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**DOI: 10.15199/180.2021.3.1**

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# COBALT AS A CRITICAL RAW MATERIAL

## KOBALT JAKO SUROWIEC KRYTYCZNY

***Summary****: In the paper, the basic information on cobalt – the element classified, for many years, in the group of critical raw materials has been presented. The current demand on the mentioned metal is higher and higher, caused mainly by the development of new technologies and also, by energetic transformation, including a development of electric cars' market. The subject connected with obtaining of critical raw materials is nowadays a key problem due to a high dependence of the EU countries on import. The obstructed access to raw materials may dramatically affect the break of the supply chain and, in consequence, affect negatively the manufacture of materials and equipment where cobalt is a component, increase the production costs and finally, limit technological development. The present article has a review character.*

***Keywords****: cobalt, critical raw material, non-ferrous metals, recycling*

***Streszczenie****: W artykule przedstawiono podstawowe informacje na temat kobaltu, pierwiastka, zaliczanego od wielu lat do surowców krytycznych. Obecnie zapotrzebowanie na ten metal jest coraz większe, głównie z powodu rozwoju nowych technologii a także transformację energetyczną, w tym rozwój rynku samochodów elektrycznych. Tematyka związana z pozyskiwaniem surowców krytycznych jest obecnie kluczowa, ze względu na wysokie uzależnienie krajów Uni Europejskiej od importu. Utrudniony dostęp do surowców może drastycznie wpłynąć na przerwanie łańcucha dostaw, a co za tym idzie, wpłynąć negatywnie na produkcję materiałow i urządzeń w których kobalt stanowi składnik, podwyższyć jej koszta, a ostatecznie ograniczyć rozwój technologiczny. Artykuł ma charakter przeglądowy.*

***Słowa kluczowe****: kobalt, surowiec krytyczny, metale nieżelazne, recykling*

## Introduction

According to Organisation for Economic Cooperation and Development (OECD), the world demand on materials in 2060 will be equal to 167 billion Mg. Ensuring the access to the resources becomes a priority of all countries with the aim to enable their industrialization, digitalization and also, the passage to climatic neutrality via manufacture of low-emission technologies and products [1–2]. In 2020, in connection with the above fact, the European Commission submitted the list of 30 raw materials being recognized as the Critical Raw Materials (CRM), having a strategic importance for manufacturing industry of the European Union and for the improvement of our life quality. Critical materials are those ones, the possibilities of obtaining of which from primary as well as from the secondary sources are charged with a high risk, or there are big difficulties in their obtaining and the possibilities of their substituting are small. The list of critical raw materials, as announced in 2020, is given in Tab. 1 [1–2]:

Similarly as in 2014 and 2017, the group of critical raw materials included cobalt.

Cobalt is a silver-grey metal, having ferromagnetic properties. The mentioned metal is found at two different degrees of oxidation (+2, +3) and has one isotope, existing in a natural form (59Co). The temperature of Co melting is equal to 1493°C. It is

*Tab. 1. List of critical raw materials, announced in 2020 [1–2]*

| **Critical raw materials 2020** |
|---|
| Antimony, Beryllium, Borate, Cobalt, Coking coal, Fluorite, Gallium, Germanium, HREE LREE, Indium, Magnesium, Natural Graphite, Niobium, PGM, Rock phosphate, Silicon metal, Tungsten, Barite, Phosphorus, Scandium, Bismuth, Tantalum, Hafnium, Natural rubber, Vanadium, Strontium, Lithium, Bauxite, Titanium |

*Fig. 1. The examples of cobalt ores: cobaltite, cariolite and linneit [4L2] [5L3] [6L4]*

estimated that the content of Co in the Earth's crust amounts to 15–30 ppm [3].

Cobalt is not present in nature independently in a metallic form. Most frequently, it is found in the form combined with copper, iron, nickel, in a form of arsenide e.g. cobaltite (CoFeAsS), skutterudite (CoAS) and sulphides e.g. cariolite ($CuCo_2S_4$) and linneit $(Co, Ni)_3S_4$ [4].

Fig. 1 represents exemplary cobalt ores: cobaltite, cariolite and linneit [4–6].

## Cobalt deposits

The deposits of cobalt are found all over the world (Fig.2), mainly in African copper belt in the Democratic Republic of Congo (DRC). Cobalt is produced in technologies, accompanying production of basic metals, most frequently of copper (44%) or nickel (50%). In the EU countries, and especially in Belgium and Finland, the different products are made of cobalt (metal, oxide, and hydroxide) on the basis of imported primary raw materials, mainly from the Democratic Republic of Congo (DRC) and Zambia [7].

## Production of cobalt

According to the data found below in Fig. 3, mining production of cobalt increased dramatically in 2009 and since the mentioned period it has been maintained at the constant level.

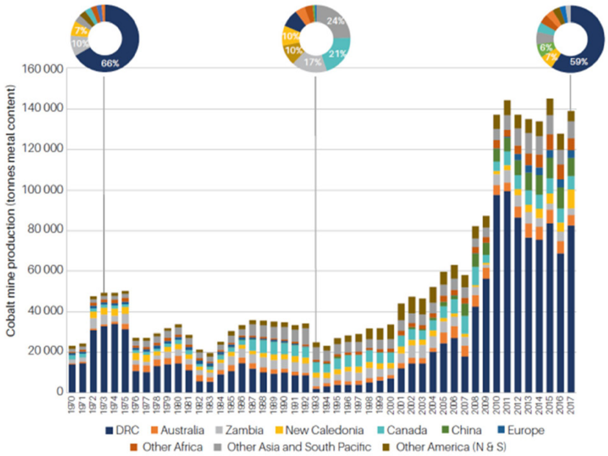


*Fig. 3. Mining production of cobalt in the period of 2005–2015 [9]*

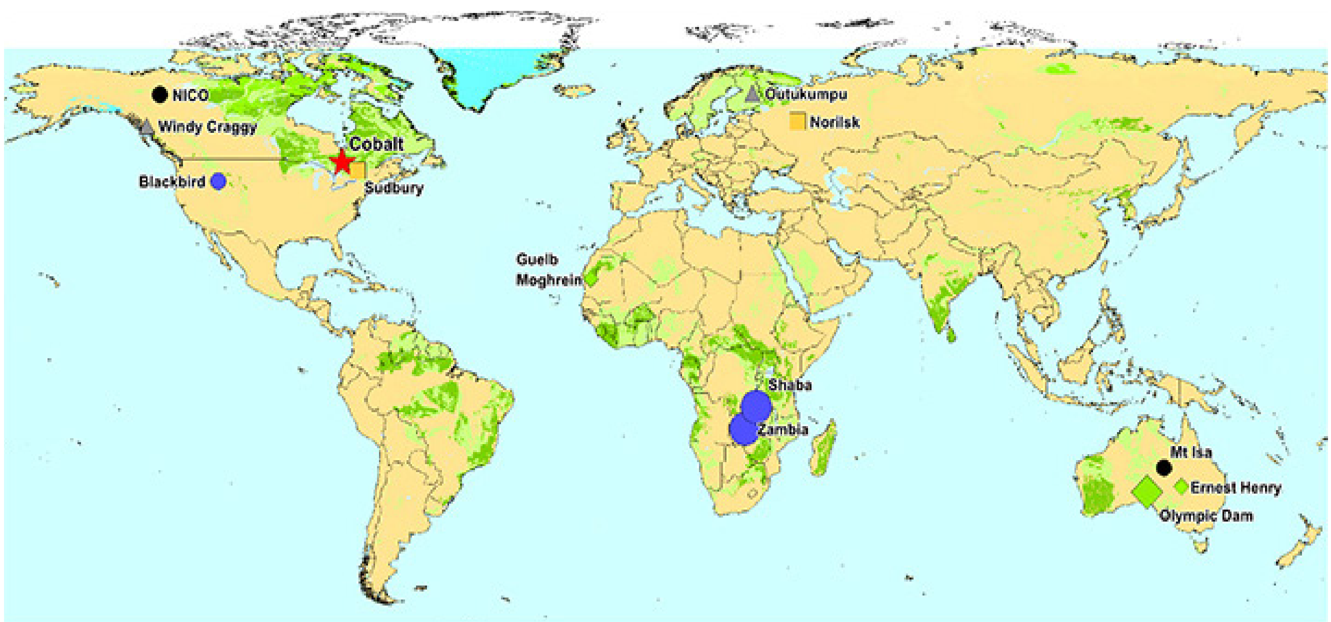


*Fig. 2. Cobalt deposits [8]*

*Fig. 4. Example of one of the mines where the extraction of cobalt is performed by "handicraft" method [27]*

At present, almost 60% of the global cobalt production is implemented in the Democratic Republic of Congo. The cobalt-rich regions form there big mining complexes. The process of cobalt extraction in the DRC takes place in the mines differing from those ones which are functioning in the developed countries. The mines in the DRC create a group of small mining plants, having a typical handicraft character i.e. heavy mining machines are not employed. It is estimated that 15–30% of the cobalt obtained in the discussed country comes from the mines which do not meet the safety and hygiene standards and their functioning is not regulated by the state organizations of mining supervision. The United Nations informs that 40 thousand children are working in the mentioned type of manufacturing plants. A lack of real control of mining of the raw materials in Congo results from numerous ethnical conflicts, or still recurring epidemics of Ebola virus at the discussed territory [10].

During the recent years, a part of the companies, mainly of Chinese ones, has undertaken the implementation of the projects aimed at formalization of handicraft mining what is expected to lead to safety increase as well as observing the human rights in such work places. The formalization of the activities of the discussed above complexes, consisting of small handicraft mines is based upon the verification of the workers who want to obtain an access to the site of extracting the raw materials. The verification consists, *inter alia*, in control of soberness or monitoring of the age of the employed persons (the worker must have 18 years completed). Additionally, the periodical risk assessment and medical training are carried out [11].

## *Metallurgy of Cobalt*

The processes, employed in cobalt production are based on pyrometallurgical process of processing the cobalt-containing ores i.e. ores of copper and nickel (at high temperatures) and then, hydrometallurgical processes, with the aim to extract cobalt from the obtained alloys in a metallic form or in cobalt compounds.

Manufacture of cobalt from sulphide ores of nickel is based upon melting of cobalt-containing sulphide concentrate of nickel (generated by flotation of sulphide ores) and production of nickel matte, containing considerable quantities of iron. Then, the obtained stone is subjected to converting process, in consequence of which the iron-poor matte is produced which is subjected to hydrometallurgical processing with the aim to recover cobalt from nickel. From the concentrate, obtained by the mentioned method, we obtained nickel and cobalt in a pure form [3].

Initially, the manufacture of nickel from laterite ores was not integrated with production of cobalt and the iron-nickel alloy was a final product of the described process. In the fifties of the 20$^{th}$ century in Cuba, there were employed the first integrated methods of nickel metallurgy, allowing the separation of cobalt from laterite ores. The mentioned method was based on the hydrometallurgical high-pressure leaching of cobalt from laterite ore, using sulphuric acid (VI) and successive its recovery from water solutions. At present, the discussed technology is universally employed [3].

Production of cobalt as copper-accompanying metal is practised, first of all, in relation to the deposits in Africa. The extracted ore is usually subjected to leaching and copper is separated from cobalt by the application of extraction with solvent. In effect, water solution of cobalt is obtained and it is precipitated using magnesium oxide to cobalt hydroxide. The cobalt hydroxide may become a commercial product, or may be later processes by electrolytic methods to obtain metallic cobalt [3].

## Application of cobalt

Due to its hard fusibility and resistance to corrosion, cobalt is used in many applications such as super alloys, additives to highly-cutting steels, machining tools and, also, in electronics e.g. in lithium-ion batteries. The discussed metal has also magnetic properties; therefore, it is employed in production of permanent magnets (samarium-cobalt, Sam-Co); alnico – compound of aluminium, nickel and cobalt).

## Superalloys based on cobalt

From among super alloys, we can distinguish super alloys based upon the nickel, iron and cobalt. Owing to additives of carbon and other metals such as wolfram and molybdenum, the alloys which are based on cobalt preserve their properties at the increased temperatures better than the alloys based on nickel. Additionally, cobalt super alloys contain often the addition of chromium (Cr); owing to this fact, such alloy is exceptionally resistant to corrosion. The elements made from cobalt super alloys are less resistant to cracking as compared to nickel alloys [12].

Table 2 shows the example of the composition of the selected cobalt alloys and their application.

*Tab. 2. The composition of the selected cobalt alloys [13–15]*

| | Chemical composition, % | Properties | Application |
|---|---|---|---|
| **Haynes 25™ Alloy L605 [13]** | C- 0,05-0.15; Mn-1.0-2.0; P-0.4; S-0.03; Si-0.4; Cr-19.0-21.0; Ni-9.0-11.0; W-14.0-16.0; Co-balance | Temperature strength and oxidation resistant to 2000˚F (ca. 982˚C). Resistant to acids, body fluids and marine environments | Gas turbine engine components; Springs; Heart valves; High temperature ball bearings and bearing races |
| **High-Performance Alloy6B [14]** | C- 0.9-1.40; Mn-max. 2.0; Si- max. 2.0; Cr- 28.0-32.0; Ni-3.0; Mo-1.50; Fe 3.0; W-3.50-5.50; Co-balance | corrosion and wear resistant high hardness at elevated temperatures | Medical blades; Valve parts; Pump plungers; Knives; Bearings |
| **NASA Co-W-RE Cast Cobalt Alloy [15]** | C-0.40; Cr- 3.0; Co-67.6; Nb-1.0; Re-2.0; W-25; Zr-1.0 | - | High-temperature space applications |

## Magnets

Permanent magnets are such materials which preserve their magnetic properties after exposition to magnetic field effect. They are found in a wide spectrum of materials, employed in many industrial and commercial applications. They include micro-engines and condensers used in computers, audio-visual equipment (loudspeakers, video recorders etc), cars (electric windows, ABS, computers in dashboard etc) and electronic household appliance and equipment (dishwashers, washing machines, air conditioners etc.). Permanent magnets are also used as time engines in industrial robots, military and cosmic technologies and in clocks [16–17].

Permanent magnet materials are identified by the following principal magnetic properties [17]:

— Maximum value of energy product, $BH_{max}$ (MGO);
— Residual induction, $B_r$ (gauss);
— Coercive force, $H_c$ (oersteds).

Types of permanent magnets according to their chemical composition:

— Alnico
— Ceramic
— Rare-Earth
— Iron-Chromium-Cobalt.

## AlNiCo magnets

Alnico magnets are the alloy of aluminium (Al), nickel (Ni), cobalt (Co), copper (Cu) and iron (Fe). The mentioned magnets are the oldest permanent magnets. The development of Alnico alloys was commenced in the thirties of the 20th century. Alnico alloys are characterized by a high resistance to demagnetization (i.e. high coercion). In spite of the fact that other permanent magnets (e.g. Sm-Co) are more frequently applied, Alnico magnets are still employed in aircraft or car industry (in sensors).

*Tab. 3. Parameters of AlNiCo magnets [17]*

| Original MMPA Class | Chemical composition | | | | | | Magnetic properties | | | | Working temp. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Al | Ni | Co | Cu | Ti | Fe | BHmax | Br | Hc | Hi | T |
| | % | | | | | | MGOe | Gauss | Oersted | | ˚C |
| **Alnico 1** | 12 | 21 | 5 | 3 | - | balance | 1.4 | 7200 | 470 | 480 | No data |
| **Alnico 2** | 10 | 19 | 13 | 3 | - | balance | 1.7 | 7500 | 560 | 580 | 450 |
| **Alnico 3** | 12 | 25 | - | 3 | - | balance | 1.35 | 7000 | 480 | 500 | 450 |
| **Alnico 5** | 8 | 14 | 24 | 3 | - | balance | 5.5 | 12800 | 640 | 640 | 525 |
| **Alnico 5 DG** | 8 | 14 | 24 | 3 | - | balance | 6.5 | 13300 | 670 | 670 | 525 |
| **Alnico 5-7** | 8 | 14 | 24 | 3 | - | balance | 7.5 | 13500 | 740 | 740 | 525 |
| **Alnico 6** | 8 | 16 | 24 | 3 | 1 | balance | 3.9 | 10500 | 780 | 800 | 525 |
| **Alnico 8** | 7 | 15 | 35 | 4 | 5 | balance | 5.3 | 8200 | 1650 | 1860 | 550 |
| **Alnico 8HC** | 8 | 14 | 38 | 3 | 8 | balance | 5.0 | 7200 | 1900 | 2170 | 550 |
| **Alnico 9** | 7 | 15 | 35 | 4 | 5 | balance | 9.0 | 10600 | 1500 | 1500 | 550 |

Table 3 shows the parameters of Alnico magnets according to the standards, defined by [17].

## SmCo magnets

Samarium-cobalt magnets (Sm-Co) are applied at high temperatures. They have working temperature reaching to 350°C [18]. Table 4 contains the most important parameters of Sm-Co magnets [18].

Sm-Co magnets have a high resistance to corrosion in wet, acid or alkaline environment. Due to the discussed properties, they may be employed in engines of traction railway locomotives and heavy industrial engines and generators [19]. Besides it, Sm-Co magnets are also used in medical implants and tools [18]. Fig. 5 represents the percentage participation of SmCo magnets in various applications [19].

*Tab. 4. Parameters of Sm-Co magnets [18]*

| Goudsmit Grade code | Type | Remanence Br | Normal coercivity HcB | Maximum energy produckt $BH_{max}$ | Maximum operating temperature |
|---|---|---|---|---|---|
| | | typical value (mT) | Typical value (kA/m) | Typical value (kJ/m³) | Tmax (°C) |
| **S20** | SmCo5 | 950 | 756 | 175 | 250 |
| **S22** | SmCo5 | 1000 | 772 | 191 | 250 |
| **S24** | Sm2Co17 | 1040 | 796 | 199 | 350 |
| **S26** | Sm2Co17 | 1060 | 820 | 215 | 350 |
| **S28** | Sm2Co17 | 1100 | 820 | 231 | 350 |
| **S30** | Sm2Co17 | 1120 | 828 | 247 | 350 |
| **S32** | Sm2Co17 | 1150 | 796 | 239 | 350 |

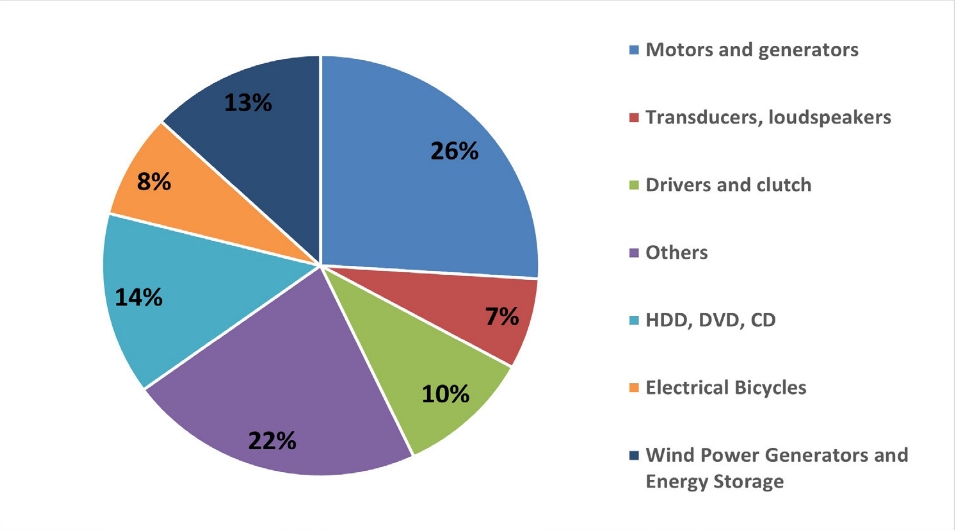


*Fig. 5. Application of Sm-Co magnets [19]*

## Rechargeable batteries

Lithium-ion cells belong to the most popular rechargeable batteries [26]. They are characterized by a high density of the stored energy in comparison to the remaining types of rechargeable batteries [21]. Lithium-ion cell consists of five components: anode, cathode, electrolyte, polymer separator and nickel-covered steel or aluminium casing. Cathode is made of oxides of transitory metals (most frequently cobalt, manganese, nickel). The electrode material is laid on copper and aluminium foils. The electrodes are separated with the separator in a form of polyethylene or polypropylene. The electrode materials are immersed in electrolyte solution which enables movement of lithium ions between the electrodes [26]. Cathodes are - most frequently -

*Tab. 5. The approximated composition of lithium-ion batteries (LCO, NMC)*

| Marking | Cathode | Anode | Application | Approximate content |
|---|---|---|---|---|
| **LCO** | $LiCoO_2$ | graphite | Mobile telephones, tablets, laptops, cameras | Li 2,7%; Co 22,8%; Ni 0,2%; Cu 8% |
| **NMC** | $LiNi_xMn_yCo_zO_2$ | graphite | Electric cars, medical equipment, scooters, electric bicycles, electric tools | Ni 39 g/kg; Co 39 g/kg; Mn 36 g/kg; Li 14 g/kg |

cobalt spinels ($LiCoO_2$; LCO), manganese spinels ($LiMn_2O_4$; LMO) intercalated with lithium ions. On the other hand, graphite is employed as anode material [21]. Table 5 shows the examples of the employed cathode materials and the approximated composition of lithium-ion batteries [2, 20].

## Demand on cobalt

Development of lithium-ion batteries (LIB) has experienced a tremendous growth during the recent years; it is connected with the increasing production of mobile devices and with the constantly growing demand in the sector of electric vehicles (EV). It is estimated that the demand on lithium-ion batteries will be increasing annually above 30% during the coming 10 years. Manufacture of lithium-ion batteries employs mainly such raw materials as copper, graphite (natural or synthetic), cobalt, lithium, manganese, aluminium and nickel [1, 22]. The EU countries (EU-27, without Great Britain) produce at present only 1% of all raw materials, necessary for manufacture of batteries. Asia, as being represented by China, Japan and the South Korea, supplies 86% of the processed materials and components for production of lithium-ion batteries all over the world. The Peoples' Republic of China accounts for 66% of global production of lithium-ion batteries. A full dependence of the EU countries on import of cells and batteries creates a serious threat to the raw material deficit and potentially high costs connected with the application of technologies of lithium-ion batteries. Due to a high demand on cobalt and a strong dependence on the supplies from other countries, there is a high necessity of recycling of cobalt from various applications [1–2].

## The methods of recycling

The technologies of recycling of the raw materials, containing critical metals, are based on the pyrometallurgical and hydrometallurgical processes [23].

Table 6 shows the examples of the employed processes of recycling the rechargeable lithium-ion batteries [2; 24].

Table 7 presents the advantages and disadvantages of the processes, employed in recycling of lithium-ion batteries, with the consideration of mechanical processes [25].

The high temperature processes are characterized by a high charge to the environment in connection with the generation of dusts and gases and high energy consumption [23]. The hydrometallurgical processes are characterized by lower energy consumption and a high selectivity of the recovered metals. The

*Tab. 6. Examples of recycling technologies of lithium-ion batteries [2, 24]*

| Company | Recovered metals | Proces | Country |
|---|---|---|---|
| **Glencore Recycling** | Ni, Co, Cu | thermal preparation + pyrometallurgy + hydrometallurgy | Canada |
| **AkkuSer** | Ni, Co, Cu, Fe | mechanical process | Finland |
| **Recupyl** | Ni, Co, Cu, Fe, Li | mechanical process + hydrometallurgy | France |
| **Umicore** | Ni, Co, Cu, Fe | pyrometallurgy + hydrometallurgy | Belgium |
| **Accurec** | Ni, Co, Cu | thermal preparation + pyrometallurgy + hydrometallurgy | Germany |
| **Kyoei Seiko** | Ni, Co, Fe | pyrometallurgy | Japan |
| **JX Nippon** | Ni, Co, Cu, Fe, Mn, Li | thermal preparation + mechanical process + hydrometallurgy | Japan |
| **Dowa** | Ni, Co, Cu | thermal preparation + pyrometallurgy + hydrometallurgy | Japan |
| **GEM** | Ni, Co, Cu, Fe, Mn, Li | mechanical process + hydrometallurgy | China |
| **Brunp** | Ni, Co, Cu, Fe, Mn | mechanical process + hydrometallurgy | China |
| **Telerecycle** | Ni, Co, Cu, Fe, Li | mechanical process + hydrometallurgy | China |
| **Kobar** | Ni, Co, Cu, Fe | mechanical process + hydrometallurgy | Korea |
| **Retriev** | Ni, Co, Cu, Fe | mechanical process (in liquid) + hydrometallurgy | United States of America |
| **Batrec** | Ni, Co, Cu | mechanical process | Switzerland |

*Tab. 7. Advantages and drawbacks of hydrometallurgical, pyrometallurgical and mechanical processes [25]*

| Process | Advantages | Disadvantages |
|---|---|---|
| **Hydrometallurgy** | High recovery rate<br>High purity product<br>Low Energy consumption<br>Less waste gas<br>High Selectivity | More wastewater<br>Long process |
| **Pyrometallurgy** | Simple operation and short flow<br>No requirement for categories and the size of inputs<br>High efficiency | Li and Mn are not recovered<br>High energy consumption<br>Low recovery efficiency<br>More waste gas and the cost of waste gas treatment |
| **Physical recycling process** | Short recovery route<br>Low energy consumption<br>Environmental friendly<br>High recovery rate | High operational and equipment requirements<br>Incomplete recovery |

main disadvantage of the discussed process consists, however, in generation of waste in a form of sewages, containing the dangerous substances [23].

## Summing up

In spite of the existing and functioning plants which process the cobalt-containing waste, the EU countries are still dependent on the supplies of the discussed raw material from other countries. The mentioned metal has been recently widely employed in lithium-cobalt batteries. Cobalt is a metal, affecting the development of the newest technologies; additionally, in certain applications, it cannot be replaced by another raw material.

The Research Network Łukasiewicz – Institute of Non-Ferrous Metals has conducted, for many years, the studies on the technologies of waste management in Poland; their solutions were introduced in many enterprises. The Research Network Łukasiewicz is the third – in respect of size – research network in Europe. It supplies attractive, complete and competitive technological solutions. It offers the unique system of "Challenging" to the business; owing to the mentioned system, is undertakes the business challenges during not longer than 15 days and submits, free-of-charge, the direction of solving problem and the ideas of the research project to the entrepreneur [28].

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*Article reviewed*
*Received: 07.07.2021 r. /Accepted: 29.07.2021 r.*