RECOVERY OF COBALT FROM PRIMARY AND SECONDARY MATERIALS - AN OVERVIEW

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Abstract:
Introduction/purpose: Cobalt is a strategic metal for industrial application. Cobalt recovery from oxidic ores such as laterite and sulphidic ores, and from secondary materials during acidic treatment and precipitation is a highly used strategy ensuring different products such as cobalt hydroxide, cobalt oxide, and finally metallic cobalt.

Methods: Familiarity with cobalt behavior in hydrometallurgical processes such as dissolution at atmospheric and high pressure, precipitation, neutralization, filtration and hydrogen reduction is most important for cobalt recovery from ores and secondary materials. Pyrometallurgical methods such as roasting and flash smelting are applied for the treatment of sulphidic ores combined with solvent extraction and electrolysis in order to obtain cathodic cobalt.

Results: Powders of nickel-cobalt hydroxide were obtained from ores using sulphuric acid under high pressure in an autoclave and after precipitation with MgO. Solvent extraction was used to separate cobalt from nickel. The final step of cobalt recovery from a solution is using electrolysis. Cobalt and cobalt compounds such as cobalt carbonate and cobalt hydroxide can be obtained from secondary materials in hydrometallurgical operations.

Conclusion: Hydrometallurgical and pyrometallurgical processes are mostly applied for cobalt recovery from primary ores (oxidic and sulphidic
compounds) and from secondary materials (cemented tungsten carbide, polycrystalline diamond blanks, and waste cathodic materials from lithium-ion batteries).

Key words: cobalt, hydrometallurgy, cobalt hydroxide, powder, recycling.

Introduction

Cobalt, an element with atomic number 27, is a ferromagnetic transition metal located between iron and nickel in the periodic table of elements. Because of its application in lithium-ion batteries, cemented carbides and catalysts, and high demands in future, cobalt belongs to critical metals. The latter has especially influenced several worldwide economies due to a rising demand for electric mobility and green energy buffering (Wang, 2006, pp.47-50). Future demand for cobalt is likely to increase - even the importance of cobalt recycling – not only because of cobalt positive influence on wear resistance and thermal stability of superalloys and cemented tungsten carbides but also due to its value and rising demand in the field of advanced alloys, entertainment electronics, and Li-ion battery technology.

Cobalt production processes are usually energy-intensive because cobalt often comes as a passenger in copper and nickel bearing ores and has to be refined and purified by the methods of successive solvent extraction, electrowinning, and/or precipitation, for instance (De Graaf, 1979, pp.47-65).

Another aspect of cobalt is the location of resources versus the location of production. In most cases, production sites are far from mines. For example, while large quantities of cobalt are mined in the Democratic Republic of Congo in the form of Coltan (columbite-tantalite, linked to conflict minerals) the metal is produced in China, Finland or Norway. Long supply chains and socioeconomic issues have already contributed to smuggling and armed conflicts connected to the value of cobalt in the past and present times (Wakenge et al, 2018, pp.497-522).

Cobalt is usually available in lateritic ores with approx. 0.1-0.2 % (Moskalyk & Alfantazi, 2002, pp.593-605). Processing of lateritic nickel ores was performed in an electrowinning process for metal winning. Studies on the kinetics of dissolution of the Nigerian lateritic soil in acid media including hydrochloric, nitric and sulphuric acids have been undertaken (Olanipekun, 2000, pp.9-14). The elemental and mineralogical characterization, the loss of mass on ignition, the moisture content and the pH value of material suspension in water were determined in order to study the content of nickel and cobalt with
impurities. The effects of the acid concentration, the process temperature, the stirring rate and the particle size on the dissolution rate were investigated. Experimental results indicated that laterite dissolution was greatly influenced by hydrogen ion concentration and the leaching data fitted a diffusion model.

Beneficiation of laterites to enrich cobalt, besides recovery of associated chromite, is not only important to countries totally devoid of nickel bearing sulphides but is also of a significance to other countries, since laterites account for a greater percentage of these metals in the world (Narasimhan et al, 1989, pp.425-429). Unfortunately, primary resources were highly treated in the last century and connected with environmental problems and high production costs. On the other hand, small amount of cobalt in primary ores and their very complex mineralogical and chemical compositions are the reason for using secondary materials in cobalt recovery. Therefore, recycling is a chosen strategy for metal recovery in contrast to traditional primary metallurgy (Stopić & Friedrich, 2016, pp.1033-1047). The recycling of cemented carbide WC-Co was performed using dissolution with nitric acid and subsequent ultrasonic spray pyrolysis (Gürmen et al, 2006, 1882-1890). An increase of ultrasound frequency from 0.8 to 2.5 MHz decreases an aerosol diameter of cobalt nitrate to 2.2 µm, which leads to the formation of submicron particles after drying and precipitation in a furnace above 500°C in hydrogen atmosphere.

Other important secondary materials for recovery of cobalt are waste nickel metal hydride and lithium-ion batteries (Müller & Friedrich, 2006, pp.1498-1509). The recycling processes of waste Li–ion batteries were performed using three strategies: pyrometallurgical, hydrometallurgical, and pure mechanical treatment (Georgi-Maschler et al, 2012, pp.173-182). More than 10 companies are recycling thousands of metric tons of spent portable and industrial Li–ion batteries annually. The companies, such as Umicore (Belgium), Xstrata Nickel (Canada), Accurec (Germany), Inmetco (USA), S.N.A.M (France) and Sony-Sumitomo (Japan) use the pyrometallurgical strategy as the main recycling process to recycle rechargeable portable and industrial Li–ion batteries also including NiMH and NiCd batteries. Valuable metals, such as Co and Ni, are fully recovered in the form of alloy at high temperature in contrast to Al, Li and Cd, which stay in slag or flue dust (Wang & Friedrich, 2015, pp.68-178).

The third secondary material for recovery of cobalt is polycrystalline diamond (PCD) in blanks. Diamond is the hardest material put to use on commercial and industrial scales. It is used, for example, for working edges of cutting tools or for grains in the hardest abrasives. Due to
advancements in the field of high strength steels and super alloys, the demand for hard cutting and forming tools is highly increased (Strong & Chrenko, 1971, pp.1838-1843). Industrially used diamonds can be found in the form of a naturally grown and mined crystal or as a man-made product with mono- or polycrystalline microstructure. PCDs are made at high temperature and during a high pressure process which requires cobalt (Co) as a solvent catalyst. Cobalt is incorporated in the final product resulting in a multi-phase-compound that is PCD. This multiphasic character renders PCD vulnerable to thermal stress since cobalt and diamond have different thermal expansion coefficients. The only way to make these PCDs stable for industrial applications at high temperatures, such as hot forming of metals, is to remove inclusions from the cavities in the framework of diamond grains. This study will include some results concerning an optimization of the leaching process of cobalt from polycrystalline diamond blanks using a conventional leaching method augmented with ultrasound.

The main purpose of this study is to present some processes and results regarding cobalt recovery from primary materials (lateritic and sulphidic ores) and secondary materials such as WC-Co, lithium-ion batteries and polycrystalline diamond blanks.

Thermochemistry of cobalt dissolution in acidic medium

The Pourbaix diagram (potential Eh-pH) of cobalt in water solution at room temperature confirms the presence of cobalt in the form of $\text{Co}^{2+}$ and $\text{Co}^{3+}$ in the pH-area below 0 (very acidic systems), as shown in Figure 1. At an increased potential between 2.0 and 3.0 V, cobalt is available only as $\text{Co}^{3+}$.

Huang et al (2004, pp.77-90) conducted experiments on the precipitation of cobalt and molybdenum from effluents and used HSC software to compute potential-pH-diagrams for the system Co-H$_2$O at temperatures of 20°C, 40°C, 60°C, and 80°C. An increase in temperature did not show any influence on the presence of cobalt-ions. Using a mixture of hydrochloric acid and nitric acid ("aqua regia"), namely without external potential, $\text{Eh} = 0$, and at pH values close to zero, the stable form of cobalt is a divalent cation within this temperature range. It was reported that the equilibrium for this reaction should be on the right side of the balance, since the divalent cobalt cation is a stable form at pH<<1 and without external potential. In many cases, the most cost- and energy-efficient way to extract metal from gangue or scraps is to oxidize and
dissolve it in a leaching solution, which means this method is useful for hydrometallurgical treatment as well as recycling.

Regarding cobalt leaching, Han & Meng (1993, p.709) found that cobalt dissolution is dependent on diffusion while the dissolution of divalent oxides is reaction controlled. They reported that the leaching rate of cobalt is generally faster than that of their respective oxides.

Cobalt extraction refers to the techniques used to extract cobalt from its sulphidic ores (cobaltite) and oxidic ores (nickel laterite) based on final separation of cobalt from copper and nickel and other elements. The chosen processes for cobalt recovery from primary and secondary materials are presented in this review.

**Recovery of cobalt from primary materials**

*Recovery of cobalt from complex sulfidic concentrates*

Over 91 % of cobalt and 84 % of copper were recovered from cobaltite concentrate by a process that included: 1) Oxidative pressure leaching, 2) Jarosite precipitation, 3) Ferric arsenic precipitation, 4)
Selective solvent extraction of copper with a mixed hydroxyamine-extractant, 5) Electrowinning of copper from recirculating acidic strip liquor, 6) Selective solvent extraction of cobalt from copper solvent extraction raffinate with an alkyl phosphinic acid extractant, and 7) electrowinning of cobalt from recirculating weak acidic strip liquor (Dannenberg et al, 1987, pp.1-20). The electrowon copper was 99.89% pure, and the electrowon cobalt was 99.8% pure, as shown in Figure 2.

Figure 2 – Conceptual flow diagram for cobalt solvent extraction and electrowinning
Рис. 2 – Концептуальная диаграмма экстракции кобальта в растворе и извлечения электролитическим путем
Слика 2 – Концептуални дијаграм тока производње кобалта помоћу раздвајања течно-течно и електролизе

The cobalt solvent extraction with its many recirculating streams takes more time at steady state conditions, where any build-up of impurities in these streams can cause serious problems. These batch experiments have confirmed that scale-up is possible only by using a continuous feed reactor.
In the Sheritt-Gordon process of nickel, sulfide concentrates can firstly be treated by either roasting or flash smelting to produce matte from which nickel and cobalt can be recovered hydrometallurgically, or they may be treated by an ammonia solution pressure leach. The chemistry of the ammonia pressure process for leaching Ni, Cu, and Co from Sherritt Gordon sulphide concentrates was described by the laboratory and pilot plant studies carried out by Sherritt Gordon Mines Ltd., Metallurgical Research Div. (Forward & Mackiw, 1955, pp.457-463)

Bioleaching of cobalt from an arsenidic ore is a new research subject, where an addition of citric acid can improve cobalt liberation and result in a more stable activity. In Australia, the BIOX-process was developed regarding the tank bioleaching of sulphidic concentrate.

**Meta Nickel Cobalt Process for the treatment of lateritic ores, Turkey**

Turkey Meta Madencilik Ltd. Şti. was founded in 2000 by a group of professional engineers and it developed Turkey’s first nickel-cobalt project from lateritic ores with approx. 0.1-0.2 % Co. The following operations are used: 1) Ore preparation and classification of ore particles, 2) High Pressure Acid Leaching (HPAL) - a leaching method to extract nickel and cobalt, 3) Primary Iron Removal & Re-Leach Area Solid Liquid Separation (CCD or SX), 4) Secondary iron removal (secondary neutralization), 5) MHP (Mixed Hydroxide Product) Precipitation-1, 6) MHP (Mixed Hydroxide Product), Precipitation-2, 7) Manganese removal, and 8) final neutralization.
Recovery of cobalt from secondary materials

Treatment of cemented tungsten carbide

The chemical composition of cemented tungsten carbide used in this work was as follows (wt %): 75.86 W, 8.14 Co, and 6.07 C. The process used is shown in Figure 4.

After grinding and sieving, the chosen fraction below 90 µm was treated with nitric acid. The leach solution of nitric acid leaching of cemented tungsten carbide scrap was used as the starting material for this strategy. After leaching and purification of the cobalt-nitrate solution, the final concentration of cobalt amounted to 0.08 mol Co/l. This solution was used for cobalt production by the ultrasonic spray pyrolysis (USP)
method in hydrogen atmosphere after leaching and the purification of cobalt-nitrate solution was used for cobalt production by the ultrasonic spray pyrolysis method in hydrogen atmosphere. The particle size of the produced cobalt powder can be controlled by the change of reaction temperature. Partly-agglomerated spherical cobalt particles with a mean diameter below 500 nm were obtained at 800°C using a concentration of cobalt nitrate of 0.4 mol/l, as shown in Figure 5.

Figure 5 – Cobalt powders obtained at 800 °C, C =0.04 mol/l by USP

Hydrometallurgical treatment of polycrystalline diamond (PCD) blanks with a grain size of 5µm

This strategy developed at the RWTH Aachen University focuses on polycrystalline diamond blanks made by Redies Deutschland GmbH & Co. KG, Aachen a manufacturer of wire drawing dies. Cobalt is incorporated in the final product (max. 1.6 % Co) resulting in a multi-phase-compound. This study was performed at between 60°C and 80°C aiming at optimizing the process of leaching cobalt and cobalt compounds from polycrystalline diamond blanks using the mixing of nitric and hydrochloric acid (aqua regia) in a conventional leaching method augmented with ultrasound. The reactor used is shown in Figure 6. The experiments were carried out in two reactors simultaneously set up in a fume cabinet. The reactor vessels were three-necked round bottom flasks with a capacity of 500 ml. Below the aforementioned setup,
ultrasonic baths of Bandelin Sonorex RK 52H type were placed on the lab jacks so they could be lowered for sampling and batch changes. This arrangement made disassembly easier and did not require readjusting the upper structure with every batch change. These ultrasonic baths have an effective nominal frequency of 35kHz and 60W output while their maximum power output is in the range of 240W. Ultrasonic irradiation, solid-to-liquid-ratio, temperature and particle size are the varying parameters in this study. Ultrasound has been found to enhance leaching processes and is varied from zero to intermittent to permanent. The results from this study have suggested that the leaching of used fraction does not require 80°C bath temperature but can be done at 60°C. Ultrasound can accelerate the leaching process so much that PCD can reach a desaturated state with less than 10% of metallic inclusions remaining after three to four days if they are leached at low solid-to-liquid-ratios close to 15g/L.

![Figure 6 – Reaction vessel in an ultrasound bath](image)
Some problems are present since the mixing of aqua regia involves volatile or gaseous species such as chlorine gas or hydrochloric vapor. It is possible that hydrochloric acid evaporated rapidly from the hot freshly-mixed solution while also forming NOCl. Applying neutralization with NaOH at the end of the experimental setup can solve this problem. The scale-up of this process can be a challenge in the future work.

**Highly efficient hydrometallurgical recycling process for automotive Li–ion batteries**

A highly efficient hydrometallurgical recycling process including pretreatment for used automotive Li–ion batteries has been developed at the RWTH Aachen University, showing the possibility of using a unique process to recover high-grade graphite, cathode metal salts and lithium carbonate, as shown in Figure 6.

![Figure 7 – Developed hydrometallurgical recycling process for Co (Wang & Friedrich, 2015, pp.168-178)](image-url)
The chemical composition of the electrode powder is assayed by the ICP–OES method, showing very high Co and Ni of about 22 and 9.9 %, respectively. Al, Fe, Mn and Cu have low content values, in the range of 0.2–1.18 %. The cathode metal (Co, No, Mn) compounds such as carbonates, sulphide and hydroxides are very valuable products obtained from this precipitation process. The recycling rates of Co, Ni and Mn can reach 95 % in the developed hydrometallurgical process. Regarding the application, the cathode metal salt could serve as a raw material (precursor) to prepare a new cathode material.

**Potential-controlled selective recovery of manganese and cobalt from a cobalt slag leaching solution**

Cobalt separation from other metals was usually performed using solvent extraction. Another strategy is a method based on an electrochemical study where manganese and cobalt were selectively separated from zinc in a leaching solution of cobalt slag by potential-control oxidation with ozone as shown in Figure 8.

![Figure 8](image-url)

*Figure 8 – Flowsheet of the two-stage method for manganese & cobalt recovery by ozone (Tian et al, 2017, pp 201-206)*

*Рис. 8 – Двухступенчатый метод извлечения марганца и кобальта с помощью озона (Tian et al, 2017, pp 201-206)*

*Слика 8 – Двостепени метод за издавање мангана и кобалта коришћењем озона (Tian et al, 2017, pp 201-206)*
When ozone was pumped into the solution in order to increase the oxidation potential, manganese (II) was oxidized and precipitated firstly, and then cobalt(II) was separated from the solution in the same way. Partial zinc was lost in the precipitates in the form of encapsulated inclusions. The effects of the dilution rate, the solution pH value and the system temperature on the manganese and cobalt separation were investigated, and high-grade cobalt precipitate and highly purified liquid were obtained in certain conditions.

Conclusion

Hydrometallurgical and pyrometallurgical processes are mostly applied for cobalt recovery from primary ores (oxidic and sulphidic compounds) and from secondary materials (cemented tungsten carbide, polycrystalline diamond blanks, waste cathodic materials from lithium-ion batteries and slag from zinc metallurgy). Hydrometallurgical operations such as dissolution at atmospheric and high pressure, precipitation, neutralization, filtration and hydrogen reduction are most important for the recovery of cobalt from secondary materials. Additionally, ultrasonic spray pyrolysis with hydrogen reduction leads to the formation of nanosized cobalt powders. The final product of the acidic leaching of lateritic ores under high pressure in an autoclave after precipitation and filtration is mixed nickel-cobalt hydroxide. The influence of the parameters such as temperature, solid/liquid ratio, pressure, acid pH-value and concentration is of high importance for the reaction kinetics. The techniques for cobalt separation from other elements such as nickel, manganese, and zinc are solvent extraction and potential-controlled selective leaching and precipitation. Finally, the main advantages of cobalt recovery from secondary materials are higher content of cobalt (approx. 1 to 20% in contrast to 0.1-0.2% in ores), higher selectivity, and a smaller number of required operations. However, these recycling processes are not industrially developed in comparison to traditional primary metallurgy. Therefore, the scale-up of these processes is a big challenge in future.

References


ИЗВЛЕЧЕНИЕ КОБАЛЬТА ИЗ ПЕРВИЧНЫХ И ВТОРИЧНЫХ МАТЕРИАЛОВ - ОБЗОР

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Резюме:

Введение/цель: Кобальт является стратегическим металлом в промышленном применении. Извлечение кобальта из оксидных руд, таких как латеритные и сульфидные руды, а также из вторичных материалов во время кислотной обработки и осаждения является широко используемым методом, обеспечивая получение различных соединений, таких как гидроксид кобальта, оксид кобальта и металлический кобальт.

Методы: Гидрометаллургические процессы, такие как растворение при атмосферном и высоком давлении, нейтрализация, осаждение и извлечение водородом, использовались для выщелачивания кобальта из руд и вторичных материалов. Пирометаллургические процессы, такие как обжиг и автогенная плавка сульфидных руд, сочетались с экстракцией растворителем и электролизом при получении катодного кобальта.

Результаты: Порошки гидроксида никеля и кобальта получены из руды с использованием серной кислоты при высоком давлении в автоклаве и осаждением оксидом магния. Никель и кобальт
разделяли с помощью экстракции растворителем. Конечный раствор с кобальтом использовали в процессе электролиза для получения кобальта. Кобальт и его соединения, такие как карбонат кобальта и гидроксид кобальта, получены из вторичного сырья с помощью гидрометаллургических операций.

Выводы: Гидрометаллургические и пирометаллургические процессы в основном используются для выделения кобальта из первичных руд (оксидных и сульфидных соединений) и вторичных материалов (цементированные карбиды вольфрама, полиэлектролиты пластины и отходы катодных материалов литий-ионных аккумуляторов).

Ключевые слова: кобальт, гидрометаллургия, гидроксид кобальта, порошок, вторичная переработка.
и кобалт хидроксид добијају се из секундарних сировина помоћу хидрометалуршких операција.

Закључак: Хидрометалуршки и пирометалуршки процеси већином су применети за издавање кобалта из примарних руда (оксидна и сулфидна једињења) и секундарних материјала (цементирани карбиди волфрама, поликристалне дијамантске плочице и отпадни катодни материјали из литијум-јонских батерија).

Кључне речи: кобалт, хидрометалургија, кобалт хидроксид, прах, рециклирање.

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