickel-manganese-cobalt oxide (NMC) cathodes are the main drivers of demand although the composition is being modified towards substitution for pricing reasons. Therefore, long-term forecasts should be treated with caution due to ongoing technological

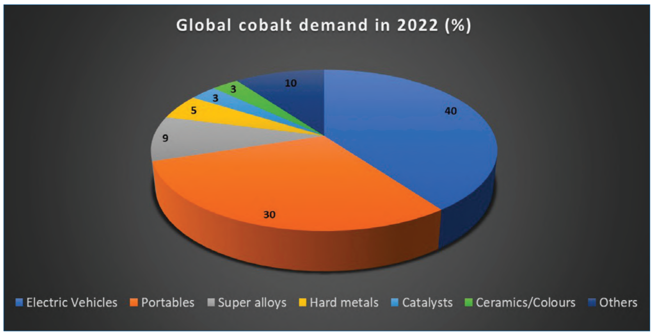

Fig. 1 - Global cobalt demand, in % (from Cobalt Market Report 2022, Cobalt Institute, May 2023)

advancements especially concerning energy density and operational reliability. In 2022, the portable electronics sector contributed with 30% of the market, while super alloys (i.e., high stability alloys employed in aerospace, nuclear power, and turbines) are the largest "traditional" sector with 9% market share. Hard metals (cutting tools, mining, drilling), catalysts, magnets, and ceramics/pigments complete the products list (Fig. 1) [9].

Considering the megatrends for transportation and energy technologies, the market is expected to expand significantly in the mid-term with EV being the dominant sector, followed by energy storage and superalloys [10].

Cobalt's important catalytic activity is displayed in several fields of homogeneous (*e.g.*, synthesis of terephtalic acid, di-methyl terephthalate, isophtalic acid, adipic acid, and hydroformylation) and heterogeneous catalysis [mainly hydrotreatment (HDT) and Fischer-Tropsch synthesis (FTS)] [11-13].

Cobalt-catalyzed reactions represent the largest group of homogeneous liquid phase oxidations in the chemical industry. Major product is terephtalic acid (TPA), a precursor in the production of polyester for textiles, recyclable plastic bottles, and packaging. Population growth and increasing per-capita consumption for polyester fibers are prominent growth factors and in 2021 TPA output was 78 million metric tons [14]. Direct liquid phase catalytic oxidation process of *p*-xylene with air in presence of cobalt and manganese acetates with acetic acid as solvent is the prevailing industrial process since the mid-1960s. Operating temperatures and oxygen pressures are 190-205 °C and 15-30 bar with *p*-xylene conversion higher than 98% and selectivity to crude TPA at 95% [15]. Catalyst recovery rates are higher than 98% and it is estimated that global cobalt consumption for homogeneous catalysis was over 3,000 metric tons in 2022.

Catalytic hydrotreating (HDT) is a key process in the petroleum refining industry. It concerns the conversion and removal of organic sulfur, nitrogen, oxygen, and metals from petroleum crudes at high hydrogen pressures accompanied by hydrogenation of unsaturates and minor cracking of high molecular hydrocarbons [16]. Sulfur is the most abundant heteroatom impurity: its content generally varies between 0.1 wt% and 4 wt% and must be reduced to a few parts per million. HDT industrial capacity has been growing steadily due to crude quality, downstream processing requirements, and environmental standards for fuels. Development started from the cracking and hydrogenation processes in the 1930s and the market is expected to expand in the decade despite the progress of electric mobility. A reaction scheme is the following:

$$\text{R-SH} + H_2 \rightarrow \text{R-H} + H_2S$$

where R represents a hydrocarbon chain. Main variables and process parameters are feedstock type, reaction temperature, pressure, liquid hourly space velocity (LHSV), and H_2/Oil ratio, all differing according to the fraction. For example, temperature and pressure vary from 250 °C and 10 bar for naphtha up to 400 °C and 120 bar for vacuum gas oil. Catalysts choice is determined by specific activity, side reactions, pressure drop, and regeneration procedure: for some systems the optimum solution involves several types of catalysts in composite beds. In the case of hydrodesulfurization (HDS) cobalt and molybdenum are the most common couple of active elements and the composition is usually 8-16 wt% Mo and 1-4 wt% Co on a γ-alumina support [17]. Cobalt promoter atoms are present on the edges of the MoS_2 slabs and facilitate the formation of sulfur vacancies by weakening the interaction with adsorbed H_2S. Deactivation factors are sintering and decomposition of the active phase, fouling, coking, and metal sulfides deposits. The lifetime is 1-3 years and the volume of spent HDS catalyst is estimated to be 120,000 tons per year with a cobalt content around 2400 tons [18].

Fischer-Tropsch Synthesis (FTS), a process dis-

covered in Germany in the 1920s, concerns the production of liquid hydrocarbons and chemicals from synthesis gas (CO and H_2) and is facing one of its recurrent revivals linked to oil price spikes [19]. Global current productive volume is around 700,000 barrels per day and remains tiny compared to the total crude oil production.
The process is simplified by the following reaction:

$$CO + 2H_2 \rightarrow -CH_2- + H_2O$$

The main products include a wide range (C_1-C_{70+}) of hydrocarbons, primarily *n*-alkanes, linear olefins, *iso*-alkanes and cyclic hydrocarbons. The exothermic reaction can be operated in high and low temperature modes. The first is catalyzed by iron-based catalysts at 320-350 °C to produce gasoline and linear low molecular mass olefins; the second utilizes cobalt catalysts at 200-250 °C to synthesize high molecular mass, linear waxes. Reaction pressure is 30-40 bar and overheating adversely affects product selectivity and catalyst lifetime [20].
A stepwise carbon chain growth process on the catalyst surface explains the FTS product distribution and the key role of catalyst choice. Co-based catalysts contain 15-30 wt% cobalt, 1-10 wt% structural oxidic promoter (ZrO_2, La_2O_3), and 0.0-0.1 wt% reducibility promoter (Pt, Ru, and Pd) on a high surface area support (*e.g.*, SiO_2, TiO_2, Al_2O_3). After preparation the catalyst usually contains cobalt in an oxidic form that must be activated by reduction to metallic state [21].
Several deactivation mechanisms are possible: fouling by carbon deposition, sintering, and poisoning (*e.g.*, by S, Cl, Mg, Na). The high cost of Co catalysts requires intermediate regeneration steps and total lifetime depends on reactors type, operation conditions, and proprietary process details. Best longevity standards reach 5 years and yearly cobalt consumption for FTS catalysts is estimated above 100 metric tons.
Novel sectors of cobalt-based catalysts are related to sustainable energy and environmental applications [22].

Production & market

The global mined cobalt supply rose to 198,000 metric tons in 2022, up by 21% on a yearly basis; its production was just above 100,000 metric tons in 2012. Large multinational and local companies dominate the business, although price and scarcity are kindling the rush of artisanal mining (ASM) [7].
Pure cobalt is not found in nature and is mainly obtained as a by-product of copper and nickel, whose prices determine the level of cobalt extraction. Even the best ores offer only low concentrations of the element: the Central African Copperbelt typically contains about 0.3 wt% Co and 3 wt% Cu, whereas nickel sulfide ores content is about 0.01-0.15 wt% Co and 1.5-3 wt%. Today, the majority of Co is produced as a by-product of Cu production, with 20 wt% as a by-product of Ni mining, and 8 wt% from either Cu or Ni operations: only about 2 wt% is derived from specific cobalt mines [23].
The element shows siderophile and chalcophile tendencies and commercially exploited minerals are sulfides and arsenides such as carrollite $CuCo_2S_4$, cobaltite CoAsS (Fig. 2), linnaeite Co_3S_4, and skutterudite $(Co,Ni)As_3$, which are commonly associated with the iron sulfides, pyrite, arsenopyrite and pyrrhotite [24].
Both open-pit and underground mines are operative. The first is typical for low-grade ores and is generally low-cost, the second necessitates capital intensive operations justified by higher grade ore. After extraction the ore undergoes usual comminution by crushing and grinding and the extraction

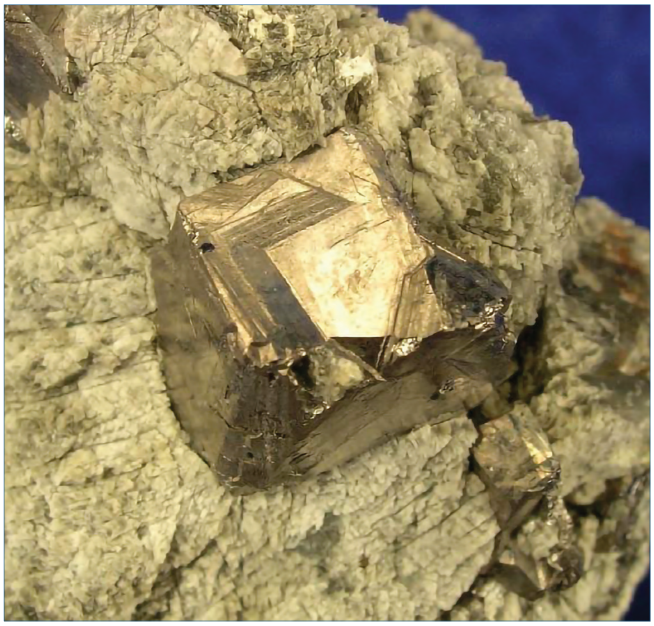

Fig. 2 - Cobaltite crystals from the Sudbury District (Canada). Photograph by R.M. Lavinsky, distributed under a CC-BY 3.0 license

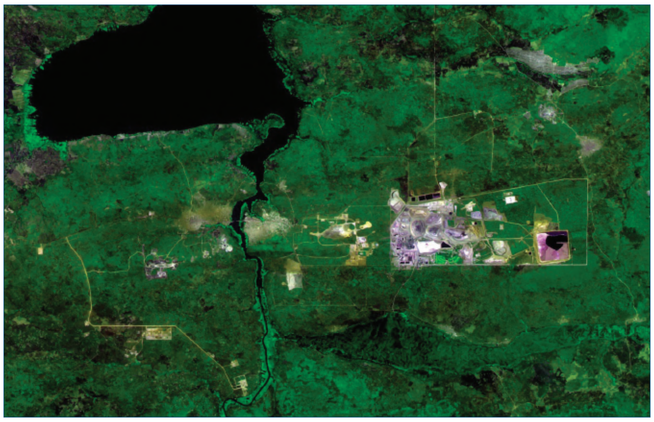

Fig. 3 - Satellite image of the Mutanda mine in Congo in 2018. Image by O. Barros (DSR/OBT/INPE) from www.dsr.inpe.br distributed under a CC-BY 3.0 license

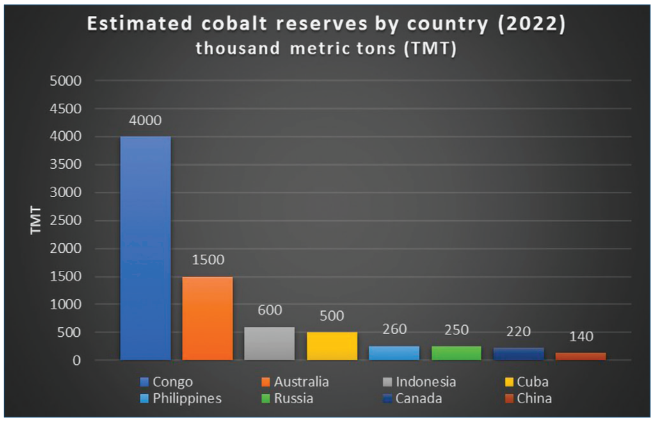

Fig. 4 - Cobalt reserves in thousand metric tons (from U.S. Geological Survey, Cobalt, Mineral Commodity Summaries, January 2023)

procedures vary according to the associated metal, whose market price and recovery efficiency affect overall profitability. Hydrometallurgical, pyrometallurgical, vapor-metallurgical, electrolytic processes, or combinations of them are used. Sulfide ores are treated via a combined froth flotation-pyrometallurgical route while for oxide ores a hydrometallurgical route (leaching-solvent extraction-electrowinning) is preferred. Cobalt recovery only takes place as last step after the primary metal extraction and concentration: final electrowinning of 99.95% pure cobalt is done from chloride or sulfate solutions [25].

Congo is the major producing country with 73% of global output in 2022 and the metal is the most important national export product after copper [26]. Recovery from copper ores began in 1924, and the country has been one of the world's largest producers ever since (Fig. 3). Once, about one-third of the export went to Belgium for further processing; nowadays, many operations are fully or partially Chinese-owned and a share of ASM around 20-30% poses severe environmental and social challenges [27]. The ore deposits consist of an upper layer of carbonates and hydroxides and a lower layer of sulfides.

The second productive country, Indonesia, follows distantly with a rising 5% share and a considerable Chinese infrastructure. Refining occurs mainly in China, with about 76% of worldwide activities in 2022, followed by Finland with 10%, and only 1% in the major producing country. China is also the world's leading consumer, with about 80% of its consumption used by the rechargeable battery industry for EV development. Currently, Europe accounts for 2% of mined and 12% of global refined cobalt and the shares are unlikely to change substantially. Reserves are reckoned to be around 8.3 million tons with Congo and Australia holding the main shares at 4.0 million tons (48%) and 1.5 million tons (18%) respectively. New mining and processing projects were recently started in Indonesia, ranking third with 0.6 million tons (7%) and with the potential to modify the mining distribution in the next years. Resources at a multimillion tons scale have been theoretically identified on the ocean floor: although sporadically quoted among the reserves, their exploitation remains unaccomplished (Fig. 4) [28].

Similarly to other critical elements, a restricted burn-off time of around 40 years (defined as the ratio between known reserves and average annual mining rate at the current consumption rates) can be calculated: in 1994 the ratio was over 200 years. Model curves for production indicate that maximum output of known reserves is being reached [29] and the commodity is subject to sharp price variations (*e.g.*, peaks in Q1 2018 and Q1 2022). Since mining and refining suffer a relevant concentration which could potentially threaten a sustainable demand, the supply risk is reputed high: Japan (1984), the European Union (2010), and the US (2018) included the metal within the respective critical materials lists [30].

Recovery & sustainability

Price volatility, geopolitics, and environmental issues drive the recovery of the metal. However, recycling plays a minor role: in 2022, secondary production only accounted for around 5% of total supply, with a weak rise in the last years. Process scrap from the manufacturing of cells accounts for the 74% of the pool, with only 26% from end-of-life materials [7]. In the future, scrap volume and primary production deficits might lead to notable growth; nowadays, integrated concepts are still to be implemented despite the regional legislative focus. In Europe, the regulation for collection and recycling of batteries dates to the EC Directive 2006/66 and was reinforced by the EU battery Regulation 2023/1542 [31, 32].

Batteries, scrap metal, and spent heterogeneous catalysts constitute the main end-of-life source, since the use as pigment is dispersive, while homogeneous catalysts, superalloys, and hard alloys are recycled within the specific industrial sectors. The product lifespan is a primary factor in recycling rates: lithium-ion batteries last 3-8 years in electronic devices, and 8-10 years in EV. Such as for other metals, achieving a high collection rate of portable devices such as smartphones is challenging, and recycling should not be regarded as a stand-alone business but rather as a closed-loop model encompassing every critical resource. Furthermore, every EV requires between five and fifteen kilograms of the metal, roughly a thousand times the amount in smartphone batteries, but specific recycling is lengthy, complicated, and safety-concerned, albeit more than 80% of the contained valuable substances is recoverable [33]. Techniques are based on the cobalt industry infrastructure with both pyrometallurgical and hydrometallurgical processes [34]. Emerging options, such as the bio-hydrometallurgical process, are reported for batteries and catalysts, but need further advancement before shift to a commercial scale. Spent heterogeneous HDS catalysts are treated for the recovery of valuable metals (Co, Mo, Ni, V) and many companies operate with proprietary techniques, but volumes are low with respect to the global business [35]. Intersectoral methods are being investigated: for example, the preparation of cobalt-manganese-acetate as homogeneous catalysts for the synthesis of terephthalic acid by hydrometallurgical recovery of Co and Mn from spent battery cathodes represents an interesting option [36].

The recycling process presents meaningful geographical differences, depending on the scrap pool: however, even in China, the world's largest EV market, the share of recycled cobalt is limited to 7% [37-39].

Cobalt derives its name from the German word Kobold -goblin-: in the footsteps of its eponym, the element is playing an ever-increasing role in the future of a sustainable society but only an efficient recycling phase will be able to maintain its attractiveness for green technological innovations.

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Cobalto: prospettive

Il cobalto, metallo di transizione dalle particolari proprietà fisico-chimiche, è un elemento chiave critico che svolge un ruolo importante nel processo globale di decarbonizzazione, con particolare riguardo alle batterie, alle leghe speciali ed ai catalizzatori. Il presente articolo si propone di fornire un sintetico aggiornamento sui principali usi attuali e futuri, produzione, riserve e prospettive di riciclo.