Raw Materials and Possibilities of their Obtaining in Poland

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Abstract

The deficit or lack of certain minerals in EU countries forced efforts to secure the supply of mineral resources within the European Union. Forecasts indicate that demand for critical raw materials and "high-tech" metals will grow along with the development of innovative technologies. Critical raw materials in the EU includes 20 commodities of major economic importance, which availability on the EU market is increasingly under threat. The analysis of the data presented in the article shows that the acquisition of critical elements in Poland would be possible with both primary and secondary resources. The study suggests areas for acquisition of certain, critical in national conditions, elements.

Keywords: critical materials, critical metals, sources

Introduction

Activities connected with obtaining raw materials at the current stage of development of EU countries are mainly dictated by:

• the growing disproportion between the demand for mineral resources and the possibilities of their obtaining,

• limitation of their sourcing in the EU countries due to the exploitation of some raw materials deposits ,

• willingness to become independent of the suppliers from countries outside the EU,e.g. from China, Russia etc.,

• rational economy and their sustainable consumption.

For those reasons the EU prefers solutions that allow for:

• improving the efficiency of material resources utilization,

• improvement of technology of products winning,

• increasing the use of secondary raw materials – urban mining - municipal waste being the source of critical raw materials,

• establishing the directions for research and innovation in methods of mineral extraction and processing,

• developing material engineering towards the use of substitutes.

These solutions should lead to improved competitiveness of the raw materials economy, in particular in the so-called critical raw materials. The data is necessary to develop not only the chemical and technological concepts of critical elements winning but also to develop the process design, namely:

• the demand for the product and its characteristics,

• world trends in methods of production and technical solutions,

• characteristics of the proposed method of production,

• characteristics of raw materials,

• characteristics of main product, by-products, waste and so on.

This paper focuses on critical raw materials and the possibility of obtaining some critical elements.

Critical Raw materials and their application

The fundamental objective for the development of basis of common European Union raw material policy in the field of non-energy commodities was to evaluate the mineral potential in the EU [Radwanska-Bank, 2011].

Raw materials are considered as critical for the EU economy when the lack of their primary or secondary sources makes it impossible to undertake the production. This concept has been developed under the EU Raw Minerals Initiative [Critical Raw Materials for the EU. Report of the Ad-hoc Working Group on defining critical raw materials 2014] based on three groups of criteria:

• economic effects of supply constraints,

• the risk of supply constraints resulting from the political and economic stability of countries producing critical elements,

• environmental risks arising from the reduction of production capacity related to the requirement of maintaining environmental quality standards.

Tab. 1. Some directions of critical elements application

Tab. 1. Niektóre kierunki zastosowania pierwiastków krytycznych

Element	The basic directions of applications
Antimony	Antypiryn- plastics industry, special batteries with lead-antimony, alloys bearing
Beryllium	Alloys - for aircraft industry and aerospace, material for nuclear reactors, neutron sources, neutron moderator speed and cladding of the fuel in nuclear reactors
Fluorite	sole- fluorides, pacifying in the production seal frit, in metallurgy, synthetic cryolite
Gallium	semiconductors (electronics), lasers, such microchips, batteries solar optical disks, the liquid thermometer, in equipment and diffusion vacuum pumps
Germanium	semiconductors, such microchips, computers, optical fibres, chemotherapy, optical glass
Graphite	refractory materials, brake linings, in the manufacture of lubricants, in foundry operations
Indium	Semiconductors (electronics), computers, optical disks, bearing alloys
Cobalt	Super alloys, ceramics and glass, catalysts, ferromagnetic alloys
Magnesium	Light alloys used in the aircraft industry, in aerospace, as compounds for the production of refractory materials
Niobium	In aerospace, aviation, as getter (binding of small amounts of residual gas, steel industry including super alloys, the arms industry
Platinum group metals	Catalysts, desalination of sea water, fiber optical, chemical equipment and laboratory
Rare earth elements	Lasers, magnetic materials (car starters, magnetic resonance etc.) microwaves, lasers, phosphors, optical glass, anti-reflective layer
Tantalum	Electronics, aerospace, telecommunications, chemical industry, in nuclear technology, surgery
Tungsten	Feet, fibers and cathodes for electron tubes, heating pipes, cutting tools (cemented carbides)

Additionally these materials are frequently listed in the following groups:

• strategic raw materials,

• scarce raw materials,

Materials which demand in the EU is greater than the supply are considered to be scarce raw materials. Their demand is covered with import from outside of the EU.

According to [Galos et. al.] critical raw materials are considered to be those that are essential to ensuring the defensive capabilities of the EU countries (development of aviation, aerospace or military technologies, and the like).

Most of the critical raw materials are found in countries outside of the EU. The largest producer of critical elements such as rare earths, gallium, germanium, fluorspar, indium, graphite and other elements is China. For example, gallium production in this country accounts for 70% of world's production of this metal, out of which 60% is obtained from electronic equipment waste (WEEE).

Two of the dominant platinum producing countries are South Africa and Russia. About 90% of the platinum is extracted from ore and the remainder is obtained from recycled materials substantially from scrap automobile catalytic converters, waste catalysts used in chemical technologies, eg. nitric industry. The increasingly important source for the recovery of platinum is WEEE.

Another example of the uneven distribution of resources is cobalt, with Congo being the major supplier. This element is usually obtained from raw materials, eg. from sulfide ores of nickel-cobalt-copper or copper-cobalt ore. Secondary materials such as metallurgical slag, spent catalysts, scrap stainless steel, etc play an important role in

Tab. 2. Indicators replacement of critical raw materials [Annex to the Communication]

Tab. 2. Stpień zastępowalności surowców krytycznych [Aneks do Komunikatu]

Critical element	Substitutability index
Antimony	0,62
Beryllium	0,85
Borates	0,88
Chrome	0,96
Cobalt	0,71
Coking coal	0,68
Fluorite	0,80
Gal	0,60
Germanium	0,86
Indium	0,82
Magnesite	0,72
Magnesium	0,64
Natural graphite	0,72
Niobium	0,69
Phosphorite and apatite	0,98
The platinum group metals (PGE)	0,83
Heavy metals, rare earth	0,77
Light rare earth metals	0,67
Silicon metal	0,81
Tungsten	0,70

the acquisition of cobalt. The common feature of above named commodities is their dispersion in the lithosphere.

Based on the above criteria, a list consisting of 14 raw materials essential to the economies of the EU and characterized by an increased risk of supply disturbances or risk of deficiency was prepared (Critical... 2010). The list contains: antimony, beryllium, fluorspar, gallium, germanium, graphite, indium, cobalt, magnesium, rare earths (REE), niobium, tantalum, platinum (Platinum Group Elements PGE) and tungsten. The commodity market observes a significant increase in demand for critical raw materials resulting from the emergence of new technologies and "high-tech" products.

The demand for these raw materials is therefore complemented by imports from countries outside of the EU. The third group contains critical materials. The resources of most of the critical raw materials are not found in Poland. The domestic demand is met by their import.

Recently, the list of critical raw materials was adjusted. It has been expanded to include such raw materials as borates, chrome, coal coking coal, magnesite, phosphorite and apatite and silicon metal with a list of the removed tantalum. By 2013 the critical raw materials accounted for 14 elements. Currently, this list includes 20 critical raw materials (tab.1). Indicators replacement of critical raw materials are shown in Table 2.

This list has been expanded to include such raw materials as borates, chromium, coal coking, magnesite, phosphorite and apatite and silicon metal. while tantalium has been removed from this list. Additionally rare earth metals were placed into two groups: the cerium group and yttrium group. In total, the list includes 35 critical metals essential for the EU economy. These metals are classified into three groups:

- antimony, beryllium , boron, chromium, cobalt, gallium, germanium, indium, metallic magnesium, niobium, metallic silicon and tungsten (12)
- platinum group of elements: platinum, palladium, iridium, rhodium, ruthenium, osmium (6)
- rare earth elements: scandium group –scandium, lanthanum and yttrium (3) and group cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium (14)–(17).

For example, the production of electric cars require lithium and neodymium, fiber optics and IR optical systems can't function without germanium. In the Table 1 directions for use of the critical elements are presented.

This list shows that among critical elements there are 12 critical metals. Adding to that the rare earths (REE), which include cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium,

Tab. 3. The size and their demand in Poland

Tab. 3. Wielkośc zapotrzebowania w Polsce

Critical element	Production	Import	Type of raw material	Source of supply
Antimony		1000 Mg 50-163 Mg	Oxides, antimony not work powder	Mainly China, to a small extent Japan and the countries of the EU (re)
Beryllium			Metal powder	Mainly China, in a small way UE (re)
Borates		161 Mg	Natural boric acid natural borates metallic boron	Turkey Italy, Czech Republic, Slovakia
Chrome		9-38 th. Mg chromite	Chromites, chrome metallic sodium dichromate	South Africa, Pakistan, Germany
Cobalt		6,3-9,7 th. Mg	Fluorite metallurgical and ceramic materials, in small amounts Chemical	Mexico, Germany, Czech Republic
Coking coal		4,8 Mg	Type 36, 37, 38	Czech Republic
Fluorite		(12-25kg)	Clean metal, untreated	USA, Slovakia, Germany, France, Sweden
Gal		17-34 kg	Oxide, pure unprocessed metal scrap	France, Britain, China, Germany, USA
Germanium		3,0-5,7 th. Mg	natural graphite	
Indium		9-84 kg	Metal	China, Belgium, United States, Switzerland
Magnesite		25-39 Mg, 18-14 Mg	Powder metal, oxides, hydroxides	USA, Finland, the countries of the EU (re)
Magnesium		4,8 Mg 81,4 Mg	Raw Magnesite, Calcined magnesite, roasted and processed cheeses	Brazil, China, Slovakia
Natural graphite		1,34 - 5,38 th. Mg	Unprocessed metal scrap	China, Germany, Czech Republic, Hungary - in small amounts several other countries
Niobium		18-187 kg	Untreated metal, Powder products	EU countries, China, USA
Phosphorite and apatite	Pt -25-30 kg/y Pd -15-20 kg/y	229-1045 kg, 1-62 kg	intermediate, metal powder	EU countries, Japan, USA, Germany
The platinum group metals (PGE)		4,9 -62,7 Mg 0,6-6,8 Mg	The compounds of rare earth metals, Rare earth metals	China, EU countries, USA, Netherlands
Heavy metals, rare earth		11 943 Mg 30-45 Mg	Silicon metal, polycrystalline silicon	Brazil, France, the Netherlands, Taiwan
Light rare earth metals		8,1- 17,1 Mg 8,7- 22,0 Mg	Metal powder	Czech Republic, Great Britain, Austria, China, China, Spain, Russia

ytterbium, lutetium and third transition group metals - scandium, yttrium and lanthanum, it can be concluded that the critical elements list is dominated by a total of 33 critical metals.

In 2014 a corrected list of critical raw materials was presented. Currently, this list includes 20 critical raw materials. It has been expanded to include such raw materials as borates, chromites, coking coal, magnesite, phosphorite and apatite and silicon metal with a list of the removed tantalum. Directions of the use of these critical elements are given in Table 2.

Boron and its compounds thereof are used for the production of: glass fibers, silicon or borosilicate glasses detergents. Recently boron compounds are introduced into mineral fertilizers as an essential trace mineral. In addition, this element is used as an oxygen scavenger in non-ferrous metallurgy as well as an alloying addition to steel and aluminum.

Chromium is present in nature in the form of chromite, from which ferrochromium is obtained, which is used as an alloying addition for the production of stainless steels, acid-proof, heat-resistant like. Furthermore, chromites are used in technology of chromium compounds (chromium acid anhydride, dichromate, etc…) and in the refractory industry.

Coking coals are the basic raw material for the production of coke for metallurgy and foundry industry. The product is a reducing agent and an energy carrier in the manufacturing of pig iron in a blast furnace. EU countries feel the shortage of coking coal (type 35, 36, 37).

Another raw material found on the revised list is magnesite. This raw material is used in production of refractory materials and Sorel cements. Magnesium compounds are increasingly frequently used in the rubber industry, agriculture and pharmaceuticals industry. Recently magnesium compounds with nano-structure e.g. flame retardants became very popular [Radomski et al., 2014]. Production of metallic magnesium is limited due to the high-energy-consumption process (16 MWh/Mg) and not due to the lack of raw materials. Technological assumptions have been developed in Poland for producing metallic magnesite from dolomite.

Phosphorus plays a vital role in the transformations occurring in living organisms and is a component of proteins. This element is found in nature in the form of apatite and phosphorite, which are basically processed into phosphate fertilizers. Living organisms can acquire phosphorus in foods of plant origin or in the form of a food additives for example di-calcium phosphate.

Silicon is one of the most abundant elements in the lithosphere but still it is one of the critical elements. In modern technologies silicon is used in semiconductor electronics as transistors, photocells, rectifiers and solar cells. Technology of manufacturing silicon in the form of a monocrystalline silicon of high purity is a complex process and requires a melting zone. This element is also used in metallurgy of as an additive alloy, for example, for the preparation of ferro-silicon.

Attached to the Communication is a list of the critical raw materials and their substitutability indexes (table 2). This data suggests that raw materials such as apatite and chromites are considered as particularly scarce raw materials.

That the probability of substituting both phosphorus and chromites is close to zero. substitutability index is a measure of the difficulty in substituting the material, scored and weighted across all applications. This index has a value in the range of 0-1 where 1 represents lack of substitutability of a raw material [Annex to the Communication].

Feasibility analysis of obtaining critical raw materials in Poland

Review of literature shows that Poland lacks minerals being the source of the critical raw materials. [Bilans, Radwanek-Bak]. The size and their demand in the country is shown in Table 3. Both the import size and type of imported raw materials differ significantly. Current and prospective aspects of obtaining critical raw materials in domestic conditions are presented in Table 3.

Antimony – in Poland there is no raw materials containing this metal and therefore its supply needs to be imported into Poland. First of all, antimony oxide is imported mainly from China. These compounds are used in the rubber, glass and other industries. A potential source of secondary antimony in Poland is the alloy scrap containing this element.

Availability of beryllium is very similar. Unfortunately, in Poland there is no primary sources of beryllium. The potential sources for this metal's wastes are ashes from the burning coals of the Upper Silesian Coal Basin. These resources are estimated at about 97 thousand tones of beryllium. One major obstacle is the lack of appropriate technology of beryllium recovery from such materials.

Another critical raw material that is not mined and produced in Poland is boron. Minerals of this element are found in rock salt deposits derived from "Kłodawa". These resources are estimated at 6000 thousand tones of borium B with its content ranging from 0.01 to 0.09%. Mainly borates, eg. calcium borax or sodium-calcium borate and boron metal are traded internationally.

Chromium – chromites are the primary sources of this raw material and all of them are imported into Poland. Since 2006, Poland abandoned the production of ferrochrome and sodium chromate. Currently, the main domestic consumer of chromites is refractory industry (mainly Zakłady Magnezytowe "Ropczyce"). At the turn of the century we developed and implemented a modified method of producing sodium chromate in Poland, which allowed for the utilization of various chromium waste materials [Kowalski]. This technology is a low-waste method and much less energy consuming compared to the existing dolomite method. Unfortunately, ZCh. "Alwernia" have changed their production profile. Therefore, the need for chromites in Poland has been significantly reduced. Apart from chromites, ferro- chromium, chromium metal and disodium chromate is being traded.

Fluorite - the basic raw material of fluoride is fluorite. In Poland, fluorite is found in the deposit Stanisławów but its acquisition is unprofitable at the moment. KZPN "Bonarka" developed a method of producing synthetic fluorite using hydrogen fluoride originating from the manufacturing process of feed phosphates. These plants have changed the technology of production of feed phosphates and thereafter KZPN "Bonarka" were closed down. ZCh. "Siarkopol" produces a small amount of criolyte in the course of the manufacturing process phosphoric acid extraction method. The domestic demand is converted by import.

Phosphorite and apatite concentrates are found in the "new" list of critical raw materials. They are the basic raw material for the production of "life-giving" phosphorus, ie. phosphate fertilizers and feed phosphates. In Poland, small phosphate rock deposits are found, which have no economic significance. Domestic production of phosphorus compounds is based on the import of phosphorus raw materials. Therefore, in many countries, including Poland, studies were undertaken on the recovery of phosphorus from the waste.

Gallium – bauxite is the main source of primary gallium, which is processed with Bayer's method. It is estimated that about 90% of gallium obtained from raw materials is derived from bauxite. However, in Poland there is no bauxite. Another source for obtaining gallium is zinc and lead sulfide ores. In domestic deposits of these ores gallium is found in the amount of about 0.002%. Domestic resources are estimated at 120 tonnes Ga.

Germanium – germanium sulfide Zn-Pb ore and copper are the main sources of germanium. This metal is found in a dispersed form. Zn-Pb ore deposits from the Silesian-Cracow's deposits are the potential source of this metal in Poland. The resources of this element in these deposits are estimated at 120 tonnes Ge [Jarosiński 2013]. This paper presents the technological aspects of the preparation of gallium and germanium. Ashes from coal combustion are also a potential source of germanium in Poland.

Natural graphite – in Poland there are no deposits of this critical raw material. Synthetic graphite is produced in plants in Nowy Sacz and Raciborz. Production yields 40–60 tonnes. Both synthetic and natural graphite are used for the manufacture of crucibles, graphite lining of electric furnaces or graphite electrodes.

Indium is dispersed in some sphalerite and copper-bearing shales. Polish deposits of Zn-Pb ores do not contain indium and for these reasons Indium's domestic demand is covered by imports, mainly from China.

The cobalt content in the lithosphere is estimated at 0.001%. This metal is generally obtained in the processing of ore concentrates Ni-Co-Cu. The presence of cobalt was confirmed in Polish copper ore deposits in Przedsudecka Monocline. The amount of this element in these deposits is about 109.2 thousand tones. In the course of domestic copper production from concentrates by pirometallurgical process (shaft furnace) part of cobalt contained in the initial material can be recovered. The remainder of the metal is concentrated in the converter slag, which represents a potential source of cobalt. Also, waste from the processing of cobalt scrap eg. stainless steel, used carbide cutting tools are considered as a secondary source of cobalt.

Metallic magnesium – generally obtained by means of thermoectrolysis. Raw material base is rich - from magnesite, dolomite up to the magnesium salt contained in seawater. The main drawback of the technology for producing magnesium metal is its energy-intensiveness. Dolomites, which are easily found in Poland, are a potential source of magnesium. The preferred method for obtaining magnesium from dolomite is to reduce roasted dolomite. This method has not been implemented primarily due to economic reasons.

Magnesite exists in two forms: crystalline or cryptocrystalline. The first form is used in refractory industry, while both forms of magnesite are an initial material for the production of calcined magnesite. This compound is a raw material used in the building, chemical, glass and ceramic industries. Magnesite deposits are found in Lower Silesia. Six tonnes deposits have been documented with total resources of 14 704 thousand tones. Only Zakład Magnezytowy "Grochow" Sp. z o.o. performs extraction of the raw material from the deposit "Braszowice". Mainly roasted, calcined and melted magnesite is being imported from countries such as Slovakia, China and Brazil [Gawlik and Mokrzycki].

The platinum group metals – the source of this group of metals in Poland is copper-shale ore. Practice shows that these elements are introduced with the raw material copper and almost entirely pass to the final stage of production, ie. electrorefining of copper. Platinum group with silver, gold, selenium and tellurium, the so-called pass. anode sludge. The increasing participation in the preparation of these metals falls on secondary sources – scrap and waste products derived from domestic and foreign producers. Hydrometallurgical method of acquiring precious metals, including platinum, out of WEEE was developed and implemented in Poland. In Poland the consumption of platinium group metals amounted to 1060 kg out of which approximately 30 kg is derived from domestic copper production.

Rare Earth Elements (REE) – these elements are present in nature and form a dispersed light lanthanide-rich mineral with a larger ionic radius and itrium-earth minerals - heavy lanthanides-rich with smaller ionic radius. In the area of Szklarska Poreba there are deposits of REE, whose resources are estimated at about 65 thousand tones. Average REE content amounts 0.26%. The minerals of these elements found in the Bogatynia region contain up to 1.55% REE, however they do not have a deposit character and therefore REE are not extracted there.

Phosphogypsum wastes from the manufacture of phosphoric acid from apatite concentrate are the primary secondary raw materials of rare earth in Poland, containing 0.69% REE. The landfill ZCh. "Wizów" during many years has accumulated about 2 million tones of phosphogypsum apatite, which is almost 8.3 thousand tones of REE. This amount of phosphogypsum contains more than 200 tones of yttrium and 33 tones of europium. There have been different variants developed of the recovery of these elements from apatite phosphogypsum. These researches including REE recovery with simultaneous utilization of phosphogypsum were verified in pilot scale. [Jarosiński, Kijkowska... 1993 Jarosiński, Kowalczyk... 1993]. Certain amount of REE is recovered domestically during the processing of WEEE according to the procedure proposed by Góralczyk and Uzunow 2013. Ashes from the burning coals recovery can be potential resource of REE, in which the content fluctuates in the range of 0.2% REE [Kiss Moszko J., Bielecka].

Silicon metal – this term refers to a metallurgical method of producing silicon. Particularly sought after is the semiconductor metallic silicon with a high degree of purity (99.997% Si) obtained from imported polycrystalline silicon. The sole domestic producer of silicon semiconductor is Cemat-Silicon. Semiconductor silicon single crystals are used in electronics - transistors, rectifiers, photocells, solar cells. Technical-grade silicon can be produced based on national quartzites and crystalline quartz core. The only Fe-Si producer in Poland is "Huta Laziska" SA.

Coking coal - the basic direction of processing this type of coal is the production of blast furnace and foundry coke. Almost 90% of coke is designed for blast furnace process - production of pig iron and pyrometallurgical processes for the production of non-ferrous metals. In Poland there are several coking plants and the largest of them is in Zdzieszowice. Poland is a significant producer of metallurgical coke, which amounts to 4813 thousand tones [Bilans... 2009].

Tungsten – according to the data presented in paper [Radwanek-Bak], it is believed that occurrence of tungsten ore deposits in Poland is practically none. The only exception is the Mo-W-Cu ore of porphyric type found in the area of Myszków. The bed was not explored until now.

Remarks

The presented data shows that Poland does not have its own sources of most of the critical raw materials. Poland lacks raw materials such as antimony, beryllium, natural graphite, indium, niobium and others. However, Poland has own sources of coking coal, from which metallurgical coke is obtained. Poland is a major exporter of this product to the EU countries.

Secondary raw materials play an increasingly important role in the area of critical raw materials. In Poland, there is a growing interest in WEEE from which both precious metals, including platinum and rare earths – mostly yttrium and europium are derived.

The data presented in the article suggests the possibility of obtaining gallium and germanium from the waste products deriving from the process of the metallic zinc winning from the domestic ores of Zn-Pb. Further development of domestic zinc industry is connected with search of new zinc sources and their complex processing. This solutions take into account environmental issues and social conditions. New deposits in Poland contain germanium and gallium.

Within the framework of research projects, both national and European, there were actions taken in Poland aiming at the recovery of precious metals and rare-earth metals from secondary raw materials (WEEE).

Domestic industry of phosphate fertilizers is based on raw materials imports. Lack of phosphorus raw materials stimulates obtaining phosphorus from waste, such as municipal sewage and sediment.

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Streszczenie

Deficyt lub brak niektórych surowców mineralnych w krajach UE wymusił działania zmierzające do zabezpieczenia podaży surowców mineralnych w ramach Unii Europejskiej. Prognozy wskazują, że popyt na surowce krytyczne oraz metale „high-tech" będzie wzrastał wraz z rozwojem innowacyjnych technologii. Do krytycznych surowców w UE zalicza się 20 surowców o istotnym znaczeniu gospodarczym, których dostępność na rynku UE jest coraz bardziej zagrożona. Z analizy danych przedstawionych w artykule wynika, że pozyskiwanie pierwiastków krytycznych w Polsce byłoby możliwe zarówno z surowców pierwotnych, jak i wtórnych. W pracy zasugerowano kierunki pozyskiwania niektórych pierwiastków krytycznych w warunkach krajowych.

Słowa kluczowe: surowce krytyczne, metale krytyczne, źródła