

REVIEW

Exposure to cobalt metal (without tungsten carbide) and some cobalt compounds: a literature review

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ABSTRACT

Cobalt is a natural metallic element with extensive applications across multiple industries, and a critical metal for lithium-ion battery production. Cobalt's only known biological function is its role as a metal component of vitamin B12. Other cobalt compounds have been described as toxic to the environment and the human body following excessive exposure. The International Agency for Research on Cancer (IARC) has classified cobalt, including cobalt metal and soluble cobalt(II) salts, as Group 2A, meaning it is probably carcinogenic to humans. This review aims to present a comprehensive overview of historical and current sources of cobalt in diverse exposure settings, along with its various intake routes. An extensive literature search was conducted between September 2021 and January 2022, analysing over 300 publications. The primary goal of these studies was to identify cobalt sources, intake routes, and exposure pathways. Workers may be exposed to various cobalt compounds and metal powders primarily through inhalation, but

exposure can also occur via skin contact or ingestion. For the general population, food typically arises as the predominant source of cobalt exposure. Furthermore, exposure may occur through ambient air, tobacco smoke, and medical implants.

KEYWORDS: exposure pathways, human health, dietary intake, environment, industry.

1. INTRODUCTION

Cobalt is a natural metallic element of group VIII of the periodic table, specifically the first-row transition metals [1]. It is a hard, silvery grey and ductile metal element, exhibiting chemical properties that closely resemble those of iron and nickel, which are also part of group VII. [2]. Cobalt exists in different valence states depending on its form. Metallic cobalt, which is widely used in various metal alloys, is present in the 0-valence state. Cobalt in compounds predominantly exists in two oxidation states (+2 and +3 valence states). From these, Co^{2+} is the most commercially and environmentally available. [1]. Further information on cobalt mining and production can be found elsewhere. [1]. Cobalt has extensive applications across multiple industries, including cutting and grinding tools manufacturing, pigments, paints, coloured glass, medical implants, and electroplating, and its role is increasingly significant in lithium-ion battery production (Figure 1). [3]. Lithium cobalt oxide batteries, which contain about 89 per cent cobalt, are used in mobile phones, laptops and cameras. Lithium nickel-manganese-cobalt oxide batteries, which typically contain between 9 and 31 per cent cobalt, are used in e-bikes and electric vehicles. (<https://www.bgs.ac.uk/news/cobalt-resources-in-europe-and-the-potential-for-new-discoveries/>)

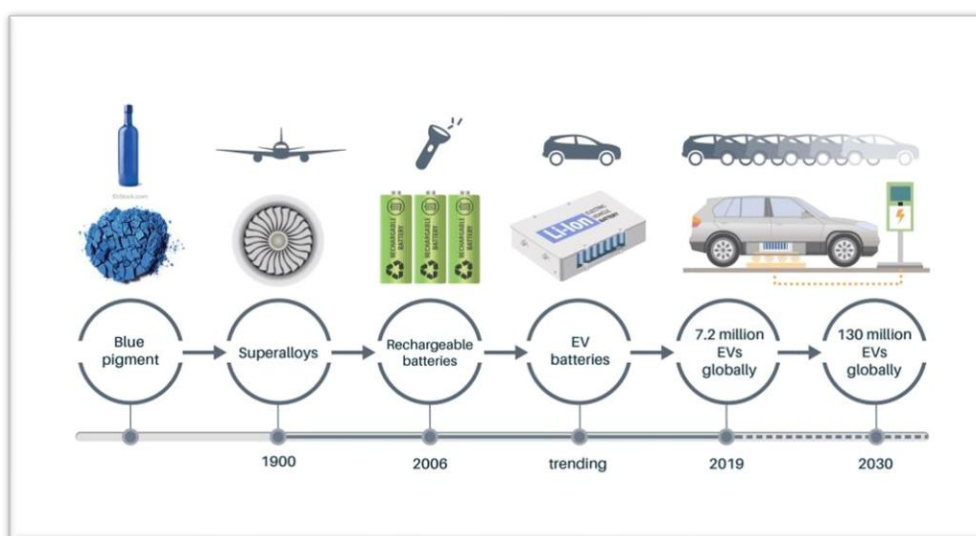


Figure 1 — Cobalt: industrial uses timeline. The main application of cobalt has evolved throughout history, progressing from being utilized for pigments to superalloys and, more recently, to batteries. Some future forecasts predict a global electric vehicle fleet of at least 130 million electric vehicles by 2030. Source: <https://www.bgs.ac.uk/news/cobalt-resources-in-europe-and-the-potential-for-new-discoveries/>. Image: BGS © UKRI.

Since 2013, consumption has been increasing by over 5% annually, primarily due to the demand for cobalt in lithium-ion battery production. [4] Europe is a significant consumer, predominantly for use in batteries, nickel-based alloys, and tool materials, accounting for approximately 25% of global consumption in 2020. Cobalt's only known biological function is its role as a metal component of vitamin B12, also named cyanocobalamin [5]. Other cobalt compounds have been described as toxic to the environment and the human body following excessive exposure. [2, 6]. The International Agency for Research on Cancer (IARC) has classified cobalt, including cobalt metal and soluble cobalt(II) salts, as Group 2A, meaning it is probably carcinogenic to humans. [1] This review aims to provide an overview of historical and current sources of cobalt in various exposure settings, as well as the intake routes. Some information gaps are highlighted.

2. MATERIALS AND METHODS

A thorough literature search was conducted between September 2021 and January 2022 that aimed to meticulously identify studies focused on cobalt sources, intake routes, and exposure pathways. The exhaustive search was performed across the PubMed and PubChem databases, employing a carefully defined set of keywords. The inclusion of studies in this review was determined based on their quality, taking into account aspects such as study design, methodology, and the comprehensive reporting of results.

3. RESULTS

3.1. Sources

In this review, the sources were grouped into the following categories: (1) industry, (2) environment, (3) diet and (4) tobacco, cosmetics and other products.

Industry

For centuries, cobalt ores have been used as blue colourants in the production of glass and pottery. However, it wasn't until the 20th century that the metal itself found various industrial applications. Cobalt combined with tungsten carbide creates a strong metal, which has proven invaluable in manufacturing high-strength steel. Cobalt is also used as an element in alloying and is a valuable source for chemical production. Specific cobalt alloys find applications in dental materials, surgical implants, bone replacement, and repair. Cobalt salts are predominantly employed

as pigments in the glass, ceramics, and paint industries, as well as catalysts in the petroleum industry, paint driers, and trace metal additives in agriculture and medicine. [1]. Cobalt chloride has also been associated with the construction industry. [7].

Environment

Cobalt is a naturally occurring element that can be found in various environmental components, including rocks, soil, sediment, surface and groundwater, and even in the air. Although it is usually undetected in drinking water, trace amounts of cobalt can be measured in lakes, spring water, groundwater, and well water, typically ranging from a few $\mu\text{g/L}$. In soil, cobalt concentrations usually range from 1 to 50 mg/kg and are often in the form of cobalt(II). [8]. In the atmosphere, cobalt is mainly associated with soil particles that become airborne. In unpolluted areas, atmospheric cobalt levels are usually below 2.0 ng/m³. [2, 8]. However, human activities like mining, smelting, coal combustion, and vehicular traffic have increased the levels of cobalt and its compounds in the environment.

Diet

Trace elements may be present in food naturally as minerals and may originate from environmental contamination derived from agricultural practices (e.g., pesticide residues) or food processing and packaging. [9]. When examining data on food prepared as consumed by the general population, the highest average concentrations were found in chocolate, butter, coffee, shellfish, nuts, vegetables (such as spinach and sweet potato leaves), and ice cream. [2, 9-10].

Tobacco, cosmetics and other consumer products

A few studies have highlighted the release of cobalt from electronic devices, including rechargeable batteries, flat panel displays, LCD computer monitors, and laptops [1-2, 11-12]. The element was also detected in leather goods, jewellery, coins, and various household items [1-2, 11-12]. It can also be found as an impurity in cosmetics [13-14]. Furthermore, cobalt, among other trace elements, has been identified in tobacco smoke [15].

3.2. Exposure pathways

Occupational exposure

Workers are most likely to be exposed to cobalt through inhalation of dust, fumes, or mists, making the respiratory tract the main route of occupational exposure. [16]. Various organizations have suggested occupational exposure limits for numerous hazardous substances, including cobalt, to minimize potential health effects. Specifically, exposure limits have been established for inhalable dust fractions in the air of work environments. [1]. Industries involved in hard-metal production, cobalt powder production, cobalt-containing pigment and drier use, battery production and

electronics recycling are most vulnerable to occupational exposure, with welders, dental technicians, and machinists being the most exposed groups. [1].

Skin exposure to metallic cobalt has been reported in various industrial and construction settings, with several studies documenting hypersensitivity to cobalt chloride among construction workers. [17-18]. Inadvertent ingestion by workers due to hand-to-mouth contact is also a potential route of occupational exposure. Nonetheless, the lack of data limits our understanding of the role of ingestion in overall occupational exposure to cobalt. [1]

Exposure of the general population

Figure 2 summarises the main environmental cobalt exposure pathways to humans.

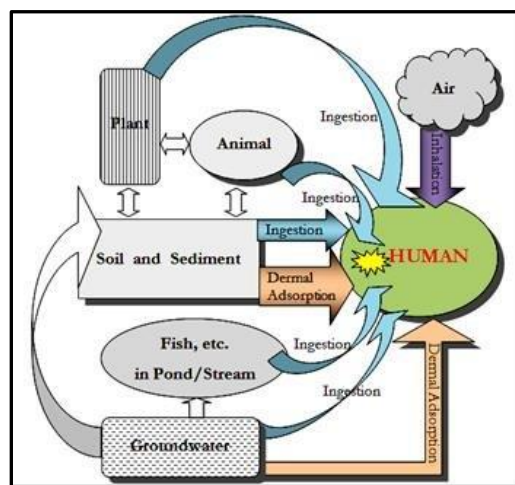


Figure 2 — Exposure pathways of trace elements, including cobalt, to human beings in the environment.

Dietary exposure

For the general population in non-polluted areas, dietary intake, estimated as ranging from 3–40 mg cobalt/day, represents the primary source of cobalt exposure. [1, 3, 9, 10]. Cobalt has no known nutritional purpose except as a component of vitamin B12. Humans obtain their required dietary vitamin B12 from animal products (such as milk, cheese, butter, meat, poultry, and eggs) unless the animal lives in a region lacking in cobalt. [1]. Microflora does not provide a significant amount of the vitamin B12 humans need. [19]. Biomagnification of cobalt up the food chain does not occur. [20-21]. The cobalt content in vitamin B12 varies between 4.4% and 5.8% and represents only a minor fraction of total cobalt intake. [21-22]. In addition to traditional dietary sources, people may deliberately ingest cobalt in the form of cobalt-containing energy drinks and supplements, used by consumers interested in healthy living practices with the aim of stimulating endogenous erythropoietin biosynthesis, and fat and carbohydrate metabolism. [1-2, 23-24]. Cases have been reported of intentional consumption of high doses of vitamin B12 through supplements (at a daily intake of 600 µg for three months). [25]. According to the European Food Safety Authority, the use

of cobalt(II) chloride hexahydrate for nutritional purposes as a source of cobalt in food supplements has raised safety concerns. It relates to the higher bioavailability of cobalt from cobalt(II) chloride compared to other inorganic cobalt compounds such as cobalt oxide. Currently, there is no established safe recommended dietary allowance for cobalt intake. [1]

Environment Exposure

Due to its widespread occurrence, humans can be exposed to environmental cobalt through various pathways, such as inhaling ambient air, drinking water, and consuming food grown in contaminated sites. [26 – 29]. Studies have shown that food crops, vegetables, fruits, and wild fish may uptake trace metals from contaminated soils in mining or smelting areas, which can contribute significantly to cobalt intake. [28-29]. Moreover, contaminated soil and dust ingestion is also a significant exposure pathway for humans, even at low cobalt levels, due to the potential for long-term exposure. [28-30]. When cobalt is in the solid phase, such as in soil or dust, it is distributed between highly soluble and exchangeable fractions and less reactive residual mineral phases. This distribution controls its mobility and determines the uptake extent in the human body. Bioavailability based on the form of exposure (soluble versus insoluble) has been identified as a significant factor influencing exposure to cobalt metal and its alloys and compounds. [1, 31]. Airborne particulate matter is a complex mixture of solids or liquids with varying masses, sizes, shapes, surface areas, chemical compositions, acidities, and solubilities. The origin of these particles plays a crucial role in determining their size (aerodynamic diameter), chemical composition, atmospheric transport, and potential to cause health issues when inhaled. Particulate matter with an aerodynamic diameter of 0.1 µm or less - referred to as PM0.1 (ultrafine) particles - are believed to be highly toxic due to their ability to absorb various hazardous substances like cobalt due to their large surface areas. Upon inhalation, these ultrafine particulates can penetrate deep into the circulatory system via the respiratory tract and impact various body organs. [1]. Indoor-settled dust containing cobalt may also be a significant source of exposure, especially since people spend most of their time indoors in places like homes, workplaces, and schools. [31]. Although the mechanism of cobalt permeation through human skin is not well-documented, skin contact with contaminated soil, water, or other earth materials can also increase exposure. [31-33]. Various regulations and guidelines have been set up for different environmental matrices to minimize the general population's exposure to cobalt. [1]. One example is the European Union (EU), which has set emission limit values for cobalt in waste gases generated by particular industrial activities. [1]

Exposure from medical devices

Medical devices, including orthopaedic implants, prosthetics, and stents made with cobalt-containing alloys, are a new source of exposure to cobalt. Metal-on-metal implants are primarily made up of cobalt (more than 34%) and chromium (20-28%), along with small amounts of other

metals like molybdenum and nickel [1-2]. There is some concern about the potential carcinogenic effects of metal wear or corrosion of these medical devices, which can cause metal debris and ions to spread throughout the body [2, 5, 34]. Increases in cobalt ions in serum, urine, and red blood cells of patients with metal-on-metal devices have been widely reported. [1-2]. However, based on current studies, it is unclear whether this increase correlates with implant wear. [1].

Although safety data on cobalt-containing alloys, such as those used in medical devices, were excluded from a European Chemicals Agency evaluation, European Medical Device Regulations require that medical devices containing > 0.1% w/w of cobalt are appropriately labelled with a justification for the use of the substance. [1].

Exposure to tobacco, cosmetics and other consumes products

Exposure to carcinogens can occur through both deliberate and accidental inhalation of tobacco smoke, making it a significant concern. [1, 15]. While other elements in tobacco smoke are more commonly associated with health issues, the presence of cobalt may also contribute to the harmful effects of smoking. [15].

Cobalt is present in various items such as electronic devices, leather goods, jewellery, coins, household items, and cosmetics. Nonetheless, based on existing evidence, these exposure pathways are considered negligible about potential risks to human health. [12-14, 32].

4. CONCLUSION AND DISCUSSION

This review intended to provide an overview of the most important sources and pathways of exposure to cobalt and cobalt compounds.

Cobalt has uses in metal alloys, dental materials, surgical implants, pigments, and lithium-ion batteries. Exposure to cobalt can be hazardous for workers who inhale its dust or come into contact with it through their skin or mouth. Industries involved in hard-metal work, pigments, and battery production are particularly at risk. Among those most vulnerable are welders, dental technicians, and machinists. In addition, some construction workers may exhibit hypersensitivity to cobalt chloride. Currently, limited information is available on accidental ingestion of cobalt-containing dust.

Cobalt is a naturally occurring element in rocks, soil, water, and air. Though not usually found in drinking water, trace amounts of cobalt can be measured in lakes, groundwater, and well water. However, human activities have increased cobalt levels in the environment where exposure to cobalt can occur through multiple pathways, including polluted air, water or food, and crops cultivated in contaminated regions. Long-term exposure can result from inhaling dust and soil contaminated by cobalt. The nature of cobalt in its solid phase, whether hosted by soluble or insoluble forms, influences exposure and risk to human health.

Trace elements such as cobalt can be present in food naturally or due to contamination from agriculture or food processing. Foods with the highest average concentrations of cobalt include chocolate, butter, coffee, shellfish, nuts, vegetables (such as spinach and sweet potato leaves), and ice cream. In unpolluted areas, cobalt exposure typically occurs through diet, with estimated intake ranging from 3-40 mg/day. Some individuals may consume cobalt intentionally through energy drinks and supplements.

Implants and stents made of cobalt-containing alloys are used in medical devices and can cause cobalt exposure. Metal-on-metal implants are mainly composed of cobalt and chromium, which may release metal debris and ions into the body. Patients with these devices have been observed to have higher levels of cobalt ions, but further research is necessary to establish a relationship with implant wear.

The element can be released from electronic devices, leather goods, jewellery, coins, and household items. It can also be an impurity in cosmetics and is present in tobacco smoke, which can exacerbate the negative impact of smoking.

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