



SCREEN

Coordination and Support Action (CSA)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227.

Start date : 2016-12-01 Duration : 30 Months
www.screen.eu

Circular Economy and zero waste aspects and business models of production

Authors : Mrs. Marjaana KARHU (VTT), Joanna Kotnis, Yongxiang Yang (TU Delft); Pierre Menger, Ainara Garcia Uriarte (Tecnalia); Kimmo Kaunisto, Elina Huttunen-Saarivirta, Elina Yli-Rantala, Marjaana Karhu (VTT); Lena Sundqvist Ökvist, Xianfeng Hu (Swerea MEFOS); Teodora Retegan (Chalmers); María González-Moya (IDENER); Michalis Samouhos, Maria Taxiarchou (NTUA); Michal Drzazga, Jolanta Niedbala (IMN)

SCRREEN - Contract Number: 730227

Solutions for CRITICAL Raw materials - a European Expert Network Dimitrios Biliouris

Document title	Circular Economy and zero waste aspects and business models of production
Author(s)	Mrs. Marjaana KARHU, Joanna Kotnis, Yongxiang Yang (TU Delft); Pierre Menger, Ainara Garcia Uriarte (Tecnalia); Kimmo Kaunisto, Elina Huttunen-Saarivirta, Elina Yli-Rantala, Marjaana Karhu (VTT); Lena Sundqvist Ökvist, Xianfeng Hu (Swerea MEFOS); Teodora Retegan (Chalmers); María González-Moya (IDENER); Michalis Samouhos, Maria Taxiarchou (NTUA); Michal Drzazga, Jolanta Niedbala (IMN)
Number of pages	206
Document type	Deliverable
Work Package	WP4
Document number	D4.3
Issued by	VTT
Date of completion	2018-06-05 11:46:50
Dissemination level	Public

Summary

This deliverable reports the survey done in SCRREEN project in Task 4.3 relating to environmental trends and Circular Economy (CE) aspects of CRM production. For each CRM, the Circular Economy aspects were addressed in order to identify the gaps that limit performance of the processing chains, hinder closing the loop and hinder a zero-waste CRM production. Information on processes, production, solutions and eco-design principles for closing the loop of raw materials in order to support the zero-waste point-of-view, resource efficiency and energy efficiency simultaneously were gathered. In addition, the aspects supporting Circular Economy were evaluated trying to resolve the identified challenges. Lastly, the environmental issues e.g. toxicity related to CRMs production were reviewed.

Approval

Date	By
2018-06-05 11:52:19	Mrs. Marjaana KARHU (VTT)



D4.3 Circular Economy and zero waste aspects and business models of production

Contributors:

Joanna Kotnis, Yongxiang Yang (TU Delft): Antimony, Indium, Dysprosium, Neodymium, Praseodymium

Pierre Menger, Ainara Garcia Uriarte (Tecnalia): Beryllium, Borates

Kimmo Kaunisto (VTT): Magnesium

Elina Huttunen-Saarivirta (VTT): Cobalt, Tungsten

Elina Yli-Rantala (VTT): PGMs, Natural rubber

Marjaana Karhu (VTT): Phosphate Rock, White Phosphorus

Lena Sundqvist Ökvist, Xianfeng Hu (Swerea MEFOS): Coking coal, Natural Graphite, Vanadium

Teodora Retegan (Chalmers): Bismuth, Fluorspar, Gallium, Helium, Tantalum

María González-Moya (IDENER): Germanium, Niobium

Michalis Samouhos, Maria Taxiarchou (NTUA): Europium, Gadolinium, Terbium, Erbium, Yttrium + others, Samarium, Lanthanum, Cerium, Silicon Metal, Baryte, Scandium

Michał Drzazga, Jolanta Niedbała (IMN): Hafnium

[April 2018]

1 INTRODUCTION

European Commission recently published report on Critical Raw Materials and the Circular Economy¹ suggesting that the share of secondary sources in raw material supply is one of several simplified approaches to assess circular use of raw material. Despite the fact that several CRMs have a high technical and real economic recycling potential, the recycling input rate (a measure of the share of secondary sources in raw material supply) of CRMs is generally low. One reason for that is that sorting and recycling technologies for many CRMs are not available yet at competitive costs. In addition, the supply of many CRMs is currently locked up in long-life assets, which implies delays between manufacturing and scrapping and influences negatively to present recycling input rates. One reason is also that the demand for many CRMs is growing in various sectors and the contribution from recycling is largely insufficient to meet the demand.

This deliverable reports the survey done in SCRREEN project in Task 4.3 relating to environmental trends and Circular Economy (CE) aspects of CRM production. For each CRM, the Circular Economy aspects were addressed in order to identify the gaps that limit performance of the processing chains, hinder closing the loop and hinder a zero-waste CRM production. Information on processes, production, solutions and eco-design principles for closing the loop of raw materials in order to support the zero-waste point-of-view, resource efficiency and energy efficiency simultaneously were gathered. In addition, the aspects supporting Circular Economy were evaluated trying to resolve the identified challenges. Lastly, the environmental issues e.g. toxicity related to CRMs production were reviewed.

¹ European Commission 2018. COMMISSION STAFF WORKING DOCUMENT. Report on Critical Raw Materials and the Circular Economy. Brussels, 2018. Available: https://ec.europa.eu/commission/publications/report-critical-raw-materials-and-circular-economy_en

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

2 CONTENT

1	INTRODUCTION.....	2
3	ANTIMONY.....	5
4	BARYTE	11
5	BERYLLIUM.....	17
6	BISMUTH.....	23
7	BORATES.....	25
8	COBALT	30
9	COKING COAL.....	38
10	FLUORSPAR	40
11	GALLIUM.....	44
12	GERMANIUM.....	46
13	HAFNIUM.....	56
14	HELIUM.....	59
15	INDIUM.....	62
16	MAGNESIUM.....	70
17	NATURAL GRAPHITE	74
18	NATURAL RUBBER	76
19	NIOBIUM.....	84
20	PLATINUM-GROUP METALS (PGM)	91
21	PHOSPHATE ROCK AND WHITE PHOSPHORUS.....	99
22	RARE EARTH ELEMENTS.....	108
23	CERIUM.....	108

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

24	ERBIUM.....	115
25	EUROPIUM.....	120
26	GADOLINIUM	126
27	OTHERS (HOLMIUM, LUTETIUM, YTTERBOIM, THULIUM.....	132
28	LANTHANUM.....	139
29	NEODYMIUM, PRASEODYMIUM, DYSPROSIUM.....	146
30	SAMARIUM	157
31	TERBIUM.....	165
32	YTTRIUM	171
33	SCANDIUM.....	178
34	SILICON METAL.....	184
35	TANTALUM.....	194
36	TUNGSTEN	196
37	VANADIUM	202

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

3 ANTIMONY

3.1 INTRODUCTION

Antimony is a soft, silver-grey metal, which is used to produce antimony trioxide (Sb_2O_3). Sb is important for several sectors, namely chemical industry, electrical industry, metal and mineral industry. Its main applications are flame retardants and lead-acid batteries as hardener. It is also used in lead alloys, in plastics as catalysts and stabilisers and as decolourizing agent in glass for electronics. The EU is completely reliant on importing unwrought antimony to meet the demand on Sb_2O_3 . Antimony in form of unwrought metal was assessed as critical material first in 2011 and this result remains the same in further assessments (European Commission, 2017).

3.2 CIRCULAR ECONOMY ASPECTS

Improving the efficiency of metal production requires taking a circular perspective, thinking of the whole value chain. A fully closed system is not possible to obtain, due to physical limitations. There will always be losses in the system because of the thermodynamics laws, human error, imperfect technology and economics. Yet many improvements in the area of metal production can be implemented (UNEP, 2013). The aim is to close the metal loop as far as it is possible, which can be achieved by implementing different strategies. First, material production phase has inevitable impact on the supply of resources, environment, and waste generation. Product design can contribute significantly to a more circular system by implementing better durability, design for reuse or recycling principles. Use phase, reusing or recycling the material from scrap and end-of-life products are subsequent elements of a closed-loop supply chain (European Commission, 2011; M. A. Reuter et al., 2015).

3.2.1 DESIGN

In order to assure efficient material use according to circular economy principles, reduction of generated waste is required. One of ways to achieve that is to minimise necessity of recycling by implementing better product design. The objective is to use less resources and lower material complexity (Reuter et al., 2015). In order to improve functionality of products, increasing number of different elements are mixed together. This causes difficulties in separating materials after products' end of life and therefore hinder possibility to close the metal production loop (UNEP, 2013). Antimony is mostly alloyed with lead and other elements and joined with different materials as fire resistance (European Commission, 2017).

The concept of design for recycling is a way to overcome those issues. It includes understanding of physics involved in material separation. Yet, the design for recycling is a complex challenge, since it has to provide the same functionality using less material or less complex combinations, which increase the cost of products. Presently it is not the preferable solution since the metal value is too low. The price for antimony reaches 9

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

dollars per kilogram, which is rather low comparing to other metals. The design should then focus on maximising resource recovery and efficiency of the process (UNEP, 2013).

Another concept found in the literature is design for sustainability. This approach looks into the best sustainability performance of a design, not only recyclability, but also energy efficiency and durability as aspects of a life cycle thinking. The life cycle assessment (LCA) analytical tool helps designers to find hotspots of the specific product, identify trade-offs between better performance and environmental footprint. This enable making a comparison for choosing the most optimal option (UNEP, 2013).

3.2.2 MANUFACTURING

No specific information was found on circular economy aspects of antimony during product manufacturing. There is however some research on new scrap generated during production of goods, which is also a source of antimony. In general, new scrap is usually high purity, has known properties and high value, its recycling is economically beneficial and can be easily accomplished (Graedel et al., 2011).

New scrap of antimony is generated by manufacturers of solders and Sb-alloys and also at plants using alloys for production of end-use items. The Sb-containing new scrap can be put back to the production system at the plant or transferred to external recyclers. It is estimated that in 2000 in US 2000 tons of antimony was produced from the new scrap only (Carlin, 2000). No information was found for the EU.

3.2.3 END OF LIFE RECYCLING

The main obstacle for recycling to take place is lack of economic incentives. Metal producers will only process scrap material when they can profit from that operation, otherwise the recovery would increase the overall production cost. Currently most of the recycling activities are undertaken together with large scale primary production of carrier metals (iron, copper, lead, nickel and others). For valuable and scarce metals, like antimony, the demand is too little to run a dedicated recovery plant, due to high investment costs (UNEP, 2013). Moreover, most of the recovery technologies are still in laboratory stage and upscaling them to be used in the industry is presently a serious obstacle (Dupont, Arnout, Tom, Koen, & Jones, 2016).

With increasing stocks of metals in many different products, their successful recovery depends strongly on the collection rate of products bearing them. The collection is usually a logistic challenge, but also depends on policy, which can differ from country to country. Consequently, the collection rates are hindered by lack of awareness or motivation among consumers on recycling possibilities. In the end, valuable secondary materials end up in municipal waste streams, especially small electronic devices, like batteries in case of antimony.

After the end of life, used products become a source of secondary materials, making the recycling a very important aspect of metal use in the future. One of the issues connected to recycling is the time after material will be available for recovery. The availability of secondary material depends on the lifetime of Sb-bearing products, in particular flame retardants, lead-acid batteries, lead alloys used in multiple applications and plastics.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Yet, recycling can secure only part of future demand, due to the delay in materials availability for recovery. Another aspect is the fact, that amount of metals used in production in the past was lower than it is now. Also, there are always metal losses during primary production, as well as from recycling (UNEP, 2013). Current end of life recycling rate for antimony reaches 28% and the material is obtained mostly from lead alloys found in scrap lead-acid batteries (European Commission, 2017).

Another issue hindering the recovery of antimony is high dispersion of this metal in final applications. This is the case especially with flame retardants and catalysts used in plastics (European Commission, 2017).

Incomplete material liberation from the scrap products is next issue causing the material loss. Complex products often cannot be efficiently separated into pure materials and therefore land in wrong stream of recyclates. This is caused also by randomness and physical properties of each material. The degree of liberation determines the quality of secondary raw materials (UNEP, 2013).

It is known that improved recycling technologies can be much more economically feasible than primary production, mostly due to lower energy use. Therefore, recycling techniques substantially reduce environmental footprint of metal production (UNEP, 2013).

3.2.4 RESIDUES

Industrial processes generate substantial amounts of waste, which can be a source of valuable metals. Research has shown that there are technologies tested on laboratory scale to recover antimony from residues, yet often those operations are not economically feasible. This could be overcome by implementing different metallurgical processes in order to recover higher number of elements at the same time (European Commission, 2017; UNEP, 2013). As an example, treating lead processing residues (anode slime) by chloridization leaching and controlled distillation can recover not only silver and gold, but after further processing also antimony, arsenic, copper and bismuth (Cao, Chen, Yuan, & Zheng, 2010). Residues from zinc primary production are potentially sources of valuable metals, like antimony but also silver, cobalt, germanium or indium (UNEP, 2013).

3.3 ENVIRONMENTAL ISSUES

3.3.1 PRODUCTION

Growing global demand for metals causes necessity for mining lower quality ores to meet the material needs. The overall decrease of ore grades leads to higher amounts of ground material to be extracted, higher energy use to process the material and consequently growth in greenhouse gases emissions, land disruption, higher pollution and water use. Primary production residues can pose a danger of releasing dangerous or even toxic substances to the soil or water, while being stored in ponds. Recycling of those production waste streams will recover value that would be lost otherwise but also save the environment (UNEP, 2013).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Primary and secondary production include multiple processes that are generating emissions to the atmosphere and thereby can cause environmental issues. Different production processes using furnaces with coal as a fuel can contribute to antimony emissions. Fly ash produced during the coal combustion process are carrying dangerous and often toxic elements and releasing them to the environment. The fly ash is a heterogeneous mixture of fine particles with varying composition, depending on the carbon used in the combustion. Sb is vaporised in the combustion process and constitutes the largest anthropogenic source of antimony released to the atmosphere, which can pose environmental and health risks (Smichowski, 2008). Antimony is lost by emissions to water, air and land, which happen during primary production, as well as during manufacturing. The Sb capture from the air should be improved, since in 2010 global air emissions reached 1904 tons. This is caused mostly by fuel combustion, waste incineration, brake wear and metal production. Emissions from coal fired power plants, metal production plants and municipal waste incinerators can be decreased by applying air pollution system with appropriate filters, which can be then treated for Sb recovery. Situation is more complicated with emissions from vehicle break wear, since they are not localised and presently no solution is available (Dupont et al., 2016).

3.3.2 PRODUCT MANUFACTURING

Exposure to antimony metal can pose a danger for human health. People working in antimony ore and metal processing plants as well as in production of antimony chemicals or manufacturing of products are at the highest risk of exposure to Sb. The EU investigated possible health effects of exposure to antimony trioxide based on laboratory tests. The assessment identified skin irritation, toxicity to the lungs and development of tumours in the lungs from inhalation exposure. However, the use of effective working safety practices and proper equipment minimise the exposure. Monitoring of workers in antimony trioxide production plant on a long term has not identified negative health effects. Taking into account the increasing number of application for antimony, there way is which it can get into the environment, it is advised to extend the research and monitoring of antimony effects on the environment and human health (Schwarz-Schampera, 2014). According to International Antimony Association, there is no carcinogenic risk when there is no inhalation exposure, which is the case in modern, controlled workplaces using protective equipment (International Antimony Association (VZW), 2017).

3.3.3 USAGE

Antimony is considered as potentially toxic metal at very low concentrations and doesn't have known biological functions. According to International Agency for Research on Cancer there is evidence that antimony trioxide is carcinogenic in experimental animals. However, the German Research Community and U.S. Environmental Protection Agency have not assessed Sb as carcinogenic, yet they have classified it as a pollutant (Smichowski, 2008).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

3.3.4 END OF LIFE RECYCLING

The typical concentration of antimony in flame retardants in e-waste reaches 1700 mg/kg, while annual global emission of Sb in e-waste is estimated as 34000 tons, assuming global waste production of 20 million tons per year (UNEP, 2013). Environmental aspect of metal recycling is related with inappropriate treatment of collected end of life scrap. Only one third of waste electronic equipment is reported as officially treated according to EU Directive. The rest of gathered unreported electronic waste is presumed either to be treated within the EU without appropriate environmental caution or transported illegally outside of Europe, where EU environmental and health standards are not met. There is an economic incentive for shipping waste to developing countries, where informal recycling channels often use manual recycling that cause health risks for employees (UNEP, 2013).

Presence of antimony in residues from municipal waste incineration can cause risks of uncontrolled release of toxic Sb to the environment. Therefore, it is crucial to implement treatment of incineration residues (Dupont et al., 2016). It is possible to recover antimony from plastics containing flame retardant. However, the amount of Sb in those materials is highly dependent on the type of plastic and its application. Efficient recovery of Sb from those sources would require applying proper sorting and screening technologies to select particles with high Sb content, which also increase recovery costs. Those methods are for instance X-ray fluorescence spectroscopy or X-ray transparency.

3.4 SUMMARY

Antimony is a valuable metal that is mostly used in flame retardants and lead-acid batteries as hardener. It is also present in lead alloys, in plastics as catalysts and stabilisers and as decolourizing agent in glass for electronics. One of the aspects of circular economy, that is applicable also to other critical metals, is better products design. The objective is to use less resources and lower material complexity. Concepts that were created to support it are design for recycling and design for sustainability. Another aspect of circular economy is recycling. Presently, the main obstacle for recycling to take place is the lack of economic incentives. With increasing stocks of metals in many different products, their successful recovery depends strongly on the collection rate of products bearing them. Apart from end of life products, industrial processes generate substantial amounts of waste, which can be a source of valuable metals. Residues from zinc primary production are potentially sources of valuable metals, like antimony but also silver, cobalt, germanium or indium. There are also environmental concerns that need to be considered. Primary and secondary production include multiple processes that are generating emissions to the atmosphere and thereby can cause environmental issues. Antimony is lost by emissions to water, air and land, which happen during primary production, as well as during product manufacturing. According to the performed research, there is no carcinogenic risk when there is no inhalation exposure to antimony, it is however classified as pollutant.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

3.5 REFERENCES

- Cao, H., Chen, J., Yuan, H., & Zheng, G. (2010). Preparation of pure SbCl₃ from lead anode slime bearing high antimony and low silver. *Transactions of Nonferrous Metals Society of China*, 20(12), 2397–2403. [https://doi.org/10.1016/S1003-6326\(10\)60661-9](https://doi.org/10.1016/S1003-6326(10)60661-9)
- Carlin, J. F. (2000). *Antimony Recycling in the United States in 2000*. U.S. Geological Survey. Retrieved from <https://pubs.usgs.gov/circ/c1196q/c1196q.pdf>
- Dupont, D., Arnout, S., Tom, P., Koen, J., & Jones, P. T. (2016). Antimony Recovery from End-of-Life Products and Industrial Process Residues: A Critical Review. *Journal of Sustainable Metallurgy*, 2(1), 79–103. <https://doi.org/10.1007/s40831-016-0043-y>
- European Commission. (2011). Circular Economy. Closing the loop. <https://doi.org/10.1145/948449.948453>
- European Commission. (2017). *Study on the review of the list of critical raw materials. Critical Raw Materials Factsheets*. Luxembourg: Publications Office of the European Union. <https://doi.org/10.2873/398823>
- Graedel, T. E., Allwood, J., Birat, J., Hagel, C., Reck, B. K., & Sibley, S. F. (2011). What Do We Know About Metal Recycling Rates?, 15(3), 355–366. <https://doi.org/10.1111/j.1530-9290.2011.00342.x>
- International Antimony Association (VZW). (2017). *i2a's assessment of NTP's long-term carcinogenicity studies on antimony trioxide (ATO)*. Brussels. Retrieved from <http://www.antimony.com/files/cms1/publications2016/i2a-ntp-study-assessment-final-170130.pdf>
- Reuter, M. A., Matuszewicz, R. W., & van Schaik, A. (2015). Lead, zinc and their minor elements: Enablers of a circular economy. *World of Metallurgy - ERZMETALL*, 68(3), 134–148. Retrieved from <http://www.scopus.com/inward/record.url?eid=2-s2.0-84931832896&partnerID=40&md5=51610431c1edba266b32334c182bb604>
- Schwarz-Schampera, U. (2014). Antimony. In G. Gunn (Ed.), *Critical Metals Handbook* (I, pp. 70–98). John Wiley & Sons, Ltd.
- Smichowski, P. (2008). Antimony in the environment as a global pollutant: A review on analytical methodologies for its determination in atmospheric aerosols. *Talanta*, 75(1), 2–14. <https://doi.org/10.1016/j.talanta.2007.11.005>
- UNEP. (2013). Metal Recycling: Opportunities, Limits, Infrastructure. A Report of the Working Group on the Global Metal Flows to the International Resource Panel. Reuter, M. A.; Hudson, C.; van Schaik, A.; Heiskanen, K.; Meskers, C.; Hagelüken, C.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

4 BARYTE

4.1 INTRODUCTION

Baryte or barite (BaSO_4) consists of the barium sulfate phase and also an individual mineral group which comprises also celestine, anglesite and anhydrite. Baryte is generally white or colorless, and is the main source of barium. Baryte and celestine in nature usually form a solid solution $(\text{Ba,Sr})\text{SO}_4$. Baryte occurs in a variety of depositional environments, and is deposited through a large number of processes including biogenic, hydrothermal, and evaporation, among others. Baryte commonly occurs in lead-zinc veins in limestones, in hot spring deposits, while is also frequently found in iron ores [1].

Baryte is included in recent (2017) European Commission list of Critical Raw Materials (CRMs) among 26 more materials taking into account its high supply-risk and a high economic importance [2]. Baryte deposits are indeed limited in EU member countries (minor deposits still exist in Germany, Romania and Greece). Major deposits of the mineral occur in Brazil, Nigeria, Canada, Chile, China, India, Pakistan, Guatemala, Iran, Mexico, Morocco, Peru, Turkey, South Africa and US [3]. Small vein type barite deposits occur throughout the world, but very few are exploitable. Large vein type deposits were mainly worked before 1980s and there for the discovery of new occurrences is crucial. World baryte production for 2016 was 7.3 million tonnes. The major baryte producer countries are as follows (in thousand tons according to the "Barytes Association"): China (3,100), India (1,300), Morocco (550), United States (430), Turkey (240), Russia (210), Mexico (200), Iran (200), Kazakhstan (190) and Thailand (160).

About the 69–77% of globally produced baryte is used as a weighting agent for drilling fluids in oil and gas exploration to suppress high formation pressures and prevent blowouts. The amount of required baryte increases as a percentage of the total mud mix in relation to hole' depth. An additional benefit of baryte is that it is non-magnetic and thus does not interfere with magnetic measurements taken in the borehole, either during logging-while-drilling or in separate drill hole logging. The baryte material used for oil drilling should have a granulometry $-75 \mu\text{m}$. The mineral is also used in added-value applications which include filler in paint and plastics, sound reduction in engine compartments, coat of automobile finishes for smoothness and corrosion resistance, friction products for automobiles and trucks, radiation-shielding cement, glass ceramics and medical applications. Furthermore, it is also used for the synthesis of barium carbonate which is a component of LED glass for television and computer screens (in cathode ray tubes) [4,5].

Baryte is also the main primary resource of barium, an alkaline earth metal which presents a similar chemical properties to magnesium, calcium, and strontium (such as medium specific weight and good electrical conductivity). Elemental barium is used for the construction of bearing alloys, lead-tin soldering alloys – to increase the creep resistance, alloy with nickel for spark plugs, additive to steel and cast iron as an inoculant, alloys with calcium, manganese, silicon, and aluminium as high-grade steel deoxidizers [4,5].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

4.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

4.2.1 PRODUCTION

4.2.1.1 BARITE CONCENTRATE BENEFICIATION

Barite occurrences are commonly associated with fluorite (CaF_2) concentrations while in most of cases contains a variety of impurities such as silicates, calcite, and iron as. Several processes have been developed for the beneficiation of barite concentrate prior to its use as a drilling mud. The most widely used process for barite beneficiation and enrichment consists of a combination of gravity separation and flotation techniques (Figure 1). Using this flow sheet, a chemical grade and drilling mud grade barite concentrate are produced. Flotation, which is more efficient in case of fine sized barite concentrate, can be either reverse or direct. Reverse flotation generally involves removals of base metals sulphides or pyrite leaving a concentrated barite in the tailing, which is recovered using flotation. Direct flotation of barite is performed from the ores that contain fluor spar, silicates, and Rare Earth Oxides (REO) [6]. Various agents are used at the flotation processing in relation to specific impurities. Sodium silicate is an important reagent acting as a dispersant and silicate depressant. Aluminum depresses calcite while citric acid is a fluor spar depressant and is used during barite flotation from the ores that contain fluor spar.

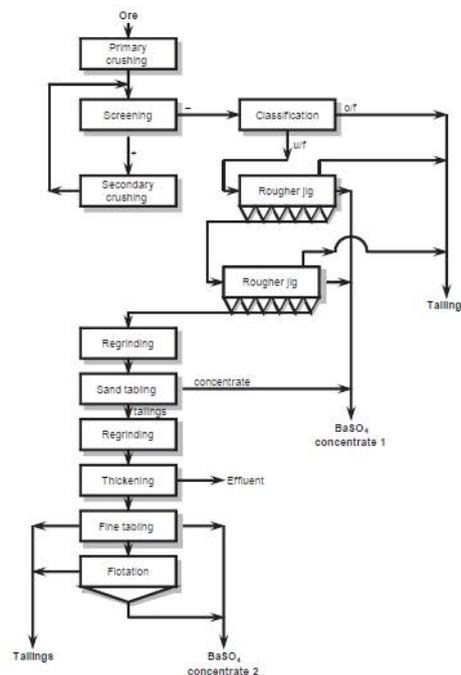


Figure 1. Beneficiation of barite ore using gravity separation and flotation [6]

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Physical separation processes for barite beneficiation have been used in the past. Since the early 1960s, a number of operating plants used a combination of gravity concentration and magnetic separation (Figure 2). The concentrate after the separation is submitted to acid leaching aiming to the removal of the remaining iron content.

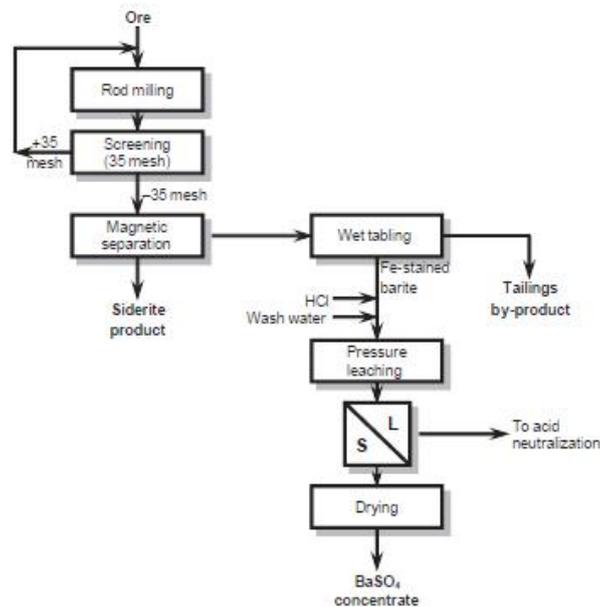


Figure 2. Beneficiation of barite concentrate via magnetic separation method [6].

After beneficiation, the barite concentrate is classified in relation to specific applications. The barite market is divided into three main product grades as (1) drilling mud, (2) chemical grade, and (3) filler grade. The typical specifications of these products is shown in Table 1.

Table 1. Specification of different barite grades.

Drilling Mud	Chemical Grade	Filler Grade
BaSO ₄ =>92%	BaSO ₄ =>96–98%	BaSO ₄ =>85–95%
Specific gravity = 4.2 g/cm ³	CaF ₂ <0.5%	Brightness = 70–95%
% 0.075 mm =<989%	SiO ₂ <1.0%	100% <0.045 m
% 0.006 mm =>70%	F ₂ O ₃ = 0.5%	
	SrSO ₄ =<2%	
	Sr/Bo =<0.017	
	100% <0.04 mm	

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

Recently, specific attention is given to the environmental impact of baryte when used as a weighting agent to drilling muds to counteract pressure in the geologic formations being drilled. It was found out that barite muds contain elevated (compared to marine sediments) concentrations of several metals. Some of these metals are bioavailable, may harm the local marine ecosystem [7]. An impact indicator can be considered the bioavailable fraction of metals that are dissolved from the nearly insoluble, solid barite into seawater or sediment porewater. Barite–seawater and barite–porewater distribution coefficients (K_d) have been calculated for determining the predicted bioavailable fraction of metals from drilling mud barite in the water column and sediments, respectively. Values for K_d barite–seawater and K_d barite–porewater were calculated for barium, cadmium, chromium, copper, mercury, lead, and zinc in different grades of barite. It was estimated that mercury, copper and lead are the metals with the higher distribution coefficients.

4.2.2 USAGE

Barite concentrate is widely used as a weighting agent in oil drilling muds. These high-density muds (Figure 3) are pumped down the drill stem, exit through the cutting bit and return to the surface between the drill stem and the wall of the well. The main functions of drilling barite rich mud include providing hydrostatic pressure to prevent formation fluids from entering into the well bore, keeping the drill bit clean during the drilling process and suspending the drill cuttings while drilling is paused and when the drilling assembly is removed from the hole. The drilling mud is also used to avoid formation damage and to limit corrosion. The advantages for barite's use in this application over other materials are: its chemical neutrality, low magnetic susceptibility and environmentally acceptable characteristics. Finally, it is far less abrasive than other materials and does little damage to drilling equipment.



Figure 3. Barite powder used for preparation of water-based mud (Wikipedia).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

4.2.3 END OF LIFE

Burial is the most common practice that used for the disposing of baryte-bases drilling mud wastes. Commonly, the solids are buried in a pit used for collection and temporary storage of waste mud and cuttings after the liquid is allowed to evaporate. Pit burial is a low-tech method that does not require wastes to be transported away from the well site, and, therefore, is widely used by many operators. On the other hand, burial doesn't consist an appropriate method in case mud wastes that contain high concentrations of oil, salt, biologically available metals, industrial chemicals, and other materials with harmful components that could migrate from the pit and contaminate usable water resources. Secure landfills are specially designed land structures which employ protective measures against off-site migration of contained chemical waste via leaching or vaporization using a synthetic landfill liner [9].

Incineration is an alternative waste management choice in case of barite mud which is frequently contaminated with oil amounts. Incineration is one of the best thermal treatment disposal options because thermally treated wastes are decomposed to less hazardous by-products. Controlled incinerators operate at sufficient temperatures for complete thermal decomposition of hazardous wastes. Non-hazardous and hazardous solids, liquids, and gases can be incinerated. However, incineration of heavy metals such as lead, mercury or cadmium, frequently contained in barite, consist a parameter that should be taken into account [9].

The use of barite mud wastes, after their drying, as an aggregate for roads construction should also be examined.

4.3 SUMMARY

Baryte (Barium Sulphate) is a chemically inert heavy mineral having a specific gravity of about 4.5 g/cm³ and its principal use is in the manufacture of oil well drilling fluids. In practice, the material used in drilling fluids has a specific gravity that ranged between 4.10 and 4.25 g/cm³. The barite market is significantly high in oil-producer countries. For example, in US more than the 97% of 2.4 million tons of barite concentrate are consumed by the crude oil industry. The average price of baryte used for gridding purposes is 120 Euros/ton. There is a lack of an estimation concerning the ranging of price in the future, however it is obvious that drilling activities worldwide have a significant impact on barite consumption. In recent years, petroleum production in the United States increased dramatically owing to advances in the application of horizontal drilling and hydraulic fracturing in shale and other tight resources [10]. The total global production of baryte was 7.46 million tonnes, while the certain reserves does not exceed 380 million tonnes.

A number of researches are focused on the environmental impact of baryte mud in marine environment [7,11]. The results show that baryte cannot be considered as a totally chemical inert material as, in several cases, it contains traces of several heavy metals (such as mercury and lead) that can be released in the marine environment at the drilling process. The disposing practice of baryte wastes is not well defined. The most common practice is the burial in pits covered with a synthetic landfill liner. The method presents effectiveness

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

and low operating cost, however, on the other hand harmful components can migrate from the pit and contaminate usable water resources. Therefore, further attention should be given to the barite disposing focusing on novel practices and valorization processes.

4.4 REFERENCES

- [1] J. Hanor, 2000. Barite-celestine geochemistry and environments of formation". Reviews in Mineralogy. Washington, DC: Mineralogical Society of America. 40: 193–275
- [2] On the 2017 list of Critical Raw Materials for the EU, COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS, European Commission, Brussels.
- [3] <http://barytes.org/statistics.html>
- [4] R. Baudis, U. Jäger, P. Riechers, H. Hermann, W. Heinz, W. Wolf, H. Uwe 2007). Barium and Barium Compounds. In Ullman, Franz. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH
- [5] M. Michael Miller, 2009. Barite, Minerals Yearbook
- [6] S. M. Bulatovic, 2015. Chapter 34 – Beneficiation of Barite Ores, in : Handbook of Flotation Reagents: Chemistry, Theory and Practice, Volume 3: Flotation of Industrial Minerals, pp. 129–141.
- [7] J. M. Neff, 2007. Estimation of bioavailability of metals from drilling mud barite, Integrated Environmental Assessment and Management, 4 (2), pp. 184–193.
- [8] Petroleum Engineering Handbook, 2007. Volume II: Drilling Engineering. Society of Petroleum Engineers. pp. 90–95.
- [9] S. I. Onwukwe, M. S. Nwakaudu, 2012. Drilling wastes generation and management approach, International Journal of Environmental Science and Development, 3 (3), pp. 252-257.
- [10] <https://minerals.usgs.gov/minerals/pubs/commodity/barite/mcs-2016-barit.pdf>
- [11] T.M. Ansari, I.L. Marr, A.M. Coats, 2001. Characterisation of mineralogical forms of barium and trace heavy metal impurities in commercial barytes by EPMA, XRD and ICP-MS, Journal of Environmental Monitoring, 3(1), pp. 133-138.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

5 BERYLLIUM

5.1 INTRODUCTION

The most important applications of Beryllium in the EU are

- Electronics and telecommunication equipment: Beryllium is used as an alloying element in copper to improve its mechanical properties without impairing the electric conductivity. Copper beryllium is used in electronic and electrical connectors, battery, undersea fibre optic cables, chips (consumer electronics + telecommunications infrastructure)
- Transport and Defence:
 - o Automotive electronics: connectors in vehicle components (CuBe) for air-bag crash sensor and deployment systems, airbags, anti-lock brake systems and many other life safety applications, for weather forecasting satellites, undersea earthquake tsunami detection monitors, air traffic control radar, fire sprinkler systems, power steering and electronic control systems, etc.
 - o Other light metal vehicle components (Be used in <10 ppms): car body panels, seat frames, car steering components and wheels, etc.
 - o Aerospace components: landing gears, engine for aircraft, mirrors for satellites, etc.
- Industrial components:
 - o Moulds for rubber, plastics and glass, made of Be ceramics
 - o Metals: Bar, plate, rod, tube, and customized forms
- Energy application: copper-beryllium is used to stop the leaking during the Oil spills, non-magnetic equipment component used to improve extraction equivalent of energy applications
- Others: among others, Be in medical application is used as beryllium foil for high-resolution medical radiography, including CT scanning and mammography; Be in explosives; beryllium oxide ceramic in lasers; beryllium as components to analyse blood and in X-ray equipment, etc.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

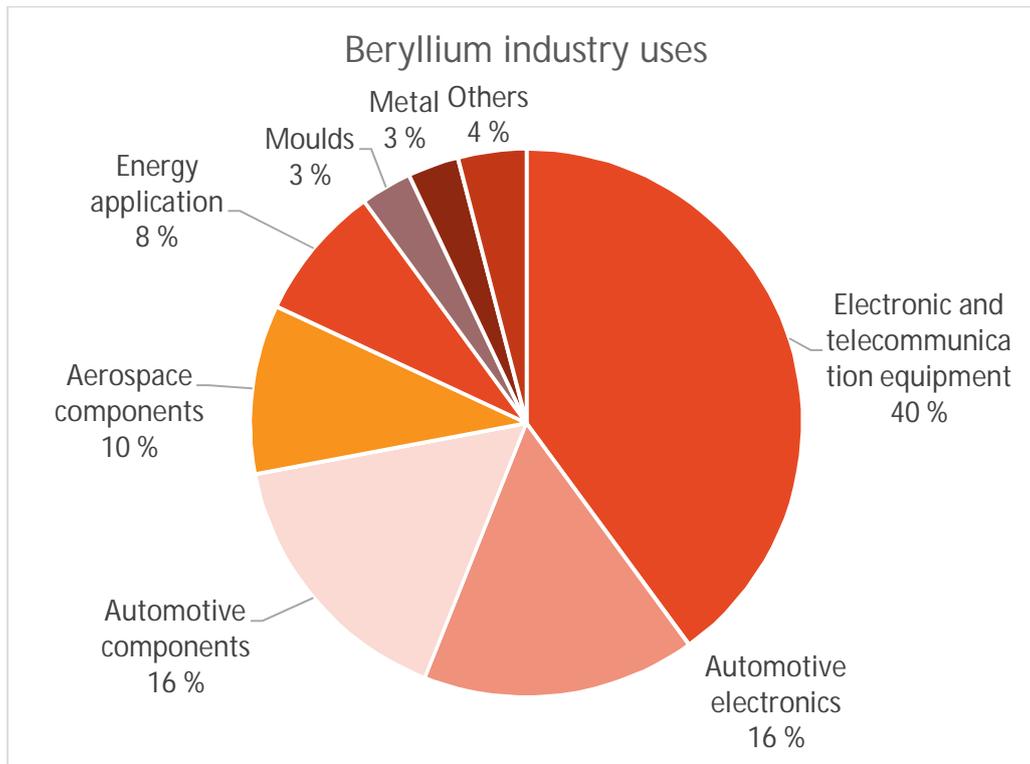


Figure 1. Most important applications of Beryllium in the EU

5.2 GAPS LIMITING CIRCULAR ECONOMY

The beryllium contained in the waste usually ends up in landfill. Beryllium is not recycled from end finished products (BeST 2018).

In the case of the pure beryllium metal components, disassembling and processing old scrap are economically viable processes only for large volumes of materials with high beryllium content, such as military aircraft parts and products used in the aerospace industry. However, pure beryllium metal components used in technological applications have extremely long lifetimes, and therefore return to the recycle stream very slowly. Some, because of applications in space, or because of their sensitive military nature, do not return at all. When pure beryllium components do finally return, they can be easily recycled.

Much of the beryllium metal is contained in nuclear reactors and nuclear weapons, which are difficult to recycle and may have been contaminated. These applications are rarely dismantled, and the beryllium may have been lost during testing (Cunningham 2004)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

In the case of the beryllium alloys components, the Beryllium alloys are lost to the beryllium industry because they are recycled with the host metal or are lost to slag during smelting. For example, the recovery of beryllium metal from copper beryllium alloys that are included in components of post-consumer scrap (like electronics) is difficult because of the small size of the components, difficulty of separation, overall low beryllium content per device and the low beryllium content in the copper beryllium alloy (average 1.25 % beryllium). Therefore, most of the scrap is recycled for its copper value

However, beryllium can be recovered from new scrap. The “new” Beryllium scrap is generated and recovered at various stages of production. Scrap generated during the manufacture of beryllium metals and alloys, and during the fabrication of beryllium products. The European industry generates a lot of “new scrap” (around the half of the beryllium input), during this manufacture step, which is totally sent back to producers outside Europe for reprocessing (European Commission 2017).

Sometimes, regulatory restrictions on the use of certain metals may hamper the development of markets or threaten their viability. The following regulatory restrictions could be a reason that the beryllium has not received more attention to increase its recycling percentage:

- REACH. The threat of being included in the Candidate List of substances of very high concern for Authorisation could be a gap. In 2014, was included in the PACT (Public Activities Coordination Tool) Beryllium has already been subjected to an RMO-Analysis and the outcome of the assessment has been that it is “Appropriate to initiate regulatory risk management action”.
- Occupational Exposure Limit (OEL). During the Risk Management Option analysis (RMOA) one of the actions defined was the “Setting of an OEL” The Setting of an OEL by the Scientific Committee on Occupational Exposure Limits (SCOEL) has set as a necessary step forwards for the regulation of beryllium. Such an OEL may serve as a basis for further regulatory measures. This regulatory option indicates the high potential for risk reduction capacity and equivalent high health benefits for the workers. On the other hand, additional costs for the measures for exposure reduction may incur e.g. plants with encapsulated equipment. However, considering the investment for the continuous improvement, the additional costs would be proportional to the benefits arising from exposure reduction. (Source: RMOA CONCLUSION DOCUMENT)

Even when a RMOA can conclude that regulatory risk management at EU level is required for a substance or that no regulatory action is required at EU level, the risk exist.

Although nowadays the Beryllium is not recycled from end finished products (BeST, 2016b), (the end of life recycling input rate is set to 0%) the market for Beryllium is expected to growth over the coming decades. In the STOA Report (2017) “Towards a circular economy waste management in the EU” examines the role of the waste management in the context of a circular economy transition. A preliminary analysis on the assessment of the opportunities for material recirculation is reported in the study, shown in the next figure. The figure plots the import dependency against the recycling rate of 28 CRMs. The materials in the top left quadrant are high potential materials, where it is appeared Beryllium.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

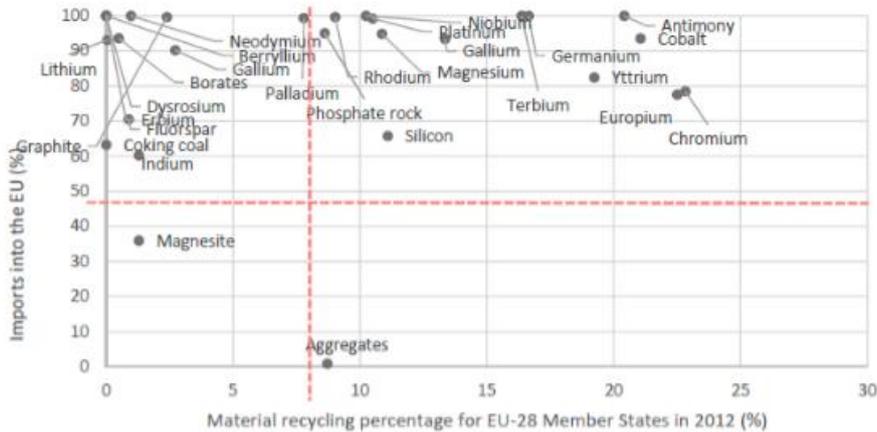


Figure 2. Assessment of the opportunities for material recirculation for CRMs (Source: STOA project 'Towards a circular economy – Waste management in the EU')

In the STOA Report, grouped these materials studied in the figure into four categories, Batteries (1), electronic and electrical products (2), other manufactured products including alloys, catalytic convertors and glass, (3) and industrial processes and construction (4). The study identified the Beryllium in this third group as high potential.

Batteries	Electronic and electrical products	Other manufactured products including alloys and glass	Industrial processes and construction
Lithium††	Indium	Beryllium	Fluorspar
Graphite	Gallium	Borates	Coking coal
Cobalt†	Rare earth elements*	Antimony	Aggregates
		Chromium	Phosphate rock
		Niobium	Magnesite
		PGMs (Platinum, palladium and rhodium)	
		Magnesium	

Figure 3. CRMs grouped by main application. Yellow shaded materials are those identified above as 'high potential' (Source: STOA project 'Towards a circular economy – Waste management in the EU')

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

5.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

One of the key challenges for a circular economy policy framework will be its integration with the existing waste management. One example or instrument is the setting of Directives and regulations for individual waste streams. (i.e ELV Directive, Batteries). Waste specific directive benefit the Circularity of some CRMs, as some of the CRM with the higher “End of life recycling input rate” belong to an end of life product with a specific waste management directive.

Among others, one regulatory challenge that need to be addressed in order to develop well-functioning markets for a circular economy is the REACH regulation. A study carried out by the Center for European Policy Studies (CEPS 2018) summarizes several challenges that need to be resolved in the transition for a circular economy. One of these challenges defined are related to substances of concern and remanufacturing. The report states that “EU legislation on substances of concern aims to protect human health and the environment. A shift towards circularity would require addressing challenges while ensuring safety. The challenges relate to difficulties in remanufacturing products, uncertainty about the substances included in products and a lack of predictability for businesses regarding future restricted substances”. Given these uncertainties, investments from private sector into achieving higher circularity performances might be hindered for some specific materials.

The principle challenges summarized in this regard are

1. A difficulty with regard to innovation and competitiveness activities, especially SMEs, because they may direct their R & D work to comply with the legislation on chemical substances of the EU but they can not know the additional costs on the compliance with it.
2. Businesses may lack predictability regarding the substances that may be restricted in the future from updates in EU chemicals legislation. This in turn can cause difficulties for companies planning to use remanufactured products or product parts
3. Directive 2011/65/EU on the restriction of hazardous substances (RoHS) in electrical and electronic equipment is another key piece of legislation for the protection of human health and the environment that also entails some challenges.
4. A further challenge relates to the access to information on the presence of hazardous substances in products and recovered materials. A report by Bernard & Buonsante (2017) assessing different case studies of products concluded that the current legal framework often fails to ensure the availability of information about the presence of substances in products and waste streams. This issue of uncertainty about the substances included in products may hinder the work of businesses that would like to remanufacture products or use recovered materials in order to produce new products.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

5.4 REFERENCES

BeST - Beryllium Science and Technology Association <http://beryllium.eu/about-beryllium/facts-and-figures/>

European commission (2017). Study on the review of the list of critical raw materials. Critical raw materials factsheets

The Public Activities Coordination Tool (PACT) List 2014.

https://echa.europa.eu/es/pact?p_p_id=viewsubstances_WAR_echarevsubstanceportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2&viewsubstances_WAR_echarevsubstanceportlet_delta=50&viewsubstances_WAR_echarevsubstanceportlet_keywords=&viewsubstances_WAR_echarevsubstanceportlet_advancedSearch=false&viewsubstances_WAR_echarevsubstanceportlet_andOperator=true&viewsubstances_WAR_echarevsubstanceportlet_orderByCol=staticField_-104&viewsubstances_WAR_echarevsubstanceportlet_orderByType=asc&viewsubstances_WAR_echarevsubstanceportlet_resetCur=false&viewsubstances_WAR_echarevsubstanceportlet_cur=4

Beryllium details of the RMOA and hazard assessment activities. https://echa.europa.eu/es/pact/-/substance-rev/1979/del/50/col/staticField_-104/type/asc/pre/4/view

Beryllium	Risk	Management	Option	Analysis	Conclusion	Document
https://echa.europa.eu/documents/10162/c482868d-14c2-e92a-eaef-458125e3902b						

Scientific Foresight Unit (STOA) within the Directorate-General for Parliamentary Research Services (DG EPRS) of the European Parliament. 2017. STOA project 'Towards a circular economy – Waste management in the EU. Oakdene Hollins (UK).

The Centre for European Policy Studies (CEPS). 2018. The Role of Business in the Circular Economy. Markets, Processes and Enabling Policies.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

6 BISMUTH

6.1 INTRODUCTION

Bismuth is a chemical element with the symbol Bi and atomic number of 83. It is a pentavalent post-transitional metal and one of the pnictogens, very chemically similar to lighter homologues: arsenic and antimony.

In earth crust bismuths is twice as abundant as gold and the most important ores of bismuth are bismuthinite and bismite. Native bismuth is known from Australia, Bolivia and China.

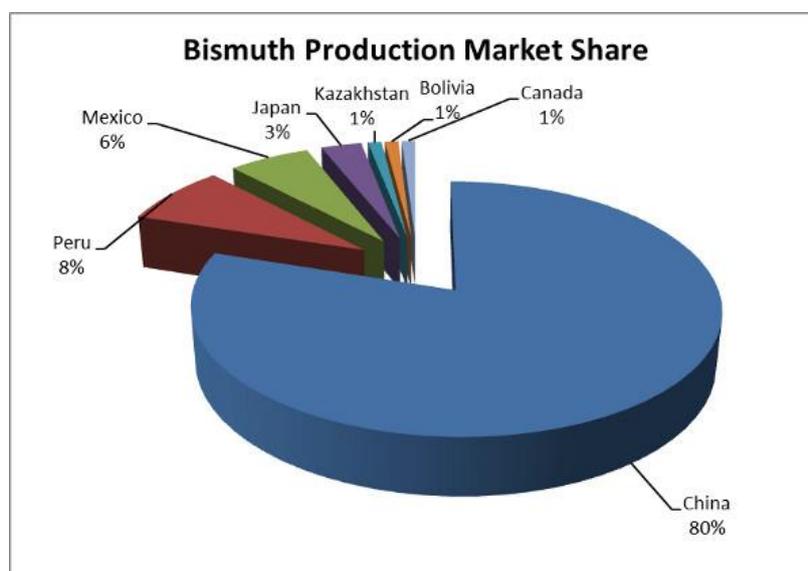


Fig. 1 Bismuth Production Market Share (InV 2014).

In China and Vietnam, bismuth is a byproduct or coproduct of tungsten and other metal ore processing. It is also a by-product of several ore-dressing operations, especially from high-grade scheelite and wolframite ores. It is in general recovered by processing lead electrorefining slimes, Kroll-Betterton dross, and other process residues which contain bismuth where almost all the time chlorine is used in order to achieve virgin material (KRU 2003).

Bismuth is currently recycled to a very low percent, about 5%, from EoL products.

Bismuth is used in chemicals used in cosmetic industry, industrial laboratory and pharmaceutical applications. Also, it is used in manufacturing of ceramic glazes, crystalware and pearlescent pigments.

Bismuth is considered to be an environmentally friendly substitute for lead in plumbing and many other applications, including fishing weights, hunting ammunition, lubrication greases and soldering alloys.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

6.2 GAPS LIMITING CIRCULAR ECONOMY

According to UMICORE, bismuth is difficult to recycle due to its "dissipative" applications (UMC 2018), such as pigments and pharmaceuticals. It is however recovered from the production of copper and lead (FUN 1992).

AURUBIS is recycling copper (AUR 2018), where bismuth gets separated together with other metals. By-elements still existing during copper production, such as lead, bismuth, antimony and tellurium, are separated in the connected lead refinery and sold as lead bullion, lead-bismuth alloy, antimony concentrates and tellurium concentrates, Figure 2.

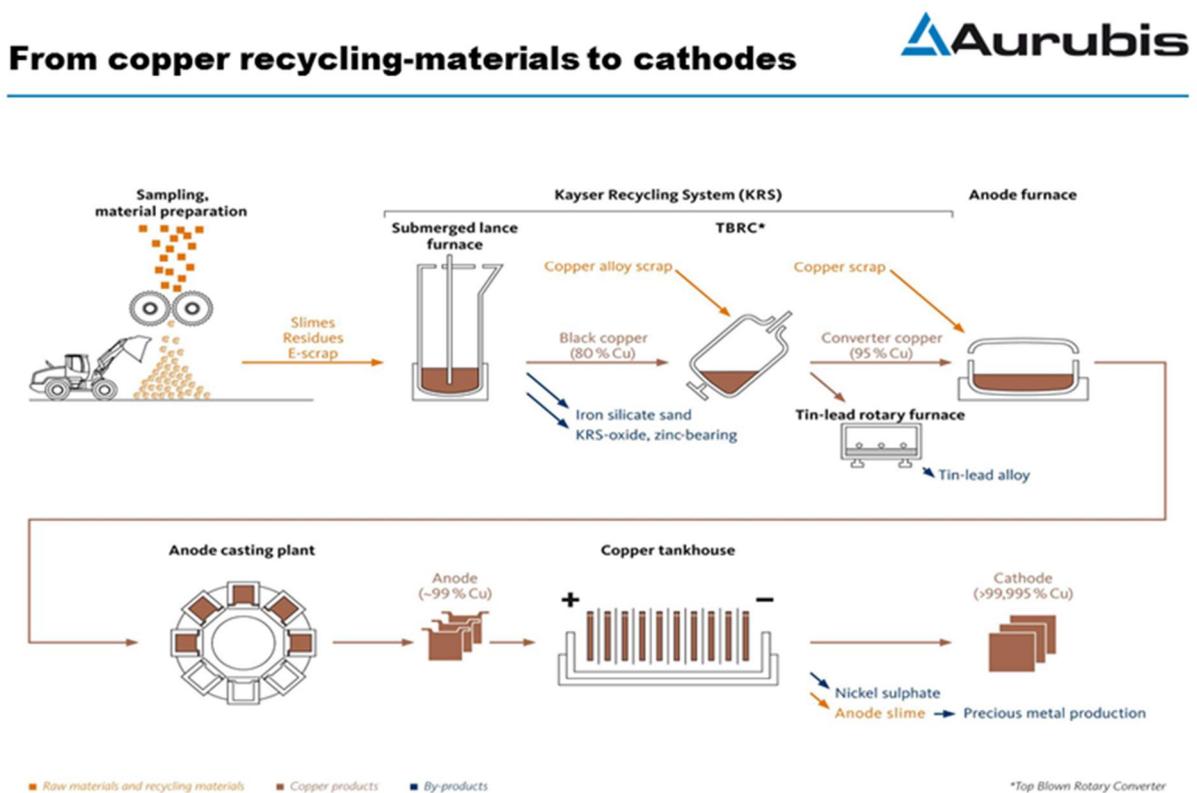


Fig. 2 AURUBIS process, where bismuth is collected together with other metals in the fraction named "By-products"

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

6.3 SUMMARY

Generally bismuth production is highly dependent on the production of the main metals of which the by-product bismuth is. Due to its rather benign properties, no special environmental harms are posed by bismuth itself, however it can be seriously affected by the main metals extraction methods, which are sometimes far away from environmentally friendly procedures.

The recycling of bismuth is a secondary process as well, no dedicated process tailored for bismuth exists currently in use.

As UMICORE highlights, the dispersive use of bismuth into other materials makes it difficult to concentrate prior to eventual recycling, thus the price of such a process would be very high.

6.4 REFERENCES

InvestorIntel – (2014) Bismuth – the X-Factor in the Chinese Dominance Challenge, <https://investorintel.com/sectors/technology-metals/technology-metals-intel/bismuth-chinese-grip/>, retrieved May 2018

Funsho K. Ojebuoboh, (1992), Bismuth – Production, properties and applications, JOM, Vol. 44, Issue 4, P. 46-49

J. Kruger, P. Winkler, E. Luderiz, Manfred Luck, H. U. Wolf, (2003) – Bismuth, bismuth alloys and bismuth compounds, https://doi.org/10.1002/14356007.a04_171

UMICORE – Bismuth – <http://www.umicore.com/en/about/elements/bismuth/>, retrieved May 2018

AURUBIS – Recycling technology - <https://www.aurubis.com/en/products/recycling/technology>, retrieved May 2018.

7 BORATES

7.1 INTRODUCTION

The global mine production is about 1 million tonnes of borates. The EU consumption is estimated at approximately 285,000 tonnes (borate equivalent), which represents around 15% of world consumption (European commission 2017)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

EU end uses of borates area shown in next figure. About half of all consumption globally of borates is used as an additive in glass. The next leading use is for frits and ceramics in the Ceramic Industries. The third use for boron compounds is as fertilizers in agriculture.

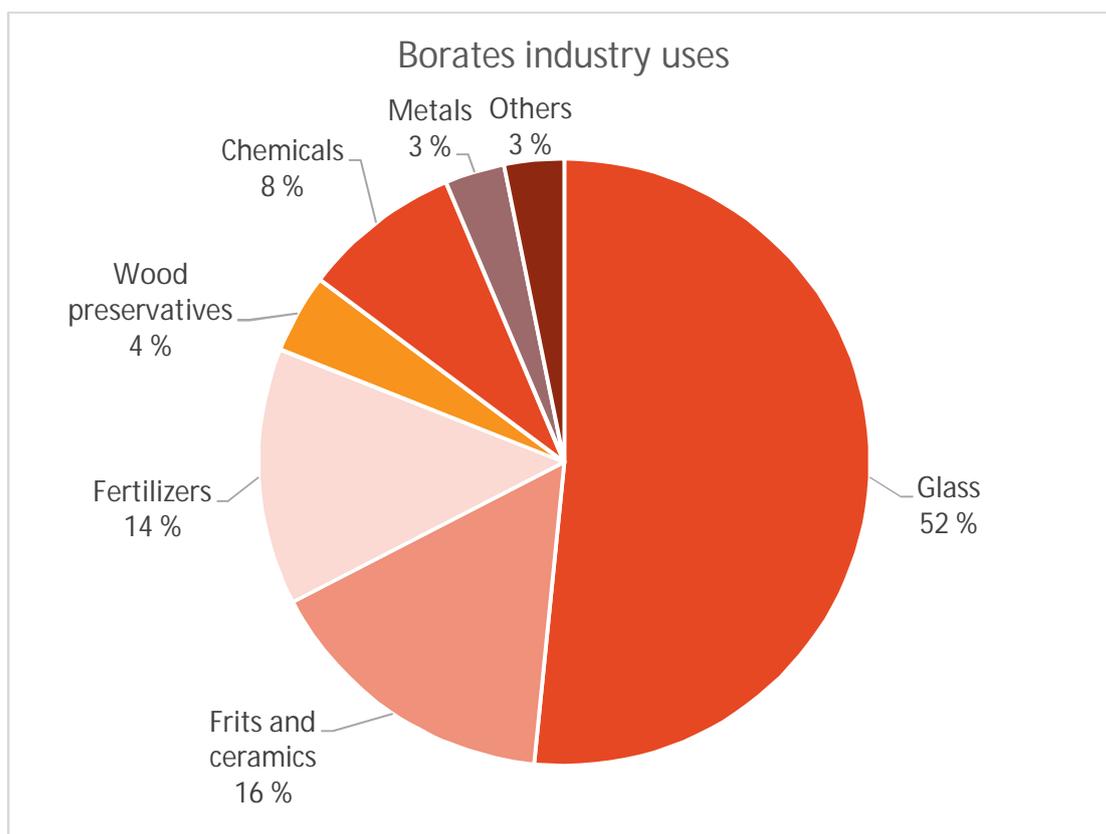


Figure 3. EU end uses of Borates. (Source: EU commission)

7.2 GAPS LIMITING CIRCULAR ECONOMY

The functional recycling of boron is thus null. (USGS 2017). The principal gap is that the products containing the borates are not likely to be recycled considering these products are consumed with use:

- Fertilisers: an essential micronutrient for plant growth, crop yield and seed development.
- Wood preservatives: Borates are used to treat wood to ward off insects and other pests.
- Detergents: Used in laundry detergents, household and industrial cleaning products. Borates enhance stain removal and bleaching, provide alkaline buffering, soften water and improve surfactant performance.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

- Chemicals (excl. Fertilisers, wood preservatives and detergents): Used for chemicals such as fire retardants.
- Industrial Fluids: Used for metalworking fluids, and other fluids used in cars, antifreeze, braking fluid etc.
- Metals: Used as an additive for steel and other ferrous metals as its presence ensures higher strength at a lower weight

And the Borosilicate glass and ceramic cannot be recycled with normal glass because these materials have a higher heat resistance and therefore higher melting point compared to conventional glass. The presence of this kind of glass during recycling causes defects in the recycled glass.

Secondary materials result mostly from non-functional recycling. Borosilicate glass is currently not separated from boron-free container and flat glass. It means that boron in waste borosilicate glass is likely to end up in the manufacture of new glass containers or glass wool and it does not replace primary boron in the new production of borosilicate glass. Moreover, waste from ceramics is mostly used as a construction material. (Deloitte, European commission 2017)

In the next table it is shown the EU stock of boron in use (180 kt), the annual amount of boron in end of life products collected and the amount of the amount of boron recycled.

Table 1 - Based on data of the Bio Intelligence Service Report, 2015

	The EU stock of boron in use(tons)	The annual amount of boron in end of life products collected (tons)	The annual amount of boron from non-functional recycling. (tons)
Glass	46.000	45.000	21.000
Frits and ceramics	98.000	13.000	10.000
Fertilizers	35.000	< 1.000	--
Others	1.000	7.000	3.000
Total	180.000	About 66.000	34.000

The stock reflects the lifespan of particular finished products, which was the longest for frits and ceramics. More than half of boron in the collected products at end of life is sent for non-functional recycling. The annual amount of products heading for disposal is about 30 kt in boron content

Although nowadays the borates are not recycled from end finished products (BeST, 2016b), (the end of life functional recycling input rate is almost 0%), the STOA Report (2017) "Towards a circular economy waste management in the EU" identifies as a high potential material. This report assesses the role of the waste management in the context of a circular economy transition. A preliminary analysis on the assessment of the opportunities for material recirculation is reported in the study, shown in the next figure. The figure plots the

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

import dependency against the recycling rate of 28 CRMs. The materials in the top left quadrant are high potential materials, where it is appeared Borates.

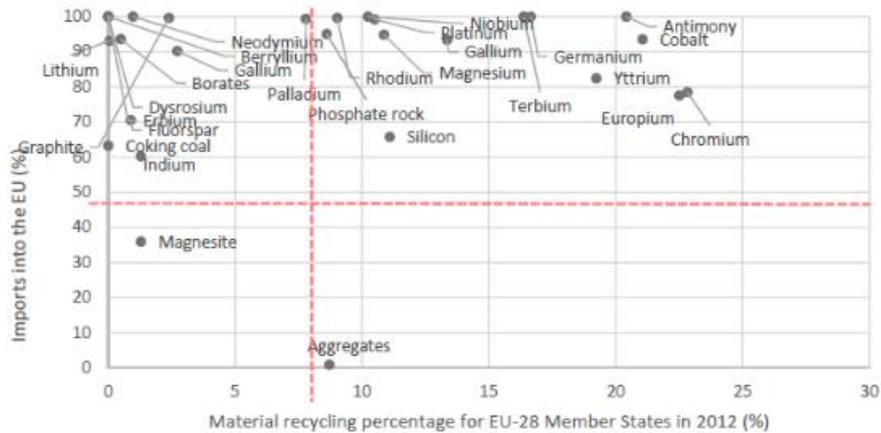


Figure 4. Assessment of the opportunities for material recirculation for CRMs (Source: STOA project 'Towards a circular economy – Waste management in the EU')

In the STOA Report, grouped these materials studied in the figure into four categories, Batteries (1), electronic and electrical products (2), other manufactured products including alloys, catalytic convertors and glass, (3) and industrial processes and construction (4). The study identified the Borates in this third group as high potential.

Batteries	Electronic and electrical products	Other manufactured products including alloys and glass	Industrial processes and construction
Lithium ^{††}	Indium	Beryllium	Fluorspar
Graphite	Gallium	Borates	Coking coal
Cobalt [†]	Rare earth elements*	Antimony	Aggregates
	Germanium	Chromium	Phosphate rock
	Silicon	Niobium	Magnesite
	PGMs (Platinum, palladium and rhodium)		
		Magnesium	

Figure 5. CRMs grouped by main application. Yellow shaded materials are those identified above as 'high potential' (Source: STOA project 'Towards a circular economy – Waste management in the EU')

Several commercial forms of borates as sodium perborate, Perboric acid, Sodium peroxometaborate, Lead bis(tetrafluoroborate), Diboron trioxide, Boric acid, Disodium tetraborate, Tetraboron disodium heptaoxide

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

(hydrate) have been identified as Substances of Very High Concern (SVHC) under REACH legislation and were added to the candidate list (ECHA 2018) These compounds have also been classified as toxic for reproduction.

7.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

The non-functional recycling is quite high in some of the end of life products. As it is shown in the table 1, the non-functional recycling of the ceramics reach almost a 75% of the amount collected. The “mixtures of concrete, bricks, tiles and ceramics» are identified in the list of C&D Waste classification (code 17 01 07) in the EU Construction & Demolition Waste Management Protocol (https://ec.europa.eu/growth/content/eu-construction-and-demolition-waste-protocol-0_en).

Some measures in the management of Construction & Demolition waste could have influenced, as some Proper regulation of C&D waste management, National waste plans, Landfill restrictions or bans to landfill disposal, R&D support in new construction materials.

7.4 REFERENCES

European commission (2017). Study on the review of the list of critical raw materials. critical raw materials factsheets.

USGS (2017) Minerals Yearbook, Boron.

BIO by Deloitte (2015) Study on Data for a Raw Material System Analysis: Roadmap and Test of the Fully Operational MSA for Raw Materials. Prepared for the European Commission, DG GROW

Scientific Foresight Unit (STOA) within the Directorate-General for Parliamentary Research Services (DG EPRS) of the European Parliament. 2017. STOA project 'Towards a circular economy – Waste management in the EU. Oakdene Hollins (UK).

ECHA. <http://echa.europa.eu> . Candidate List of substances of very high concern for Authorisation <https://echa.europa.eu/candidate-list-table>

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

8 COBALT

8.1 INTRODUCTION

Cobalt is used in a wide range of end products, either as cobalt-bearing compounds or cobalt metal. Cobalt-containing compounds find use especially in battery applications (cathode material in Li-ion batteries, anode material in Ni-MH batteries), but also in as pigments and other applications of ceramic materials (Hamut, 2017), (Ogura & Kolhe, 2017), (Llusar et al., 2001), (Delorme et al., 2017). Metallic cobalt is included in superalloys, particularly Co-based superalloys, wear-resistant cobalt-base alloys, known as Stellites, and even in biocompatible alloys of Co-Cr-Mo (Campbell, 2008).

The form in which cobalt is included in the end product, i.e., compound or bulk metal, inherently influences the circular economy aspects. Much work has been put on finding technologies to recycle and recover cobalt from battery components, primarily from cathodes of lithium ion batteries. In them, cobalt exists as lithium cobalt oxide, LiCoO_2 , or its invariants lithium nickel cobalt aluminium oxide or lithium nickel manganese cobalt oxide. In general, the recovery of cobalt from the pretreated battery waste may be achieved by pyrometallurgical or hydrometallurgical routes, i.e., by smelting or leaching. Much of the work in this area has concentrated on leaching combined with a reductive treatment of the dissolved cobalt in order to optimise the conditions for the maximum yield, e.g., (Meng, Zhang, & Dong, 2018), (Peng, Hamuyuni, Wilson, & Lundström, 2018), (Meng, Zhang, & Dong, 2017), (Albler, Bica, Foreman, Holgersson, & Tyumentsev, 2018), (Torkaman, Asadollahzadeh, Torab-Mostaedi, & Ghanadi Maragheh, 2017), (Rodrigues & Mansur, 2010), (Wang et al., 2017), (Takacova, Havlik, Kukurugya, & Orac, 2016). A proof-of-concept has also been received for a pyrometallurgical route to recover cobalt (Georgi-Maschler, Friedrich, Weyhe, Heegn, & Rutz, 2012). In addition to these, some successful attempts to recover the electrode material, LiCoO_2 , through solid-state synthesis have been reported (Pegoretti, Dixini, Smeccellato, Biaggio, & Freitas, 2017), (Sita, da Silva, da Silva, & Scarminio, 2017).

In 1998, superalloys covered 44% of the cobalt use in USA (Shedd, 1998), with aerospace and power generation being the main consumer sectors (Srivastava, Kim, Lee, Jha, & Kim, 2014). Despite the emerge of battery revolution since then, it is clear that superalloys are an important category of use for the cobalt (Ferron, 2016). In the case of cobalt-base alloys, recycling technologies exist already yet there are several challenges to overcome. In alloy applications, the recycling of the material can easiest be done at the source, i.e., where an alloy is cast or machined. These are typically very localised individual spots, which makes the collection of scrap for recycling very easy. The most convenient way to recycle cobalt is to re-melt the scrap directly provided no harmful elements (polishing grit, cutting oils,...) have been added. (Ferron, 2016) Otherwise, the main technologies to recycle superalloy scrap and even cobalt catalysts are pyrometallurgy, hydrometallurgy and their combinations, similarly to the case of batteries, and with recognized issues of environmental hazardousness and energy intensiveness. The recycling of superalloys in general is not straightforward as typical superalloys contain more than 20 alloying elements and consideration in recycling of every single element included in the composition is very demanding. For example, in 1998 in USA, i.e., before the boom of battery technologies, the

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

recycling efficiency of cobalt scrap was 68% (Shedd, 1998). Here, the cobalt scrap covered superalloy parts, cemented carbide parts, magnets, spent catalysts and other metal products, but it was clearly emphasized that some of the recycled scrap underwent downgrading, i.e., dilution to the level where its properties are not fully utilized (alloying element in e.g., steel). Furthermore, one issue that directly contributes to the recycling rate is the amount of produced scrap. Indeed, it is acknowledged that the superalloy industry releases an extremely large amount of scrap: components may have a final product yield of less than 10% due to machining and forging (Srivastava et al., 2014).

For Stellite, i.e., cemented carbide or hard metal structures, the recycling processes fall into direct and indirect ones. Direct methods include cold stream process, like gas atomization but conducted at lower temperatures, and zinc melt process, in which the material is immersed in molten zinc bath to react selectively with cobalt and to introduce a porous structure, from which the zinc can be heated away and Co and WC powders separated (Katiyar, Randhawa, Hait, Jana, & Singh, 2014), (Kim, Seo, & Son, 2014), (Hämäläinen & Isomäki, 2005). The indirect recycling methods involve sequential steps of dry and wet processes, such as chlorination, oxidation-alkaline leaching and oxidation-reduction, to enable selective recovery of the elements included in the material (Katiyar et al., 2014), (Kim et al., 2014). During the recent years, finding the optimal combination of processes and process parameters has gained a lot of research effort. (Kim et al., 2014), (J. C. Lee et al., 2011), (Kücher, Luidold, Czettl, & Storf, 2018), (Xi, Xiao, Nie, Zhang, & Ma, 2017), yet some of the processes still give very low cobalt yield rates, e.g., (J. Lee, Kim, & Kim, 2017).

Recent figures reveal that end-of-life recycling input rate (EOL-RIR) for cobalt is 35%. It is third highest among the critical raw materials (CRM) after vanadium (44%) and tungsten (42%). However, this is mainly because a wide use of cobalt in battery applications and the existing waste legislation that requires the collection of end-of-life batteries. However, still much of the waste cobalt ends up in, e.g., landfill. (Mathieux et al., 2017)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

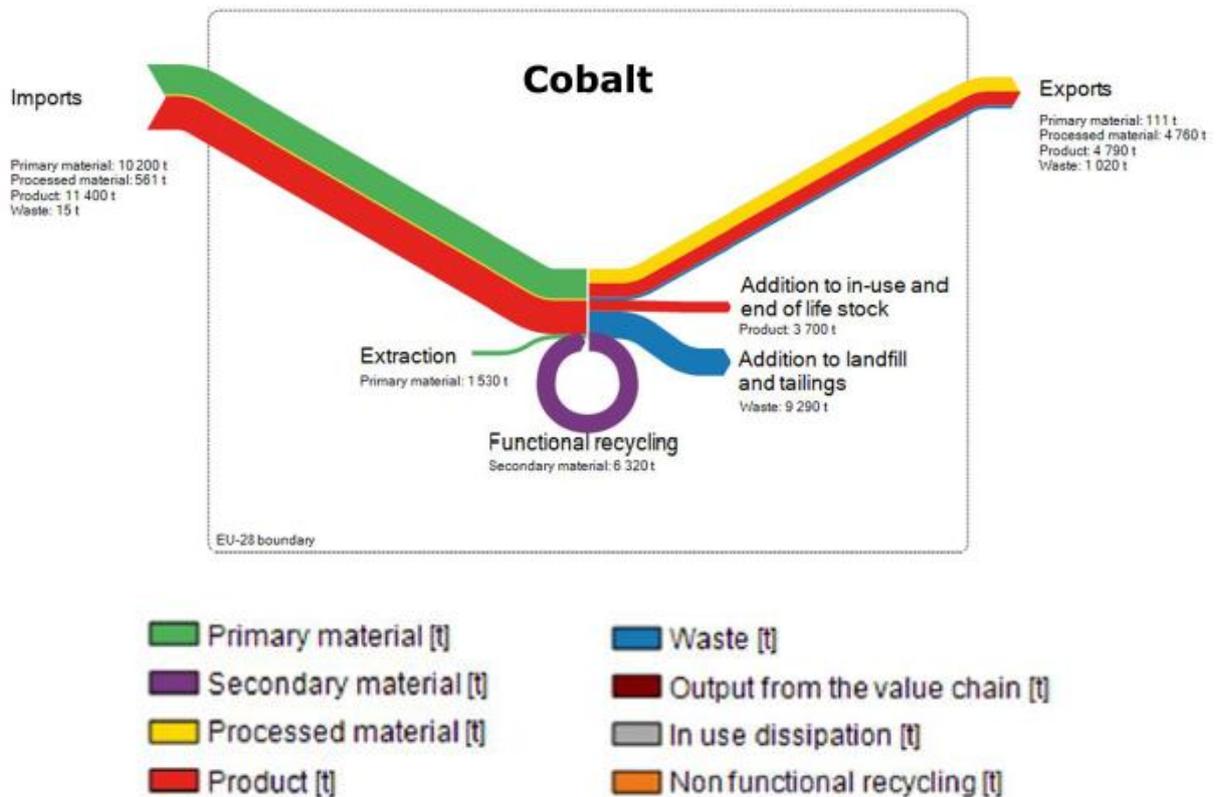


Figure 1. Simplified Sankey diagram for cobalt in EU expressed in t/year for the year 2012. (Mathieux et al., 2017)

8.2 GAPS LIMITING CIRCULAR ECONOMY

As demonstrated above, the technologies that are used in cobalt recycling are partly coherent, particularly in the recovery of cobalt from battery electrodes and superalloy scrap, but when the hard tungsten carbides are included, the processes and technologies become more complex. The technologies thus exist, although with variable yield rate and economic feasibility. The gaps that limit circular economy of cobalt are, however, very application linked and will be treated below one by one.

Concerning the recycling of batteries, the main goals are the separation and recovery of battery components and removal of waste from the environment. The following problems have been identified in the battery recycling:

- 1) The low collection rate of batteries. Limited number of battery collection points in the municipalities (although the sellers should serve for collection points, particularly in the case of consumer products) combined with an easiness of storage of old batteries in a drawer.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- 2) The intrinsic safety risk because of the high reactivity of batteries. If overheated or overcharged, as it may happen if stored in masses, the batteries may experience a thermal runaway or even explosion.
- 3) The market is in continuous evolution with the advent of many new chemistries and electrode materials.
- 4) Parallel use of various electrolyte types and compositions in batteries, making it challenging to develop an universally valid and economically feasible recycling process.
- 5) The recycling at present only covers portable batteries for consumer electronics due to limited production of batteries for, e.g., electric vehicles (EV). EV battery recycling is expected to gain importance in the years to come.

These problems then also cover cobalt included in the battery electrodes. In addition to these, the amount of cobalt (and some other valuable elements) in a battery may vary significantly, between as low as 1 % and almost 50 wt.% (Ferron, 2016), thus the recycling is not always economically viable. (Scrosati, Garche, & Sun, 2015). Figure 2 shows the steps needed to recover most of the valuable elements in the batteries, and their number well reflects the economic challenges related to recovery of cobalt and other key elements.

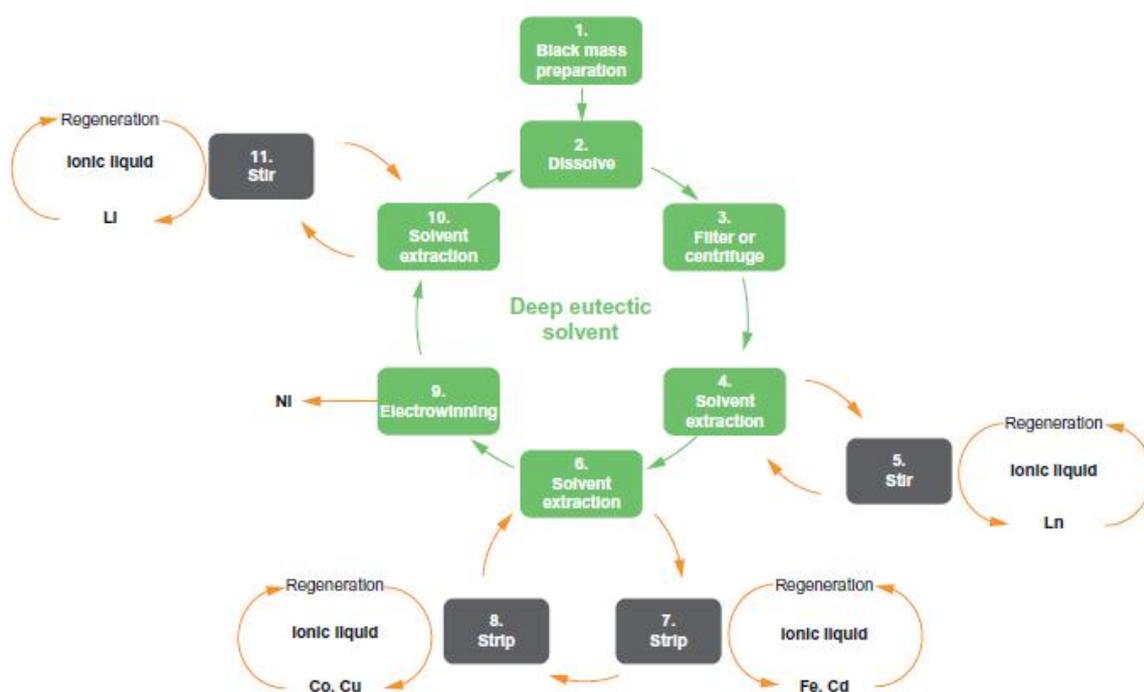


Figure 2. Flow sheet showing the recent advances in the recycling of elements included in batteries and the number of steps needed to recover the valuables. Many of the steps employ ionic liquids. Figure from ref. (Scrosati et al., 2015)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

The European Commission has mandated a Battery and Accumulator Directive to give recycling targets. In many cases, subsidies are provided to encourage the battery recycling, usually by adding a tax on each manufactured battery. The directive also prohibits to place on the market of batteries or accumulators containing more than 0.0005 wt.% mercury or 0.002 wt.% cadmium (Ec, 2000). Concerning specifically the recycling of cobalt from the battery components, the major technical challenges are the unestablished technology, documented wide variation in recycling efficiency and the use of extreme pH values in process electrolytes, requiring careful health and safety precautions.

For metallic material, the recovery is technically much easier, and there is a traceable system for scrap collection and logistics (even internationally) as demonstrated by Shedd. However, the collection and processing of cobalt-bearing scrap depends on several factors, such as the type, quality and volume of the scrap. Alloy scrap is sorted based on the shape, colour and weight of the scrap items. Other sorting methods, such as response to a magnet, may also be employed together with chemical analyses. (Shedd, 1998) However, cobalt is a very common alloying element, meaning it exists in alloys at varying levels, and the material may contain increased amount of impurity elements from the use, thus influencing the further processing. There are also some technical challenges related to the multi-element character of the alloys. All elements cannot typically be recovered simultaneously and at equal efficiencies. For example, recycling by pyrometallurgical routes may easily cause the loss of approximately 20% in the amount of alloying elements. Overall, it is not rare that cobalt undergoes downgrading upon recycling. Furthermore, in some countries, e.g., Korea, the recycling of superalloys is exclusively done by the material supplier and related to maintenance of gas turbines in power stations. (Srivastava et al., 2014) Similarly, the recycling of cobalt from hardmetal is established technology, yet it requires several steps and may not always be economically feasible due to, e.g., energy intensity. Some of the recycling processes also have specific purity requirements for the waste to be recovered. (Shemi, Magumise, Ndlovu, & Sacks, 2018)

Some end use of the metal does not lend itself to recycling because the cobalt is dispersed in such a way that it is very difficult to collect, e.g., pigments.

8.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

In the case of cobalt, the aspects that inherently support circular economy are the established technologies for recovery. Also the understanding that cobalt reserves are finite and concentrated on some local areas serves as incentive for cobalt circularity. It is also acknowledged that the recycling of cobalt occurs at lower costs than the extraction from ores, thus this is recognized the key motivation for cobalt recycling. In battery applications, the collection of end-of-life battery waste is also required by waste legislation, thus putting pressures to cobalt recycling in this sector. (Mathieux et al., 2017)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

8.4 ENVIRONMENTAL ISSUES

Cobalt has a biologically necessary role as a metal constituent of vitamin B12, but excessive exposure may induce various adverse health effects, such as neurological, cardiovascular and endocrine deficits. For example, toxic reactions have been reported in the several cases of malfunctioning metal-to-metal Co-based hip implants. It is expected that the primary toxic form of cobalt is free ionic Co^{2+} . (Leysens, Vinck, Van Der Straeten, Wuyts, & Maes, 2017) This is also good to bear in mind in the cobalt recovery through hydrometallurgical routes.

8.5 SUMMARY

Cobalt is one of the critical raw materials with relatively high recycling rate, 35%. However, still some of the end-of-life cobalt ends up in, e.g., landfill. The waste legislation requires to collect battery waste, but the circular economy is still limited by a limited number of collection points, safety risks related to their storage in masses and continuous evolution of battery designs and chemistries that makes it challenging to develop universal recycling solutions. Also the cobalt contents in batteries vary, challenging the economic feasibility of recycling processes. Metallic cobalt and cobalt included in hardmetal components are recycled through established technologies, yet in the case of superalloys, the high number of alloying elements present implies that not all of them cannot be recovered. The recovery of cobalt from hardmetal requires several process steps, thus the process volumes need to be large to be economically viable. In the recycling of cobalt-base scrap, local ecosystems play an important role, although the markets are also global.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

8.6 REFERENCES

- Albler, F. J., Bica, K., Foreman, M. R. S. J., Holgersson, S., & Tyumentsev, M. S. (2018). A comparison of two methods of recovering cobalt from a deep eutectic solvent: Implications for battery recycling. *Journal of Cleaner Production*, *167*, 806–814. <https://doi.org/10.1016/j.jclepro.2017.08.135>
- Campbell, C. F. (2008). Elements of Metallurgy and Engineering alloys, 345–347.
- Delorme, F., Chen, C., Pignon, B., Schoenstein, F., Perriere, L., & Giovannelli, F. (2017). Promising high temperature thermoelectric properties of dense Ba₂Co₉O₁₄ceramics. *Journal of the European Ceramic Society*, *37*(7), 2615–2620. <https://doi.org/10.1016/j.jeurceramsoc.2017.01.034>
- Ec. (2000). This document is meant purely as a documentation tool and the institutions do not assume any liability for its contents. *Official Journal of the European Communities*, *L 269*(September 2000), 1–15. <https://doi.org/2004R0726 - v.7 of 05.06.2013>
- Ferron, C. J. (2016). The recycling of cobalt from alloy scrap, spent batteries or catalysts and metallurgical residues - an overview. *Ni-Co 2013*, (3), 53–71. https://doi.org/10.1007/978-3-319-48147-0_3
- Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H., & Rutz, M. (2012). Development of a recycling process for Li-ion batteries. *Journal of Power Sources*, *207*, 173–182. <https://doi.org/10.1016/j.jpowsour.2012.01.152>
- Hamut, H. S. (2017). 2 Electric Vehicle Battery Technologies 2.1 Introduction, 49–92.
- Hämäläinen, M., & Isomäki, I. (2005). Thermodynamic evaluation of the C-Co-Zn system. *Journal of Alloys and Compounds*, *392*(1–2), 220–224. <https://doi.org/10.1016/j.jallcom.2004.09.033>
- K.B. Shedd, Cobalt recycling in the United States in 1998. U . S . Department of the Interior, U . S . Geological Survey, Open File Report 02-299. Reston, VA, USA, 1998. (1998).
- Katiyar, P. K., Randhawa, N. S., Hait, J., Jana, R. K., & Singh, K. K. (2014). An overview on different processes for recovery of valuable metals from tungsten carbide scrap ., 1–11.
- Kim, S., Seo, B., & Son, S. H. (2014). Dissolution behavior of cobalt from WC-Co hard metal scraps by oxidation and wet milling process. *Hydrometallurgy*, *143*, 28–33. <https://doi.org/10.1016/j.hydromet.2014.01.004>
- Kücher, G., Luidold, S., Czettl, C., & Storf, C. (2018). Lixiviation kinetics of cobalt from cemented carbides. *International Journal of Refractory Metals and Hard Materials*, *70*(October 2017), 239–245. <https://doi.org/10.1016/j.ijrmhm.2017.10.004>
- Lee, J. C., Kim, E. Y., Kim, J. H., Kim, W., Kim, B. S., & Pandey, B. D. (2011). Recycling of WC-Co hardmetal sludge by a new hydrometallurgical route. *International Journal of Refractory Metals and Hard Materials*, *29*(3), 365–371. <https://doi.org/10.1016/j.ijrmhm.2011.01.003>
- Lee, J., Kim, S., & Kim, B. (2017). A New Recycling Process for Tungsten Carbide Soft Scrap That Employs a

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- Mechanochemical Reaction with Sodium Hydroxide. *Metals*, 7(7), 230. <https://doi.org/10.3390/met7070230>
- Leysens, L., Vinck, B., Van Der Straeten, C., Wuyts, F., & Maes, L. (2017). Cobalt toxicity in humans—A review of the potential sources and systemic health effects. *Toxicology*, 387(May), 43–56. <https://doi.org/10.1016/j.tox.2017.05.015>
- Llusar, M., Forés, A., Badenes, J. A., Calbo, J., Tena, M. A., & Monrós, G. (2001). Colour analysis of some cobalt-based blue pigments. *Journal of the European Ceramic Society*, 21(8), 1121–1130. [https://doi.org/10.1016/S0955-2219\(00\)00295-8](https://doi.org/10.1016/S0955-2219(00)00295-8)
- Mathieux, F., Ardente, F., Bobba, S., Nuss, P., Blengini, G., Alves Dias, P., ... Solar, S. (2017). *Critical raw materials and the circular economy - Background report*. <https://doi.org/10.2760/378123>
- Meng, Q., Zhang, Y., & Dong, P. (2017). Use of glucose as reductant to recover Co from spent lithium ions batteries. *Waste Management*, 64, 214–218. <https://doi.org/10.1016/j.wasman.2017.03.017>
- Meng, Q., Zhang, Y., & Dong, P. (2018). A combined process for cobalt recovering and cathode material regeneration from spent LiCoO₂batteries: Process optimization and kinetics aspects. *Waste Management*, 71, 372–380. <https://doi.org/10.1016/j.wasman.2017.10.030>
- Ogura, K., & Kolhe, M. L. (2017). Battery technologies for electric vehicles. *Electric Vehicles: Prospects and Challenges*, 139–167. <https://doi.org/10.1016/B978-0-12-803021-9.00004-5>
- Pegoretti, V. C. B., Dixini, P. V. M., Smecellato, P. C., Biaggio, S. R., & Freitas, M. B. J. G. (2017). Thermal synthesis, characterization and electrochemical study of high-temperature (HT) LiCoO₂obtained from Co(OH)₂recycled of spent lithium ion batteries. *Materials Research Bulletin*, 86, 5–9. <https://doi.org/10.1016/j.materresbull.2016.09.032>
- Peng, C., Hamuyuni, J., Wilson, B. P., & Lundström, M. (2018). Selective reductive leaching of cobalt and lithium from industrially crushed waste Li-ion batteries in sulfuric acid system. *Waste Management*. <https://doi.org/10.1016/j.wasman.2018.02.052>
- Rodrigues, L. E. O. C., & Mansur, M. B. (2010). Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel-metal-hydride batteries. *Journal of Power Sources*, 195(11), 3735–3741. <https://doi.org/10.1016/j.jpowsour.2009.12.071>
- Scrosati, B., Garche, J., & Sun, Y.-K. (2015). Recycling lithium batteries. *Advances in Battery Technologies for Electric Vehicles*, 503–516. <https://doi.org/10.1016/B978-1-78242-377-5.00020-0>
- Shemi, A., Magumise, A., Ndlovu, S., & Sacks, N. (2018). Recycling of tungsten carbide scrap metal: A review of recycling methods and future prospects. *Minerals Engineering*, 122(September 2017), 195–205. <https://doi.org/10.1016/j.mineng.2018.03.036>
- Sita, L. E., da Silva, S. P., da Silva, P. R. C., & Scarminio, J. (2017). Re-synthesis of LiCoO₂extracted from spent Li-ion batteries with low and high state of health. *Materials Chemistry and Physics*, 194, 97–104. <https://doi.org/10.1016/j.matchemphys.2017.03.026>
- Srivastava, R. R., Kim, M. S., Lee, J. C., Jha, M. K., & Kim, B. S. (2014). Resource recycling of superalloys and

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

hydrometallurgical challenges. *Journal of Materials Science*, 49(14), 4671–4686. <https://doi.org/10.1007/s10853-014-8219-y>

Takacova, Z., Havlik, T., Kukurugya, F., & Orac, D. (2016). Cobalt and lithium recovery from active mass of spent Li-ion batteries: Theoretical and experimental approach. *Hydrometallurgy*, 163, 9–17. <https://doi.org/10.1016/j.hydromet.2016.03.007>

Torkaman, R., Asadollahzadeh, M., Torab-Mostaedi, M., & Ghanadi Maragheh, M. (2017). Recovery of cobalt from spent lithium ion batteries by using acidic and basic extractants in solvent extraction process. *Separation and Purification Technology*, 186, 318–325. <https://doi.org/10.1016/j.seppur.2017.06.023>

Wang, H., Huang, K., Zhang, Y., Chen, X., Jin, W., Zheng, S., ... Li, P. (2017). Recovery of Lithium, Nickel, and Cobalt from Spent Lithium-Ion Battery Powders by Selective Ammonia Leaching and an Adsorption Separation System. *ACS Sustainable Chemistry & Engineering*, 5(12), 11489–11495. <https://doi.org/10.1021/acssuschemeng.7b02700>

Xi, X., Xiao, X., Nie, Z., Zhang, L., & Ma, L. (2017). Electrolytic separation of cobalt and tungsten from cemented carbide scrap and the electrochemical behavior of metal ions. *Journal of Electroanalytical Chemistry*, 794(April), 254–263. <https://doi.org/10.1016/j.jelechem.2017.04.001>

9 COKING COAL

9.1 INTRODUCTION

Coking coal is a special group of coals belonging to hard coals that are of bituminous type. The property that really sets coking coals apart from other coals is caking ability, which is the specific property required in order to make coke suitable for making steel. When heating a coking coal without presence of air the coal becomes plastic and swells at about 350-500°C and solidifies and shrinks when further heated to 500-1000°C. In Europe coking coal is mined mainly in Poland and Ukraine but there is some minor production also in UK, Germany, Czech Republic, Spain and Turkey.^{1, 2} However, the main part of the coking coal used in Europe for metallurgical coke production is imported from Australia and North America.

The production of coke in Europe was 29384 kt in 2016. The amount of coking coal needed for the production of coke varies dependent on the volatile content but approximately 1250-1400 kg coking coal is needed for the production on 1 t of coke. The amount of coking coal corresponding to the coke production in 2016 is following 36 730 - 41 138 kt of coking coal.^{1, 2}

9.2 GAPS LIMITING CIRCULAR ECONOMY

Coking coal has special properties related to the total mined material with specific carbon structure, ash composition and volatile content. During cokemaking the coal blend of coking coal is heated and in the pyrolysis, the coal is not only dried, the tars and oils are driven off and the coal is melting. A plastic phase is formed the

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

carbon structure is transferred to coke. As by-products e.g. elementary sulphur, benzene, tar, etc. are produced. The generated coke oven gas is used for different purposes as e.g in the heating of steel slabs, heating of blast air, drying of ceramics, drying of coal, production of electricity etc. Based on all these processes and disintegration of compounds during carbonization it can be understood that the coking coal is not present any more.

Screened-off fines from produced metallurgical coke containing coking coal can be added to the coking coal blend and replace some coking coal. Due to that these fines are inert in the carbonisation process, there is no plastic phase formed, the addition will result in lowering of the coke quality. Moreover, released tar that initially was one part of the coking coal can also be added to the coking coal blend.

Further, when the coke is used in metallurgical applications the coke is ending up as carbon dissolved in the metal but mainly as CO and CO₂ in the off gases. Further, the ash in the coke will become part of the slag.

9.3 ENVIRONMENTAL ISSUES

The use of coking coal and its product coke is related to production of coke oven gas which is constitute of mainly hydrogen and methane and some other hydrocarbons but contains also some carbon monoxide. Further, when using coke in steel production carbon is transferred to CO and CO₂ causing emission of CO₂.

The generation of CO₂ from the integrated steel plant is approximately 7% of global CO₂ emission.³ In order to counteract the increase of CO₂ content in the atmosphere it should be of importance to fully valorise carbon units in the off gases and thereafter capture CO₂ from these large streams. Residual CO in the gas stream can be reacted with water under the production of H₂ and CO₂. CO₂ can be captured for use in the production of chemicals or carbonates. Letting H₂ and CO₂ react under specific conditions is one way to produce methanol. Further, if N₂ in the off gases can be used for the production of ammonia (NH₃) and the ammonia can be reacted with CO₂ for the generation of urea. In such way N, H and C in the gas phase can be the basis for chemicals.

9.4 SUMMARY

There is no possibility to recover used coking coal as it is reacted and consumed during use. In order to enable the use of coking coal with minimised impact on climate change, actions collecting greenhouse gases for storage or use in the production of chemicals are desired.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

9.5 REFERENCES

1. http://ec.europa.eu/eurostat/statistics-explained/index.php/Coal_consumption_statistics#Consumption_and_production_of_hard_coal
2. Coal industry across Europe 6th Edition, European Association for Coal and Lignite, EURACOAL (web page <https://euracoal.eu/home/>)
3. <https://www.worldsteel.org/>

10 FLUORSPAR

Calcium fluoride (Ca F₂) is a halide type of mineral, colorful in both visible and UV light. It is widely occurring mineral with significant deposits on over 900 locations. It can occur in vein deposits (together with other minerals with which forms gangue) sometimes associate with galena, sphalerite, barite, quartz and calcite. It is a common occurrence in minerals of hydrothermal origin and it is a primary mineral in granites and other igneous rocks.

In the world the reserves and production are estimated to 260 million tonnes (Mt) with the largest deposits in South Africa (about 41 Mt), Mexico (32 Mt) and China (24 Mt).

China is leading the world production with about 3 Mt annually, followed by Mexico (1 Mt), Mongolia (0.45 Mt), Russia (0.22 Mt), South Africa (0.13 Mt), Spain (0.12 Mt) and Namibia (0.11 Mt). One of the largest deposits in North America is in the Burin Peninsula, Newfoundland, Canada.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

South African fluorspar: access to global markets

South Africa set to be world's premium fluorspar provider

- SA has 17% of world's fluorspar reserves (China has 10%)
- 95% of SA acidspars exported
- strategically positioned
- excellent logistics from Richards Bay and Durban ports

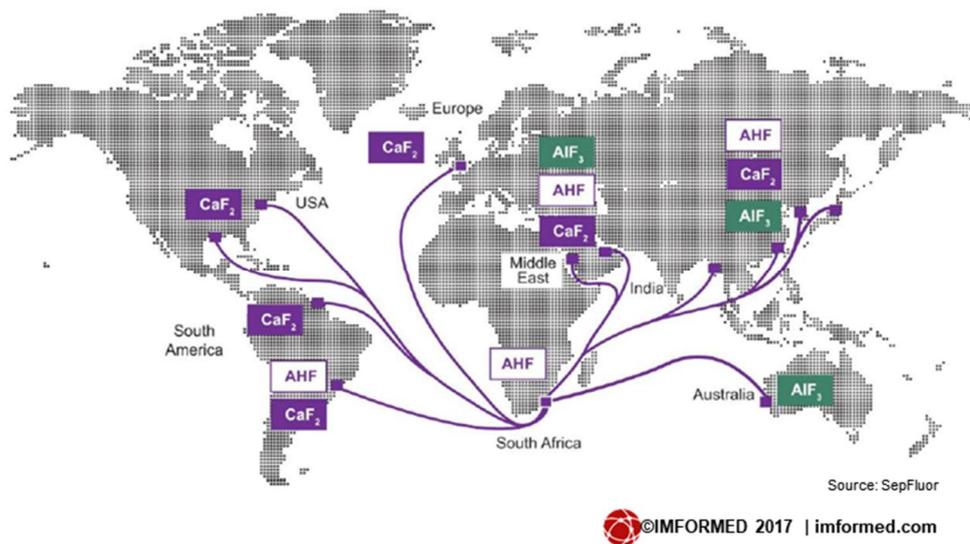


Fig. 1 South Africa prepares the ground for taking the lead in fluorspar production.

Besides the mineral resources, fluorspar can be also found in by-production of a number of minerals, among the most important ones is from limestone.

Other sources can be in the mining tailings.

There is also production of synthetic fluorspar, which can be produced from the neutralization of waste in the enrichment of uranium, petroleum alkylation and stainless-steel pickling. However, the further usage can be hindered by slight contamination from the respective production. The Aluminium producers are recycling the HF and the fluorides from smelting operations.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

The main use for fluorspar is as a flux for smelting and in the production of certain gases and enamels, as well as in the production of hydrofluoric acid. This is an intermediate product for the most fluorine-containing fine chemicals, see Figure 2.

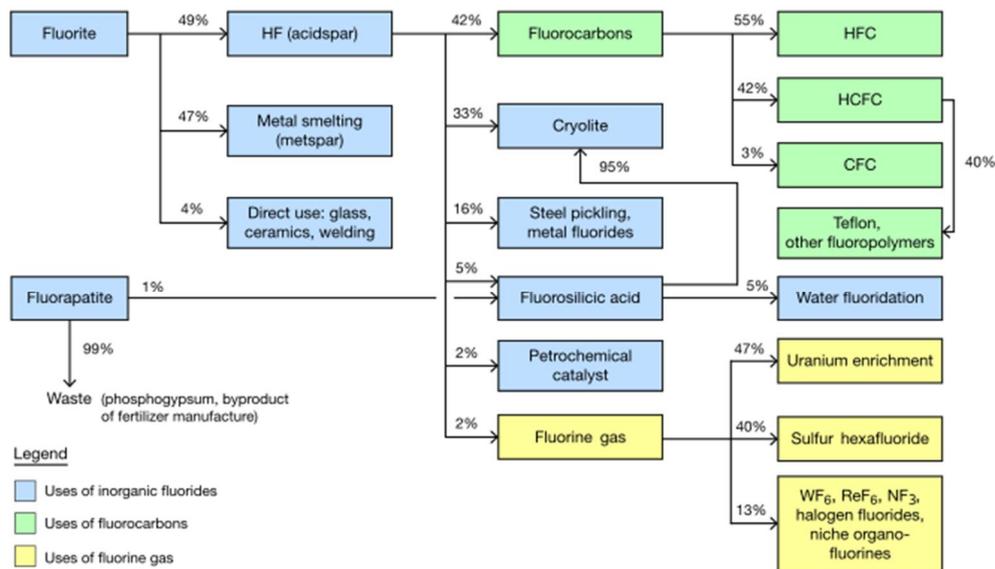


Fig.2 Uses of fluorite in different industrial application, along with waste production (Wiki)

According to Roskill (ROS 2017), fluorspar cannot be recycled, thus the only reliable source is either mining or synthetic fluorspar.

A series of mine closure in the mid 2017s in China plunged the production world-wide, China standing for 50% of the world production.

One of the clear hinder of production are the environmental aspect of production/mining, the reason of the Chinese authorities to shut down several operations especially on the South-Eastern China.

There are however several project attempts to recycle or partially recycle of partially fluorinated polymers by for example InVerTech (Bayereuth, Germany), which has the following flowsheet of materials as a possible circular economy/production:

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

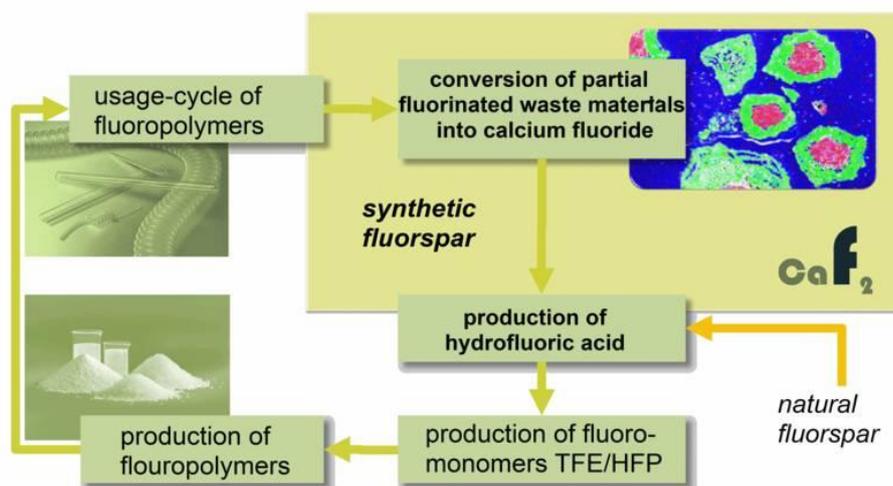


Fig. 3 Utilization cycle of synthetic fluoride, according to InVerTech.

The aim of the above-named project is to develop a flexible, environmentally friendly, high-performance process which makes it possible to convert fluorocarbon wastes into synthetic, high-quality fluorite. This fluorite shall then be directly included into value-added production as a secondary resource. The first step in this new approach to recover fluoride from organic compounds is to convert fluoropolymers and small molecular waste materials into CO_2 , HF and H_2O . This takes place within an autothermic high-temperature conversion process. The transformation of the gaseous mixture into synthetic fluorite is induced by a reaction with limestone (CaCO_3). The resulting fluorite is added to natural fluorspar and is then converted together with sulfuric acid into anhydrous HF using a conventional rotary kiln. To ensure direct use of the synthetic fluorite, the resulting material must be of high purity and have a narrow particle size distribution

10.1 SUMMARY

- There is very little interest in recycling or closing the loop of fluorspar. The new unexploited resources in South-Africa are so extensive and the technology for exploitation are new, simple and feasible, thus even with a number of mine closures around the world, the supply chain is ensured.
- The faulty exploitation of some Chinese deposits has caused some mine closures due to environmental concerns, however the prices are still high and rising, thus China is not losing momentum on the market.
- Synthetic fluorspar is feasible, however very little used and cannot compete with the natural resources.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

10.2 REFERENCES

ROS 2017 – Fluorspar – global Industry, Markets & Outlook, ISBN 978 1 91092231 6, 30/09/2017

11 GALLIUM

Gallium does not exist as a free element in the Earth's crust, and the few high-content minerals, such as gallite ($CuGaS_2$), are too rare to serve as a primary source. It usually occurs in trace concentration in aluminium ores, zinc ores and is extracted as a by-product along with the main metal, bauxites. Thus one can say that gallium production is highly dependent on the extraction of the main metal from, e.g. bauxite ores or sulfidic zinc ores. Sometimes coal can be a source of gallium as well. (Lu 2017)

Since it is a by-product, it is not easy to estimate the resources available, however it is counted that there is a minimum of 1200t/y from bauxite, 85 t/year from sulfidic zinc ores and potentially 590 t/year from coal. An approximate number is given in Figure 1. (POU 2013)

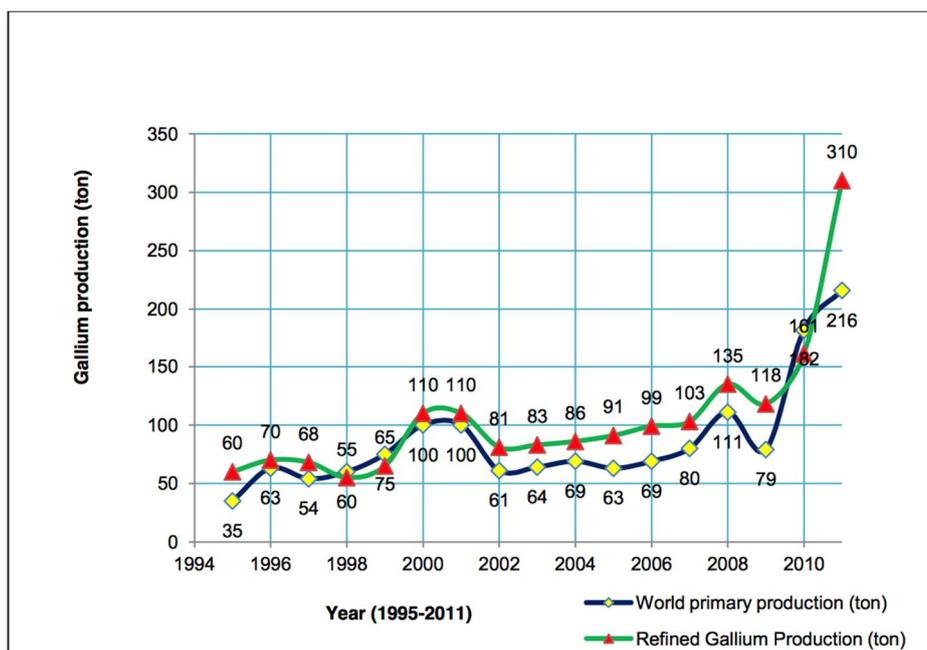


Fig. 1 World primary and refined production rate (1995-2011) (POU 2013)

Gallium is used mostly in semiconductor industry, which totals 98% of the demand for gallium. The next major application is the gadolinium-gallium garnets for use in jewelry decoration or for optical instruments. Other uses

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

are in electronic, glazing and bio-medical applications. A more special application is in neutrino detectors, where pure gallium is needed. Also, another emerging use of gallium is in the field of photovoltaics and LED. A recycling process have been developed at Chalmers university for the high-purity recycling of gallium from fabrication sputtering waste.

Another application is in mobile telephony and microwave appliances.

11.1 GAPS HINDERING CIRCULAR ECONOMY

According to UMICORE (UMC 2018), gallium, as well as bismuth is not easy to recycle on an industrial scale due to the dissipative use of gallium. The recycled materials come mostly from production spills from semiconductor industry.

11.2 SUMMARY

To summarize, gallium applications in other domains than semiconductors will increase the need of the metal in the future, however the capacitors are a good source for high-concentrate gallium, thus the recycling of these items might be a future source. Otherwise, the gallium demand and business models are highly underdeveloped if at all.

11.3 REFERENCES

UMICORE – (2018) – Gallium, <http://www.umicore.com/en/about/elements/galium/>, retrieved May 2018

Faughai Lu, Tangfu Xiao, Jian Lin & All, (2017) Resources and extraction of gallium: A review, Hydrometallurgy, Vol. 174, p. 105-115

Pouya Yarahmadi Dehnavi, (2013) Global Cycle of Gallium production, use and potential recycling, KTH PhD Thesis, ISSN 1651-064X, LWR-EX-13-23

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

12 GERMANIUM

12.1 INTRODUCTION

Ge is a greyish-white, brittle semimetal with a bright lustre. Due to its excellent electrical properties, it acts as a semiconductor, being used in several technologies. Currently, its main applications are as a polymerisation catalyst in plastics (25%), in fibre optics (30%), in infrared night vision devices (25%), and as a semiconductor and substrate in electronic circuitry and solar cells (20%) [1] [2].

Ge does not appear in its elemental state in nature, but it is found as a trace metal in a variety of minerals and ores. Today, Ge is extracted as a by-product of Zinc production (60%) and from coal (40%). Only China and Russia recover Ge from fly ash. Others Ge producers are USA and Canada. In EU, Finland produced Ge from Cobalt concentrates (OMG's Kokkola plant), but it stopped the production in 2015 [3]. World refinery production in 2012 is estimated at 136 tons. EU imports around 15 tons per year of unwrought Ge and Ge powders, primarily from China, who produced approximately 70% of world's Ge demand in 2014. This fact is very important as unstabilities in the country may affect Ge production in the future, so limit the imports from other countries and enhance own production would place EU in a better position respect to its dependence from this raw material [2]. As Ge primary production in EU is limited, and would imply new mine explorations (currently in Portugal and Slovakia according to the Minerals4EU website [3]), the most feasible options to produce Ge at short term and reduce the Ge consumption, would be minimizing the losses of the metal during processing and even more, enhancing recycling.

In EU, Umicore (Belgium) and Recylex (France), with its subsidiary PPM Pure Metals GmbH (Germany) are large global recyclers and refiners of zinc with combined Ge production, being also experts in manufacturing Ge-based products for various applications [1]. Also Chemical and Technical developments Ltd in UK recycles all kinds of scrap and waste containing Ge metal, Ge dioxide and other Ge compounds, normally from infra-red lenses and other infra-red systems. Ge is mainly recycled from production processes of various industries such as fibre optics, solar cells, LEDs and infrared optics ("new scrap"). For example, Robertz *et al.* (2015) from UMICORE stated that in the case of GeCl_4 produced from PV production scraps, the main impacts were the energy sources in the pyrometallurgical treatment and the reagents used in the pyrometallurgical and hydrometallurgical treatments, as hydrochloric acid [3]. Approximately 30% of the world's production comes from recycled new scrap, being recovered and reinserted in the production process. For example, during the manufacture of optical devices, more than 60% of Ge metal used is recycled as new scrap [2] [4].

End of life recycling (also called "old scrap" recycling) present significant challenges due to the dissipative nature of some of the applications [5]. It is estimated less than 1% of EoL recycling [6]. This fact is due to the presence of Ge in products and devices as trace metal, making it technologically and economically difficult to recover [2] [7].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Particularly in Europe, the PET sector is the most important, accounting for 29% of global volume sales [1]. Several studies agree that Ge into PET products is currently unrecyclable, as Ge dissipates completely in the product [5] [4] [8] [9] [10].

The aim of the following sections is giving a general overview of Ge circular economy possibilities in EU, to enhance recycling activities and therefore decrease the EU dependence from other countries and even foster new markets lines. All the information provided is based on bibliographic review, trying to compile all existing publications about Ge potential losses during its whole life cycle. Also, environmental issues are included in each step of the value-chain when possible.

It is worth to say that the information on this topic is scarce, so the content of this review is very general and would need more industry data about Ge producing in EU that is not available.

Although PET catalysts is the main application of Ge in EU, information about Gerecycling from fibre optics (the second main application) has also been included, as into PET catalysts Ge dissipates completely in the product and is currently unrecoverable as commented before.

12.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS OF GE MAIN APPLICATIONS VALUE CHAIN IN EU

12.2.1 GE PRODUCTION

Ge is a by-product in some sulphide ores and in some coals; therefore, surface and underground mining methods that are commonly used to extract base metal and coal are employed [1]. Typically, Ge is recovered as a by-product from zinc production residues, flue gases of zinc smelters, copper ores and fly ash from coal combustion process. Coal and coal ashes carry on average 2.2 and 15 ppm Ge, respectively [11]. Robertz *et al.* (2015), consider that coal Ge content is of 600 ppm, as a medium range of those reported in the literature [3].

After mining, the ores are processed to increase their base metal and Ge contents using conventional mechanical (grinding, sieving, magnetic separation) and flotation methods. The next diagram shows the steps of Ge processing. As said, Ge is mostly obtained from zinc smelter flue systems and dusts of smelters that process zinc ores. This process involves 1) refining zinc, 2) distillation under non-oxidising condition, 3) recovery of the distillation residue, 4) formation of Ge tetrachloride by leaching the distillation residue with hydrochloric acid, 5) hydrolysis of Ge tetrachloride into GeO_2 , and optional reduction of GeO_2 into metallic Ge with hydrogen at 760°C . Metal powder is melted and moulded into metal bars, from which highly purified metal may be produced by zone refining polycrystalline processes. Fractional crystallisation of volatile GeCl_4 is also used to separate Ge from other metals.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

The recovery of Ge from lignite includes burning the coal at 1200°C and pyro-metallurgical treatment after filtering the ashes, followed by sulfuric acid leaching [1].

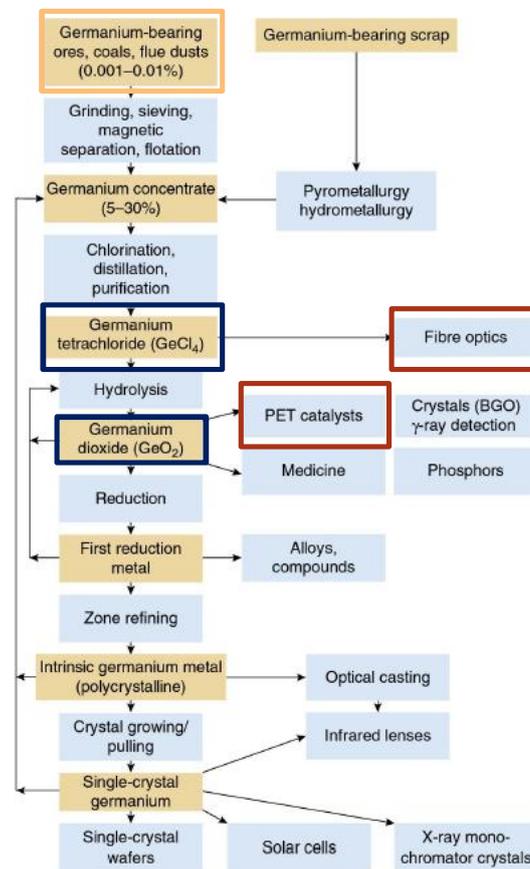


Figure 6. Ge production flow-sheet from ores, coals, flue dusts and scraps.

The main Ge fraction in the zinc ore extracted worldwide is not valued and is considered as lost (in tailings, as impurities in zinc products, etc). About 760 tonnes of Ge were present in 2012 in zinc ores mined worldwide, but only a small proportion was recovered [3]. But the data found in literature differs according to the values.

Licht *et al.* (2015) estimated that 5402 t of Ge were not being extracted from hydrometallurgical processed Zn concentrate, taking into account refining efficiencies of 68%. Further, they estimated a recoverable amount of 1910 tons as losses, considering a very conservative extraction efficiency of 50% from fly ash. Then, they stated that given low Ge-refining capacities and inefficiencies, only 42.7 and 39.9 t of Ge were produced from Zn leach residue and coal fly ash, respectively, which was less than 2% of the Ge available. This data refers to USGS data in 2011. Concerning production from scrap recycling, 35.4 t of Ge were recovered [11].

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

In Europe, currently there are not Ge production from zinc or coal, but there are lignite production in several countries as Greece, Bulgaria, Hungary, Poland, and Romania, and also large zinc production in Ireland, Sweden, Portugal, Poland, Finland, and Spain, among others [12]. So, EU has potential to produce Ge from Zn and Coal sources.

For example, it was estimated that about 2000 tons of Ge are annually discharged in stack gases to the atmosphere by the combustion of coal in the United Kingdom [7]. Also, Ayres *et al.* (2001) estimated that Ge and Ga content of coal ash exceeded primary refinery production by a factor of 200 [13]. The lack of data on Ge emission to the atmosphere by coal firing in EU impedes the estimation of possible Ge recovery [14], but as this recovery may become economically feasible, there are various leaching procedures developed [15]. Already in 2004, Moskalyk R. stated the potential of coal ash as a future source once more accessible resources become depleted [7]. Also Földessy and Gombkötö stated the economic potential of Ge extraction from coal ash in Hungary [16].

Improved efficiency in the primary production combined with the reworking of historic primary stocks, will provide a large and rather easy accessible additional Ge source [17].

Concerning environmental aspects in extraction and processing steps, Ge is not considered to cause damage to the environment, due to its low toxicity and its presence as trace element in rocks and ores, perhaps with the exception of the close surroundings of Ge production or processing sites [1].

Ge compounds have also low order of toxicity, with the exception of Ge tetrahydride [7], which is considered toxic. However, materials as arsenic and cadmium, consumed or produced as a by-product during the processing of Ge-bearing materials, may present potential problems, but they are separated out at the smelter stage and controlled in the refineries. Acids and bases used in the process are neutralised and held in tailings ponds. The largest source on input for Ge in the environment is the combustion of Ge-containing coal and lignite which is estimated to exceed emissions from its industrial production by two orders of magnitude. Ge levels found in the hydrosphere have been reported as 0.016, 0.029 and 0.079 $\mu\text{g}/\text{dm}^3$, for fresh, estuarine and saline water, respectively. Rainwater exhibited an even lower Ge concentration of 0.0088 $\mu\text{g}/\text{dm}^3$ [14, 1]. The exposure of GeO_2 to HCl emits volatile GeCl_4 which is both corrosive and irritating, and is classified as a dangerous liquid subject to international regulations for material handling. Powdered Ge metal reacts violently with concentrated nitric acid. It is not compatible with fused alkalis, strong oxidizing agents and halogens [7].

Robertz *et al.* (2015) made a comparison between impacts from Ge primary production from coal (based on literature data) and secondary production of Ge (based on UMICORE process), and stated the benefits linked to the recycling of metals, attributing the main primary production impacts to the mining and burning of the coal to produce a Ge concentrates, and concerning secondary production from PV production scraps, to the energy sources used in the pyrometallurgical treatment and the reagents used in the pyrometallurgical and hydrometallurgical treatments (for example, HCl) [3].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

12.2.2 PRODUCT DESIGN AND PRODUCTION

12.2.2.1 GE AS CATALYST IN PET PRODUCTION

As mentioned in the introduction, in EU the main use of Ge is as polymerization catalyst for PET production, in GeO_2 form. In EU, Umicore is an important producer of catalyst grade GeO_2 [1]. Ge content in GeO_2 catalysts is about 69%. The average Ge metal consumption in polyester production is about 80 ppm per tonne PET. [9].

Polyesters are made by the reaction of bi-functional acids and alcohols, in the presence of a metal catalyst. The metal catalyst are used at extremely low concentrations to promote the reactions and ensure practical economics. PET manufactured using GeO_2 catalysts is mainly used for drink bottles and shows particularly good properties in terms of brightness and shine. Ge remains in PET bottles, normally grading 10-70 ppm per tonne. Estimated world polyester production in 2009 was about 50 million tonnes per year. About a third of this production volume was used for PET bottle grade, and around 10% of the PET produced is using GeO_2 catalysts [1]. Making an estimation, this means around 16,5 kg of Ge used to PET bottle production in 2009.

However, Licht *et al.* (2015) estimated that 9.92 t of Ge ended up in waste streams of PET production, where 1,48 t were internally recycled and the remaining 8,44 t dissipated in wastewaters [11]. This data refers to USGS data in 2011. New scrap in internal production amounts to approximately 5% of the total used in new manufacture [14].

In the PET manufacturing, GeO_2 from polymerization catalysts dissipates completely into the product and is not recovered. Therefore, the potential secondary flows cannot be quantified based on the number of polymerization catalysts but on the number of PET bottles placed on the market [9]. Dissipation means that receiving medium only contains small concentrations of the material in question, making the recovery impossible or at least technically and economically unattractive [8].

However, the recovery of Ge from wastewaters from PET production process may be a field of study.

12.2.2.2 GE IN FIBER OPTICS

The manufacturing process for making optical fibers involves high temperature oxidation of silicon tetrachloride (SiCl_4) and GeCl_4 to form glass particles (SiO_2 and GeO_2) which are incorporated into a glass preform rod ("Modified Chemical Vapor Deposition, MCVD, developed at Bell laboratories). This rod is subsequently drawn in a furnace to produce the optical fiber. GeCl_4 is mainly used as a dopant for fiber optic systems to alter the refractive index. The optic fibre cable consists in general of a core, cladding and a primary coating. Generally, 96% of optical fibre is SiO_2 and 4% of GeO_2 , with small amounts of other elements, but only 0,03% to 2% of the cable is the optical core. For 2,5 km of optical fibre, about 1 gram of GeO_2 is used. The primary coating is made of materials such as silicon and nylon. There are very few companies manufacturing the optic fibre itself [18]. It is known from experimental studies that the oxidation of GeCl_4 to GeO_2 proceeds to only 25% completion whereas oxidation of SiCl_4 is nearly complete. Particle deposition is only 50% efficient, resulting in further losses

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

of Ge [19]. In 2011, 35.4 t of Ge in USA were destined to this product, of which 24,8 t were lost in the effluent of the oxidation process. [11]. Typically, the effluents contain 70-85% of the GeCl_4 used in the process. Only one study was found about the recovering of Ge from effluents of optical fiber manufacturing, by Bohrer *et al.* in 1985 [20] [20]. The process consists on a first wet scrubbing of the effluents, followed by solution filtering and recirculation, and Ge precipitation, being collected as a wet filter cake which is easily reprocessed to make GeCl_4 . Moreover, the process provides the removal of chlorine and particulates, eliminating environmental pollution.

The production of fiber-optic cables generates scrap, which consists primarily of quartz glass and synthetic materials that contain the Ge. Extraction of Ge from these scraps requires economically viable recycling processes. HZDR (Germany) is developing a recycling process that will convert the Ge and silicon dioxide in the glass scraps into chlorides. The chlorides of these elements are easily separated via distillation and can be purified for the production of new fiber-optic cables. They are also studying the mechanical processing of fiber scrap [21].

Recycling from “new scrap” in the production of Ge-containing fibre-optic cables, counting for 50 % of Ge recycled material in US economy. Most of the scrap is sent to a Ge processors for recycling which are able to recycle material containing a minimum of 2% Ge, including solutions, fibres, dust and filter mats from air-conditioning systems. Processing of scrap normally involves dissolution into GeCl_4 (which is considered toxic, as stated before). The quality of products is not affected by recycled material. Fibre-optic cables for telecommunication contain up to 60% of recycled material, from new scrap, and 40% virgin material. Around 80% of Ge containing in the scrap can be recycled [1].

12.2.3 USAGE

12.2.3.1 GE AS CATALYST IN PET PRODUCTION

A typical dissipative loss occurring during the use phase of a product into other material flows is the dissolution of Ge catalysts into the PET bottles. Zimmermann *et al.* (2013) studied the order of magnitude of dissipation for some critical materials, analysing the major applications of each metal including potential losses during fabrication/manufacturing and use phase, as well as recycling situation. The study concluded a dissipation rate assumed of >90% for Ge, but stated the existing lack of data [8].

During the use of the PET produced with GeO_2 catalysts, there are no significant losses of Ge produced, so there are not possible Ge recoveries nor environmental damage produced by Ge metal or Ge compounds [17].

12.2.3.2 GE IN FIBER OPTICS

No detailed data is available on the life span of optic fiber cable. However, for the cables an operational life span of 20 years is assumed, based on the assumption that major refurbishment and restructuring of the buildings is likely to take place and the wiring adapted and renewed for renewed needs.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

Through the use phase, energy consumed is that required by converters (max. 90W). Heat generation also occurs [18].

12.2.4 END OF LIFE

12.2.4.1 GE AS CATALYST IN PET PRODUCTION

Since the Ge dissipates completely into the PET, the PET bottles have to be considered the relevant product for analyzing the end-of-life chain. PET bottles represent the end-use product with the highest share of Ge (19,6 t) and the highest losses, because even though PET bottles are normally recycled, Ge is not recovered. Thus far, recovery of Ge from obsolete PET material is not possible [11]. Within the current end-of-life treatment of PET bottles, the recovery of Ge is not an issue in any form and a complete loss has to be noted. No findings exist regarding potential options to recover Ge from PET.

PET bottles are normally re-used or shredded and sold for other applications. As PET post-consumer scrap, Ge is totally lost.

In the study on the review of the list of Critical Raw Materials from European Commission, in June 2017, it is stated that PET catalysts end-uses are not occurring in the EU [22].

12.2.4.2 GE IN FIBER OPTICS

Fibre-optic cables have a long residence time in their applications, thus recycling volumes for old scrap are rather low. This source and technology associated has not been fully developed [4]. However, in the future, they may have considerable post-consumer recycling potential.

In comparison to metal containing cables where the recovery of metal is economically reasonable, there are no valuable materials in optic fibre cable that would encourage recycling. In particular, the presence of sticky gel makes cost-effective recycling hard to achieve. Although research is underway to improve recycling techniques, they have not yet been widely applied [18]. It is assumed that used cables are disposed of by incineration.

12.2.5 RESIDUE TREATMENT

12.2.5.1 GE AS CATALYST IN PET PRODUCTION

As said before, in EoL PET products Ge is totally lost and unrecovered. Wastes are treated outside EU and not recovery of Ge is stated.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

12.2.5.2 GE IN FIBER OPTICS

All used optical fibres go into non-functional recycling in C&D waste. There are few companies that recycle fiber optic cables. Communicom, in US, recycles Fiber Optic Cables and Fiber Scrap, which is converted back to its basic components and made into Plastic Pallets and other resalable products, but no evidence of Ge recovery is stated [22].

12.3 SUMMARY

Ge is mined outside EU, so the possibilities to extract Ge from mining by-products and wastes does not exist. In EU, few companies have been identified as refiners, being the most important UMICORE, who produces Ge products from zinc concentrates. There are some mine explorations in EU that maybe in a future could produce Ge, but not in a short term. What already exist in EU is zinc and coal production, that although not Ge production exist at the moment, maybe with new environmentally and cost-efficient processes would imply a source of Ge in EU.

The results of the analysis of the complete value chain of Ge, focusing on PET and fiber optic applications, show that the Ge recycling from EoL products is negligible, if exist. There are very few companies identified in EU which recycles Ge from fiber optics, but there are no data available. In the products manufacturing, it seems that Ge scraps produced are internally recycled and, especially in fiber optics, account for high percentage in new product manufacturing. However, little fiber optic production is identified in EU. The big producers of fiber optics are in USA and China, so even the recovering of Ge from fiber optic production effluents may become feasible, it is not realistic to maintain a supply for EU. However, the scraps of quartz glass and synthetic materials that contain the Ge generated in the process may be bought, but there would be essentially based on non-EU imports. No studies about Ge recovery from PET manufacturing waste waters have been found, but once Ge concentration in these waters have been analysed, maybe it could be also a Ge recycling source in EU.

Summarizing the potential Ge production in EU from production to PET and fiber optic applications, there is a need of:

- More data from EU industries that take part in the Ge value chain, and if possible clustering of EU industries manufacturing Ge products and EU Ge recyclers, to identify the potential and unlocking Ge losses in EU.
- Studies on availability of Ge extraction from Zn and Coal by-products on EU mines, and cost-efficient and environmentally friendly techniques.

Concerning environmental issues related to Ge value chain, the important aspects are related to mining and processing activities, and as these activities are not carried out in EU, there is no problem in EU now. Moreover, except for some compounds, as GeCl_4 , Ge is not considered toxic and there are not significant losses during the products use and end of life phases, mainly to the scarce presence in the products.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

12.4 REFERENCES

- [1] F. Melcher et P. Buchholz, «Germanium,» chez *Critical Materials Handbook*, British Geological Survey, 2014, p. 178.
- [2] E. Commission, «Report on Critical Raw Materials for the EU, Critical Raw Materials Profiles,» 2015.
- [3] B. Robertz, J. Verhelle et M. Schurmans, «The Primary and Secondary Production of Germanium: A life-cycle assessment of different process alternatives,» *JOM*, vol. 67, n° 12, 2015.
- [4] J. D. Jorgenson, «Germanium recycling in the United States in 2000,» U.S Department of Interior, U.S. Geological Survey, 2000.
- [5] UMICORE. [En ligne]. Available: <http://www.umicore.com/en/about/elements/germanium/>.
- [6] UNEP, «Recycling rates of metals - A status report,» 2011.
- [7] R. Moksalyk, «Review of germanium processing worldwide,» *Minerals Engineering* , vol. 17, pp. 393-402, 2004.
- [8] T. Zimmermann et S. Göbling-Reisemann, «Critical materials and dissipative losses: A screening study,» *Science of the Total Environment*, Vols. 1 sur 2461-462, pp. 774-780, 2013.
- [9] T. Zimmermann et S. Göbling-Reisemann, «Recycling potentials of Critical Metals-Analyzing Secondary Flows from Selected Applications,» *Resources*, vol. 3, pp. 291-318, 2014.
- [10] L. Ciacci, B. K. Reck, N. T. Nassar et T. Graedel, «Lost by design. Supporting information,» *Environ.Sci.Technol*, vol. 49, pp. 9443-9451, 2015.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [11] C. Licht, L. T. Peiró et G. Villalba, «Global Substance Flow Analysis of Gallium, Germanium, and Indium,» *Journal of Industrial Ecology*, vol. 19, n° 15, p. 890, 2015.
- [12] T. Brown, S. Hobbs, N. Idoine, A. Mills, C. Wrighton et E. Raycraft, «European Mineral Statistics,» British Geological Survey, Keyworth, Nottingham, 2016.
- [13] R. U. Ayres, J. Holmberg et B. Andersson, «Materials and the Global Environment: Waste Mining in the 21st Century,» *Materials challenges for the next century*, pp. 477-480, June 2001.
- [14] E. Rosenberg, «Germanium: environmental occurrence, importance and speciation,» *Rev Environ Sci Biotechnology*, vol. 8, pp. 29-57, 2009.
- [15] F. Arroyo et C. Fernández-Pereira, «Hydrometallurgical Recovery of Germanium from Coal Gasification Fly Ash. Solvent extraction method,» *Ind.Eng.Chem.Res.*, vol. 47, n° 19, pp. 3186-3191, 2008.
- [16] J. Földessy et I. Gombkötö, «Strategic elements - Primary and secondary resources in Hungary,» chez *24th Annual General Meeting of Society of Mining Professors*, Milos island, Greece, 2013.
- [17] C. Meskers et C. Hagelüken, «Complex Life Cycles of Precious and Special Metals,» Thomas E. Graedel and Ester van der Voet, 2010.
- [18] N. Unger et O. Gough, «Life cycle considerations about optic fibre cable and copper cable systems: a case study,» *Journal of Cleaner Production*, vol. 16, pp. 1517-1525, 2008.
- [19] A. I. o. C. Engineers, «AIChE - The Global Home of Chemical Engineers,» 1990. [En ligne]. Available: <https://www.aiche.org/community/students/student-design-competition/recovery-germanium-optical-fiber-manufacturing-effluents>. [Accès le 28 September 2017].
- [20] M. P. Bohrer, J. A. Amelse, P. Narasimham, B. Tariyal, J. M. Turnipseed, R. F. Gill, W. J. Moebuis et J. L. Bodeker, «A Process for Recovering Germanium from Effluents of Optical Fiber Manufacturing,» *Journal of Lightwave Technology*, Vols. 3 sur 3, n° 13, pp. 699-705, 1985.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

[21] HZDR, «HZDR,» [En ligne]. Available: <https://www.hzdr.de/db/Cms?pNid=195>. [Accès le 28 September 2017].

[22] Communicom, «Communicom,» [En ligne]. Available: <http://www.communicomrecycling.com/Safe-Recycling-Program-Rock-Hill-SC.html>. [Accès le 28 September 2017].

13 HAFNIUM

13.1 INTRODUCTION

Hafnium is mainly used for superalloy production as an alloy additive. It is also used in nuclear plants as a neutron absorber (steering rods in nuclear reactors), ceramics (some of its compounds are fire retardant and melts only at extremely high temperatures) or as an agent stabilising ZrO₂ (prevents excessive crystal growth). Specificity of hafnium recovery (hafnium is obtained during production of metallic zirconium for nuclear applications, where complete recovery of Hf is required) causes oversupply, which is stored mainly in the form of an oxide. The main market products of hafnium are sponge and metallic hafnium containing 97-99% Hf, as well as its compounds, mainly hafnium oxide (hafnia). World hafnium resources, connected mainly with zirconium minerals (baddeleyite) exceeds 1 mln tonnes. Due to mining difficulties and insignificant abundance in Earth crust hafnium application is limited.

Recycling of hafnium is specific due to its application areas and because it is produced and used mainly in combination with zirconium. Hafnium and zirconium are miscible in each other. Amounts of one metal in another may differ and its proportions are often random. Due to hafnium application fields (nuclear technology, superalloys or microprocesors) the number of its recycling companies is limited.

13.2 GAPS LIMITING CIRCULAR ECONOMY

Hafnium is recovered as a by-product in the production of pure metallic zirconium from its concentrates. Its typical Zr:Hf content ratio is 50:1. The most significant producers are: USA, France, Ukraine, Germany, Great Britain, China and Russia. The main supplier of metallic hafnium are American corporations: Wah Chang (40% market share) and Western Zirconium (20%) as well as French Compagnie Europeene du Zirconium – Cezus (40%).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

World hafnium supply, after a long period of stabilisation, is increasing over the last 10 years. It is a result of increasing zirconium concentrate production. Nuclear industry requires pure zirconium alloys, therefore hafnium is removed (it is not desired due to strong thermic neutrons absorption in fuel rods). Additionally, lower activity of arms industry and increasing supply from Russia also have influence on stability of hafnium market. Moreover, substitution of hafnium by Ag-Cd-In alloys in steering rods of nuclear plants or by zirconium in some superalloys may be noticed. Production of hafnium is strongly associated with current situation on zirconium market.

There are almost no information about hafnium content in metallic scrap and recycled amount. Information about recycling methods of hafnium are not widely available. High quality metallic scrap is remelted into ingots and then processed. Lower quality scrap is usually oxidised and then, depending on the purity, returned to the process stream or landfilled [1]. The main difficulty in the Hf recycling is its high melting point, which strongly limits its processing methods. End-of-life recycling rate of hafnium in 2011 was below 1% [2]. Hafnium recycling rate is low and applied recycling methods are either insufficient or not widely shared.

13.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

Hafnium belongs to strategic metals. Its consumption is increasing every year. It should be noted that its production is small (ca. 65 tones) comparing to other industrial metals. It is forecasted that Hf demand will increase by even 40% to 2020 due to its application in new technologies [3].

The following table presents data concerning production, demand and supply of hafnium in European Union [4].

Raw material	Main world suppliers (2010-2014)	Main importers to EU (2010-2014)	EU demand sources (2010-2014)	Import dependence factor *	Substitution factor EI / SR **	End-of-life recycling input rate***
Hafnium	France (43%) United States (41%) Ukraine (8%) Russia (8%)	Canada (67%) China (33%)	France (71%) Canada (19%) China (10%)	9%	0.93/ 0.97	1%

* net import / (net import + EU domestic production)

** is a measure of the difficulty in substituting the material, scored and weighted across all applications, calculated separately for both Economic Importance and Supply Risk parameters. Values are between 0 and 1, with 1 being the least substitutable

*** The 'End-of-life recycling input rate' measures the ratio of recycling from old scrap to EU demand of a given raw material, the latter equal to primary and secondary material supply inputs to the EU

Price of unprocessed metallic hafnium imported from France to US market was 225 USD/kg in 2008, then in 2009 increased twice to 472 USD/kg, following zirconium proces. After small decrease in 2010 to 453 USA/kg years

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

2011-12 demand on hafnium again increased and its prices reached 530-540 USD/kg. In 2013 hafnium price reached ca. 600 USD/kg and stabilised at this level to 2015. In 2017 according to Argus Media the price of hafnium was ca. 900 USD/kg and it decreased from almost 1100 USD/kg in 2016 [5].

13.4 ENVIRONMENTAL ISSUES

Hafnium generally is not problematic. However, all hafnium compounds should be considered as toxic with limited health concerns. Metallic dust causes fire and explosion danger. Metallic hafnium is toxic. It is insoluble in water and aqueous solution of salts. Hafnium exposure may occur by inhalation, digestion or eye and skin contact. Overexposure on hafnium and its compounds may cause eye, skin and mucosal irritation. No symptoms of chronic hafnium exposure were observed.

Hafnium is not toxic for plants. They get small amounts of hafnium from soil. There is not much data concerning hafnium toxicity for animals. Tests show that hafnium compounds causes eye, skin and mucosal irritation as well as liver damage. Oral LD50 for hafnium tetrachloride for rats is 2362 mg/kg, while intraperitoneal LD50 for mice is 112 mg/kg.

Environmental hazards connected with hafnium recovery may be also associated with the presence of radioactive metals (uranium, polonium, thorium), which may be present in the scrap. It should be taken into account during processing or disposal of wastes.

13.5 SUMMARY

Production and applications of hafnium are strongly related to zirconium. Both elements are present in the same ores. Metallic hafnium is a by-product in the production of pure metallic zirconium for nuclear application. Therefore, availability of hafnium strongly depends on the current demands on ultra-pure zirconium. Zirconium and hafnium may be also used interchangeably in many superalloy applications.

Economics of hafnium recyclability depends also on the current situation on the markets of primary and secondary hafnium. Currently only recycling of large metallic pieces of pure hafnium is profitable. Processing of other hafnium-bearing scrap is limited to its neutralisation before landfilling.

13.6 REFERENCES

1. Haygarth J.C., Graham R.A., Zirconium and Hafnium, in: Review of extraction, processing, properties & applications of reactive metals ed. Mishra B., 1999
2. Graedel T.E. et al., What do we know about metal recycling rates?, J. Ind. Ecol., 2011, 15, 355-366

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

3. Schweizerische Metallhandels AG.
4. European Commission, COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS on the 2017 list of Critical Raw Materials for the EU, 2017
5. USGS, Zirconium and Hafnium, 2013-2018, Mineral Commodity Summaries
6. USGS, Recycling – Metals, 2015

14 HELIUM

14.1 INTRODUCTION

Helium is a chemical element with the symbol He and atomic number 2. It is a colorless, odourless, non-toxic, inert, monoatomic gas and is the first in the noble gas group. Helium is the second most abundant element after hydrogen in the universe and the most common is helium-4. It has the lowest boiling point among all the known elements. It was discovered by two Swedish chemists in 1895, Per Teodora Cleve and Nils Abraham Langlet, which found helium emanating from the uranium ore cleveite.

On earth helium stands for 5.2ppm by volume in the atmosphere while the terrestrial helium is created by the natural radioactive decay of heavy radioactive elements from for example, thorium and uranium, as the alpha particles emitted by their decay consists of helium-4 nuclei.

This type of helium (radiogenic) is trapped with natural gas in concentrations as high as 7% by volume.

The helium resources of the world, exclusive of the United States, were estimated to be around 31.3 billion cubic meters (USGS 2017).

In December 31, 2016, the total helium reserves of the United States were estimated to be 20.6 billion cubic meters. This included 4.25 billion cubic meters of measured reserves, 5.33 billion cubic meters of probable resources, 5.93 billion cubic meters of possible resources and 5.11 billion cubic meters of speculative resources.

The locations and the volumes of the major deposits, in billion cubic meters are: Qatar 10.1; Algeria 8.2; Russia 6.8; Canada 2.0; China 1.1.

A recent discovery of a very rich helium deposit has been done in Tanzania, where the helium is in up to 10% concentration and the company which stepped in of eventual production is called Helium One (HEL –O 2017).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

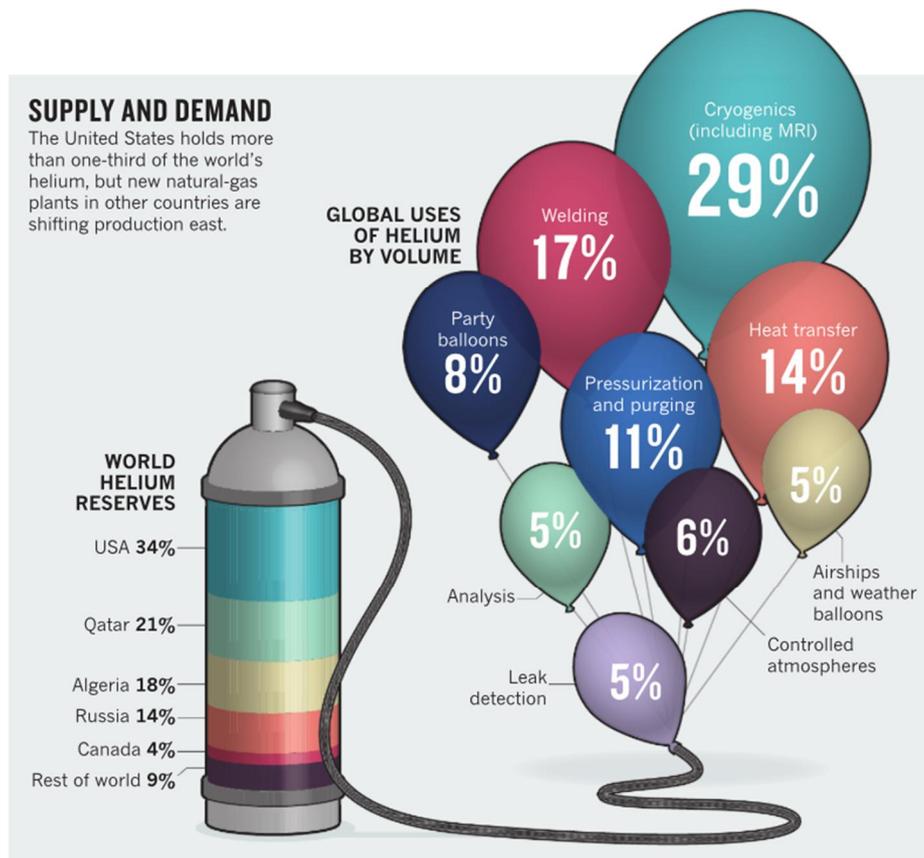


Fig. 1 The supply and demand of helium, by use (NUT 2012)

It's unique combination of properties makes helium very sought-after commodity for a lot of applications.

Just to name a few applications: MRI, laboratory, controlled atmospheres, breathing, fibre optics, leak detection, welding, purging/pressurizing, other cryogenics, lifting/balloons, electronics, etc.

Qatar is the second-largest producer of helium in the world and currently is facing a series of market and political blockades which make the production of helium very precare. A large number of scientists (which are the first to struggle with shortage of helium supply) are calling for a serious consideration of recycling helium on larger scale (NAT 2017). Only some industrial facilities have a local recycling of helium set-up and only a few national laboratories.

Already in 2012, Nuttall &All (NUT 2012) were flagging for the precarity of production, the high demand and a potential crisis.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

One of the producers of helium is in Algeria, the helium is produced by Helison Production Spa, a joint venture between the Algerian gas and oil company Sonatrach and The Linde Group, which has started operation in 2006 in Skikda, (East of Algeria). The plant has been designed and build by Linde Engineering. (Gasworld.com, from 29th of November 2007).

The nominal capacity of the Skikda plant is 600 mmscft/year of liquid helium (16 million Nm³/year), according to the company webpage (HEL 2017).



Fig 2. Image of part of the production plant, retrieved from (HEL2017).

Sonatrach supplies the feed gas which is a mixture of helium, nitrogen and methane to Helison from their three LNG plants they own and operate in Skikda.

According to the source, during the helium production process, the nitrogen is separated, liquefied and delivered back to Sonatach for use in the industry while the methane is returned to LNG complex and used to produce steam. This way the Helison plant is emission-free.

Even this particular case, as Qatar, have been facing numerous problems, mostly connected to technical problems but also some political instability in the region.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Some attempts to recycle helium from other sources have been the recycling of helium from optical fiber manufacturing (US Patent 1996).

14.2 SUMMARY

- a. Helium is largely used in many applications which are industrially and scientifically important.
- b. Since the helium is naturally produced together with natural gas (of where it is further extracted), in general countries with serious supply of natural gas resources have the possibility of production as well.
- c. US has decided to open up the helium reserve and sell part of the stock in 2005, Qatar has built-up the capacity and the production was aimed to be the highest in the world. However political unrest has lead to uncertainty of Wuatar's production and supply capability.
- d. There is no serious attempt to recycle helium, more than some small installations in some industrial applications or in some laboratories.

14.3 REFERENCES

NAT 2017 – Helium should be recycled, Nature 547, doi:10.1038/547006a

NUT 2012 – William J. Nuttall, Richard H. Clarke, Bartek A. Glowacki, Stop squandeling heliu, Nature, Vol 485, 575, 31st of May 2012

US Patent – Helium recycling for optical fiber manufacturing, Paul A. Chludzinski,US625357B1, 1996

15 INDIUM

15.1 INTRODUCTION

Indium is a soft and ductile metal that is produced as a by-product of zinc refining. Major producers are China, South Korea and Japan with an average amount of 689 tons per year. In Europe the primary production reaches 48 tons and the activities take place in Belgium and France (European Commission, 2017). In Belgium, Hoboken indium is recovered by Umicore during lead refining. The capacity of this site is 30 tons per year (Gunn, 2014). Nyrstar group, a global zinc refining company is producing indium and other valuable metals in its Auby site, France. It is the largest producer of indium in Europe that recover the metal from zinc refining waste, with installed capacity of 45 to 50 tons In per year (Les Echos, 2014).

Due to its properties Indium is used in new technologies, mostly in form of indium-tin oxide (ITO) in flat panel displays used in televisions, laptops and mobile phones, but also in solders and photovoltaic cells. Other smaller

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

applications include thermal interface material in electronics, alkaline batteries as a substitute for mercury, low melting point alloys and InGaN semiconductors in LEDs (European Commission, 2017). In the near future indium demand is expected to continue growing, mostly as a result of increasing PV cells and LED markets (Pavel et al., 2016).

15.2 GAPS LIMITING CIRCULAR ECONOMY

In contrast with a traditional, linear economy consisting of extraction, manufacturing and product disposal, circular economy focuses on, among others, the activities after the end of life. It aims to achieve a closed-loop supply chain, which saves primary resources by using disposed products as a source of secondary raw materials that can be used again in production (Gaustad, Krystofik, Bustamante, & Badami, 2017).

15.2.1 SUPPLY AND DEMAND (MARKET)

Innovative technologies in many sectors rely on so-called technology metals, which are usually rare metals required for production of high technology devices. Indium is an example of such metal, together with gallium, tantalum and rare earth elements. Growing demand for different electronic devices and subsequently higher use of technology metals can hamper reliable supply of Indium (Ueberschaar, 2017). The demand for indium for displays (indium-tin oxide) as well as LED lighting (InGaN semiconductors) is expected to grow from 30% in 2014 to 50% in 2020 (Pavel et al., 2016). Indium can also encounter a challenge in supply due to the fact, that it is obtained as a by-product of zinc ores and is available in low concentration. The economic incentive for extraction of those by-products is driven by the economics of the main metal, in this case zinc (Eunomia Research & Consulting Ltd, 2015).

15.2.2 COLLECTION MECHANISMS

Similarly to low recycling rate, collection rates for waste electronic devices, especially screen devices that are relevant for indium recovery are low at the moment (Ueberschaar, 2017). The inefficient collection of end of life products containing indium is one of the biggest obstacles to close the indium cycle (Ciacci, Werner, Vassura, & Passarini, 2018).

The logistic chains of waste streams are implemented in most of European countries. Collection of waste electronic equipment is done by partnerships between relevant stakeholders, especially those being in contact with consumers: retailers, local authorities and others. The optimal collection rate per capita for each type of product is a challenge of the take-back scheme. Next phase is transportation of appliances to treatment units, separated based on the product type. Sorting can be done at the source, by collection points or later at the regrouping centres. Here, the challenge is to optimize the logistic chain to make it economically attractive. Last

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

phase is the waste treatment and recycling in specialised plants, where the challenge is to comply with WEEE Directive and to recover the maximum material possible (Toffolet, 2016).

There is an issue with CRM-containing waste electronic devices export outside of Europe. Only one third of electronic waste is reported to be treated according to the EU WEEE directive. The rest of collected, but unreported waste is suspected to be treated within EU but without appropriate environmental care, or illegally exported to recycling sites outside the EU, where European environmental and health standards are not met. Most of the e-waste flows end up in China, India and some African countries (UNEP, 2013).

15.2.3 RECYCLABILITY

Another issue is related to recyclability of indium-bearing end of life products. The end of life recycling rate for Indium is less than 1%. Ciacci, Werner, Vassura, & Passarini (2018) claim that closing the indium cycle is hampered by lack of end of life products recovery. Presently, there are no efficient and economically attractive separation or refining technologies to recover In from display units. In displays, which have the biggest share of all applications, indium is used in very small amounts and is applied in a sandwich compound, which makes the recovery more difficult. According to the source, mass of indium found in LCDs of various devices ranges from 3 ppm in smartphones to 660 ppm in mobile phones (Ueberschaar, 2017). Therefore, the metal is lost through dissipation. Currently LCD panels containing indium are discarded in cement factories as energy input from plastic parts, copper smelters as energy input and copper recovery, or often in landfills.

The potential for indium recovery from collected waste electronic devices mostly comes from mobile phones, LCD televisions and flat screen monitors, while much lower quantities can be expected from notebooks. Tablets and smartphones are playing minor role due to low concentrations. However, the selective separation of indium is possible, based on experiment conducted for LCD panels separated from tablets and smartphones. The technology involves a composite separation and dissolution of the indium-tin oxide. As a result, about 80% of In was transferred to the oxide in the composite separation stage, from where both tin and indium can be recovered. Minor quantities ended up in foils fraction and leachate residues. One measure that can be taken is to collect and store scrap displays and other appliances for recycling in the future, when more efficient processes are developed and higher mass flows of In-bearing screen devices are available (Buchert, Manhart, Bleher, & Pingel, 2012; Eunomia Research & Consulting Ltd, 2015; Ueberschaar, 2017).

15.2.4 CAPACITY OF RECYCLING CHAIN

The capacity of each part of recycling chain is not easily available in the literature. The recycling of indium from end of life products does not exist. The fraction of indium present in those products is mostly lost. The new scrap, usually in form of spent indium-tin oxide, is the only substantial secondary source of this metal. It adds to the global indium supply about 1000 tons per year. Processing the new ITO-bearing scrap occurs mostly in the same facilities as the primary production, therefore indium undergoes usually closed loop recycling, by being utilized and recycled in the same product type. The cycle of indium in Europe is highly inefficient and improving recycling

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

rates at the end of life are required. As shown in figure 1, there is a huge potential in recovery of indium from old scrap and subsequently closing the overall material cycle (Ciacci et al., 2018).

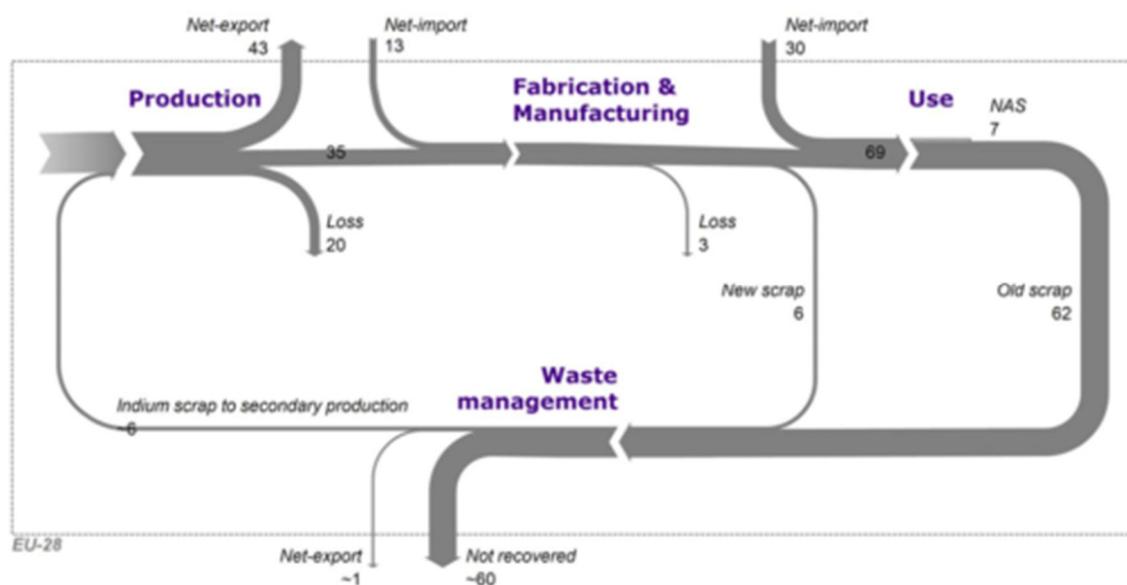


Figure 1. Net additions to in-use stock in anthropogenic indium cycle in EU-28 in 2014 (tons of indium) (Ciacci et al., 2018)

To establish and maintain the recycling system a reliable supply of secondary indium sources. It is discussed in the literature, that if the demand for indium stays at least at the same level as 70 tons per year, then closing the indium loop is possible, which will also help with decreasing the EU reliance on other indium producers (Ciacci et al., 2018).

15.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

15.3.1 SUBSTITUTION

One of the solutions for problems connected with availability and other limitations of indium is substitution, which can deal with potential supply risk and price fluctuations. In applications such as flat panel displays or amorphous silicon and CdTe PV cells, indium can be replaced with other transparent conducting oxide, for instance aluminium doped zinc oxide or fluorine doped tin oxide. Those materials are cheaper, however their performance in conductivity and transparency is lower, which are the main barriers for substitution. Other substitution paths for indium-tin oxide being under research and development are graphene quantum dots, carbon nanotube coating and antimony-tin oxide coating. However, the possibility of using those materials is still uncertain (Pavel et al., 2016). Another alternative is silver nanowire used in touch-sensitive displays. This solution

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

cannot help for other applications using indium. For instance, in semiconductors for thin-film solar cells there is no commercially available replacement for indium. However, the semiconductors account for only 2% of global PV cells production. Crystalline silicon technologies holding over 90% of PV cells market and thin-film based on other materials can be substitutes for In-bearing semiconductor compounds.

Regarding alloys, tin-indium can be substituted with tin-bismuth in low temperature bonds and solders (European Commission, 2017). Increasing use of LED technology and subsequently higher demand for CRMs including indium and gallium will also incentivise the search for alternative materials also in this sector. Although LED substituted phosphors in fluorescent lighting, it is not equivalent with complete ceasing of rare elements use. Presently, there are few European projects researching the CRM substitution possibilities in lighting and displays. IRENA aims to develop materials with high performance that can completely eliminate critical materials from electronic devices. Another two projects are part of Horizon 2020. INREP is developing transparent and conducting oxide, which could replace indium in electrodes used in multiple applications: solar cells, LED, touch screens etc. INFINITY aims to investigate inorganic alternative for indium-tin oxide using sol-gel technologies and more easily available metallic materials to eliminate indium (Pavel et al., 2016).

15.3.2 RECYCLING ACTIVITIES

Although end of life recycling input rate is very low, indium is recycled from the manufacturing waste (new scrap). According to Indium Corporation, in 2011 from about 1,500 tons of refined indium 950 tons came from recycling (European Commission, 2017). Countries producing indium-tin oxide have significantly increased recycling rates of their production, due to higher demand for In-bearing products (Gunn, 2014). There are ongoing indium recovery activities from secondary resources. An example is Xstrata Zink GmbH located in Nordenham, Germany that treat recycled materials and imported products with electrolytic zinc refining process. During this process, trace metals, such as indium, gallium and germanium and impurities are separated from the main material and sold to copper and lead smelters with minor metal concentrate. However, the amounts of recovered trace metals are not publicly available. Other German companies Haines and Maassen and PPM Pure Metals recycle indium-bearing compounds, obtaining high purity indium metal (Gunn, 2014).

15.3.3 LEGISLATION

In the European Union legislation is supporting circular economy by electronic waste collection schemes and directives, in particular Directive 2002/96/EC on Waste Electrical and Electronic Equipment. Since the collection rates of electronic appliances are still low, the legislation incentivises consumers to properly dispose their products in order to recover their value and prevent environmental issues. The EU directive also aims to improve the environmental performance on all other levels of supply chain, including producers, distributors and waste treatment operators. It puts responsibility on producers to recycle their products and make them think of product design more suitable for recycling (UNEP, 2013). The first EU Directive on WEEE has been revised in 2012 (Directive 2012/19/UE) and set a goal of 65% collection rate for products placed on the market or 85% rate for

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

WEEE arising by 2016. It also set a 5% increase in recycling rate by 2016 and requirements for traceability in order to avoid hidden trade of undeclared waste (Toffolet, 2016).

15.3.4 RESEARCH ACTIVITIES

In order to assess the potential of recycling in circular economy of indium, it is useful to find out the scale of In-bearing end of life products available for recovery. Recent work of Ciacci, Werner, Vassura, & Passarini (2018) has focused on the quantification of indium deposits in stock (urban mines) in Europe, that can constitute as future source of secondary material. They applied dynamic Material Flow Analysis to investigate stocks and flows of indium in Europe and estimate the magnitude of secondary indium available. This research has shown how inefficient indium cycle in Europe is and pointed out a great room for improvement in recovery and recycling rates. Researchers came to conclusion that there is opportunity to close indium cycle in Europe since the amount of indium potentially available from waste products exceeds the indium domestic demand.

15.3.5 BUSINESS MODELS

The circular economy is supported by already implemented business model of take-back system. It is based on a principle of extended producer responsibility for their manufactured items. They are obliged to partially or fully manage the waste end of life products. Additionally, manufacturers are encouraged to implement eco-design principles in their activities. The WEEE Directive implemented additional obligations for manufacturers, for instance marking electronic equipment with a special sign to avoid inappropriate disposal (Toffolet, 2016).

Together with take-back model, there are other tools for promoting the eco-design principles. First is the idea for detailed data collection on life cycle of products from recycling activities. Improved life cycle inventory will make the new life cycle assessment studies more accurate. Another example is a tool calculation the recyclability for electronic appliances. With real data from recyclers this tool will provide information for the best manufacturing practices for the product design, basing on the idea of designing for recycling (Toffolet, 2016).

15.4 ENVIRONMENTAL ISSUES

15.4.1 WATER POLLUTION

The main environmental constraint for indium recycling involves generation of high amounts of waste water in hydrometallurgical and chemical processes. The recycling processes of indium from LCD panels require high input of chemical substances. There is a risk that the waste water will be contaminated with toxic heavy metals, which can affect the following recovery processes (Ueberschaar, 2017), or pose a threat for the environment.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

15.4.2 CARBON FOOTPRINT

Primary production is considered energy intensive and therefore generate high amounts of greenhouse gases, especially carbon dioxide. The impact of primary production is likely to increase due to low ore grades being processed. On the other hand, recycling activities usually require less energy to obtain raw materials. Therefore, the carbon footprint of primary production is much higher in comparison to secondary refining, which is applicable for all metals. In case of indium, primary carbon footprint is calculated as 142 t CO₂/t of metal. Other rare metals used in electronic devices have even higher footprint, for example platinum with 13 954 t CO₂/t and gold 16 991 t CO₂/t of metal. Considering the fact that those metals are important for future sustainable technologies, reduction of primary production by implementation of circular economy principles will help decreasing the overall carbon footprint of metals (UNEP, 2013).

15.5 SUMMARY

Indium is a valuable critical raw material, used mostly in form of indium-tin oxide in new technologies. Most important applications are flat panel displays, solders and photovoltaic cells. Other smaller applications include thermal interface material in electronics, alkaline batteries, low melting point alloys and InGaN semiconductors in LEDs. It is presently recycled only from manufacturing scrap and the recycling rate of end of life products is lower than 1%. In order to allow circular economy implementation in indium cycle, several limitations need to be resolved. Growing demand for electronic devices and higher use of technology metals can hamper reliable supply of Indium. The stable supply of this metal will help to close the material loop. Other issues are connected with low recyclability of indium-bearing products and still not high enough collection rates. Environmental issues include risk of water pollution from recycling activities and high carbon footprint of rare metals. However, there are also aspects that support implementing of circular economy. Metal substitution can improve the indium cycle, yet it often comes with a price of reduced performance. The technology for replacing indium still need to be improved to cease from critical metals use. Moreover, there are ongoing recycling activities in order to increase share of secondary metals, supported by EU legislation, research and circular business models.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

15.6 REFERENCES

- Buchert, M., Manhart, A., Bleher, D., & Pingel, D. (2012). *Recycling critical raw materials from waste electronic equipment*. Freiburg: Öko-Institut Retrieved from <http://www.resourcefever.org/publications/reports/Recycling critical raw materials from waste electronic equipment.pdf>
- Ciacci, L., Werner, T. T., Vassura, I., & Passarini, F. (2018). Backlighting the European Indium Recycling Potentials. *Journal of Industrial Ecology*, 0(0), 1–12. <https://doi.org/10.1111/jiec.12744>
- Economia Research & Consulting Ltd. (2015). *Study on the Competitiveness of the EU Primary and Secondary Mineral Raw Materials Sectors*. Retrieved from <https://publications.europa.eu/en/publication-detail/-/publication/d066d034-e0f0-4c6a-9437-59b01dfc0070>
- European Commission. (2017). *Study on the review of the list of critical raw materials. Critical Raw Materials Factsheets*. Luxembourg: Publications Office of the European Union. <https://doi.org/10.2873/398823>
- Gaustad, G., Krystofik, M., Bustamante, M., & Badami, K. (2017). Circular economy strategies for mitigating critical material supply issues. *Resources, Conservation and Recycling*, (January). <https://doi.org/10.1016/j.resconrec.2017.08.002>
- Gunn, G. (2014). *Critical metals handbook*. American Geophysical Union.
- Les Echos. (2014). Nyrstar récupère un métal rare dans les déchets de raffinerie. Retrieved from https://www.lesechos.fr/02/12/2014/lesechos.fr/0203979367786_nyrstar-recupere-un-metal-rare-dans-les-dechets-de-raffinerie.htm#
- Pavel, C. C., Marmier, A., Alves, P., Schüler, D., Schleicher, T., Degreif, S., ... Öko-institut, V. (2016). *Substitution of critical raw materials in low-carbon technologies: lighting, wind turbines and electric vehicles*. <https://doi.org/10.2790/64863>
- Toffolet, R. (2016). *WEEE Management. WEEE Recycling: Research, Development, and Policies*. Elsevier Inc. <https://doi.org/10.1016/B978-0-12-803363-0.00001-8>
- Ueberschaar, M. (2017). *Assessing recycling strategies for critical raw materials in waste electrical and electronic equipment*. Technische Universität Berlin, Berlin.
- UNEP. (2013). *Metal Recycling: Opportunities, Limits, Infrastructure. A Report of the Working Group on the Global Metal Flows to the International Resource Panel*. Reuter, M. A.; Hudson, C.; van Schaik, A.; Heiskanen, K.; Meskers, C.; Hagelüken, C.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

16 MAGNESIUM

16.1 INTRODUCTION

Magnesium (Mg) is the sixth most common metal in the Earth's crust and the third most abundant element in seawater. Magnesium metal is a gray-white solid and the lightest structural metal used today, being 30 % lighter than aluminum. Metallic magnesium burns vigorously once molten in contrast to its alloys that possess high melting point. Magnesium is most often used in alloys for advanced applications. Magnesium alloys are widely used in consumer electronics, as well as by the steel, aircraft and automotive industries. Magnesium is the third most used metal in construction. The EU Commission classifies magnesium as a Critical Raw Material because there is no primary production of magnesium in the EU.

The lack of magnesium production in the EU is not based on a geographical lack of magnesium raw materials. High production capacity and export policy of China made the primary magnesium production redundant in Europe. As a result, the last smelter in the EU closed in 2006. Currently, the EU's demand of primary magnesium depends mostly on imports from China.

Magnesium is an attractive metal for recycling due to its high price and environmental issues of its primary production (high carbon footprint).¹ Functional recycling is mainly focused on alloying since pure magnesium metal production from the secondary sources is demanding and costly. For this reason, most of the secondary magnesium is used in aluminium and other magnesium containing alloys.

16.2 GAPS LIMITING CIRCULAR ECONOMY

Magnesium and its alloys can be easily recycled making its availability practically unlimited. Globally, about 80 % of magnesium usage goes into alloys with aluminium or other metals.² These materials are available for recycling if efficiently collected after disposal. Magnesium used in the iron and steel industry as a desulphurising agent, about 13 %, and in chemical industry, comprising about 7 %, is practically unrecyclable.² The magnesium production consumption in the EU is spread out as follows: 52 % to aluminium alloys, 34 % to other magnesium alloys, 11 % to iron desulphurization and 3 % to other.³

Figure 7 presents magnesium usage and end of life availability in the EU in 2012. Figure 7a outlines use of magnesium in the EU manufacturing, showing that 44 % is used in motor vehicles and 37 % in other aluminium alloy applications. That is, in order to significantly enhance magnesium recycling rate, use of secondary magnesium in automotive and aluminium alloy industries must be strengthened. Annual end of life availability of magnesium scrap is about 85.4 kT, as shown in Figure 7b. From the total volume of end of life magnesium, roughly 66.8 kT is available for functional recycling (mainly excluding iron desulphurisation and electrochemistry usage). The high volume of available magnesium scrap shows the enormous potential of magnesium functional recycling in the EU.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

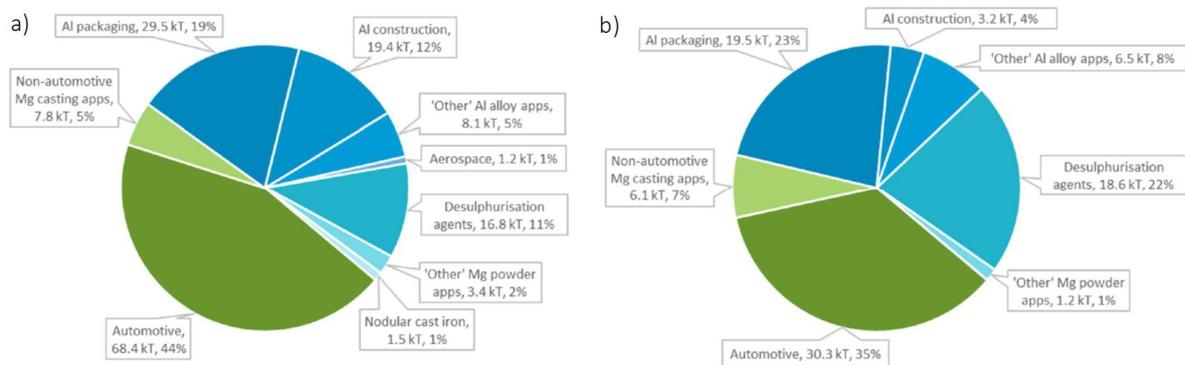


Figure 7. a) Magnesium usage in the EU manufacturing in 2012. b) End of life availability of magnesium in the EU in 2012.³

Increasing production and utilization of magnesium alloys has escalated the volume of magnesium waste. Recycling with no loss of material quality is possible but demands advanced technologies due to high oxidation tendency of magnesium. For this reason, end of life magnesium alloys are often recycled to produce secondary alloys, not primary alloys with as good as new properties. Highly contaminated magnesium alloys are typically discarded with no functional recycling.²

Magnesium recovery is getting more challenging as its alloys are increasingly diversified due to magnesium's good properties to yield lightweight materials with high strength. This sets also challenges for recycling facilities that require new technological solutions and capital for research and testing of new methods to recycle the components having many types of material combinations. The automotive industry is the most significant source of magnesium containing components, their recycling being guided by the EU legislation (95 % of the total car weight must be recovered and reused by 2015).^{2,4,5} Currently, magnesium recycling for high quality magnesium alloy production is realized only with new magnesium scrap that is obtained directly from the casting ("clean scrap"). Most of end of life magnesium scrap is used for aluminium alloying or steel desulphurisation due to contamination of the scrap by other metals and organic materials.³

Figure 8 depicts magnesium flows in the EU in 2012. The End of Life – Recycling Input Rate (EoL-RIR) for magnesium is estimated to be about 7 % according to the material flow analysis data.³ The EoL-RIR is the ratio of recycling from end of life scrap to European demand of magnesium raw material (equal to primary and secondary material inputs). The value for magnesium is lower compared to aluminium that possess 12 % EoL-RIR rate globally. This is due to the dispersive nature of products containing magnesium as well as collection and recycling inefficiencies of some of the magnesium applications.³ Taking into account also the new magnesium scrap generated in the manufacturing processes (not been sold to end-users), the magnesium recycling rate is about 32 % in the EU (Figure 8).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

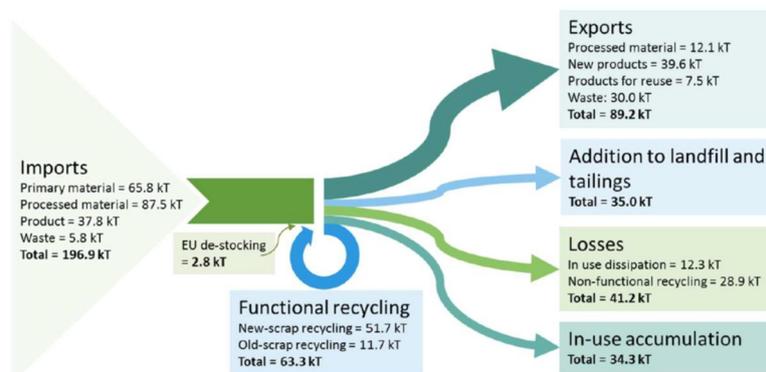


Figure 8. Simplified Sankey diagram of magnesium flows in the EU in 2012.³

The magnesium material flow complies within the aluminum recycling loop as magnesium is most often used in alloys, rather than pure metal. Magnesium and aluminium can also be separated during the recycling with the technology available, but, due to economic reasons, magnesium most often ends up into the light-metal fraction together with aluminium.⁶ Pure secondary magnesium production is an alternative recycling pathway for the use of magnesium in secondary magnesium alloys. However, there is no currently markets for such secondary alloys.⁶

16.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

Magnesium is closely tied with the aluminum recycling loop having over 90 % recycling rate in automotive and construction industry.⁶ That is, magnesium recycling infrastructure is already available, recycling rate being limited mainly by the material collection efficiency from the end-users and by the lack of suitable metal dismantling/separation technologies. The collection rate for aluminum beverage cans is about 70% and that for other aluminum packaging is about 45%,³ in which there are still room for improvements.

The main improvements to enhance magnesium recycling rate were identified by the Material Flow Analysis of Magnesium in the EU³:

- Enhanced dismantling of magnesium and aluminium alloy components from end of life vehicles
- Improved collection rate of end of life aluminium beverage cans
- Technological advances in the automatic sorting of aluminium alloy fractions from shredding
- Directing higher fraction of high magnesium content aluminium alloys to remelters that retain magnesium in their input materials (instead of to refiners that do not)
- Favouring specialized magnesium recyclers for segregated end of life magnesium alloy recycling
- Improved slag utilization by the aluminium and steel industries in non-functional recycling

Currently there are several EU funded projects seeking new technologies to enhance end of life magnesium recycling (REALCAR2, REALITY and SHREDDERSORT).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

16.4 ENVIRONMENTAL ISSUES

Magnesium demand has more than doubled since 2000 having an annual growth rate of about 6.6 %.² The primary production of magnesium using the Pidgeon process is highly energy-intensive with immense CO₂ emissions. Secondary magnesium production from the scrap is much more less energy intensive, diminishing the CO₂ emissions and production costs. This makes the secondary magnesium sources economically attractive for industry, also supporting the EU's climate actions.^{2,7}

The landfill rate (tonnes landfilled/tonnes imported) of magnesium in the EU is 18 %.³ That can be improved by enhancing the metal collection network and improving separation technologies of different metals. Salt slag recycling in the EU is hindered due to the high costs of its disposing responsibility. This might be one of the reasons why some of the scrap is being exported outside the EU to countries with lower-regulatory jurisdiction. The salt slags can be a significant source of secondary magnesium if the metal recovery is made economically viable by legislation and technology.³

16.5 SUMMARY

Magnesium plays a major role in the key industrial sectors within the EU, assuring its increasing strategic importance also in the future. The EU's 100 % reliance on magnesium imports guarantee that magnesium stays on the Critical Raw Materials listing issued by the EU. These facts alone demonstrate the importance of magnesium recycling in order to decrease the EU's reliance on magnesium imports (mainly from China). Despite magnesium's key role as a raw material for industry, there is no much data available on the circular economy aspects of magnesium in the EU. *The readers are strongly recommended to see the study of "Magnesium Recycling in the EU",³ published in 2017, for comprehensive understanding of magnesium flows within the EU.*

In general, magnesium recycling is in good level with rather high magnesium end of life scrap collection rates with certain industrial sectors. However, the magnesium EoL-RIR rate of only 7 % shows there is a need to increase the recycling level of end of life magnesium. As the business models of magnesium recycling mostly exist, the recycling can be made more attractive by the EU legislation and new technological developments. This demands technological advances e.g. in automated metal and alloy separation of end of life vehicles.⁶ The end of life scrap must be sent to remelters instead of to refiners in order not to downgrade the materials. Aluminium packing is another sector where recycling can be improved increasing also the magnesium recycling rate. In addition, the steel industry slags are a potential new sector where magnesium recycling can be enhanced, possessing no functional recycling to date.

Economic investments in research of magnesium and aluminum recycling would provide new technologies to reach the next level in their functional recycling, boosting also the economic viability of end of life collection of the components. This could be efficiently steered by the EU funding policies and legislation.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

16.6 REFERENCES

1. Mendis CL, Singh A. Magnesium recycling: To the grave and beyond. *Jom*. 2013;65(10):1283-1284. doi:10.1007/s11837-013-0701-5
2. Fröhlich P, Lorenz T, Martin G, Brett B, Bertau M. Valuable Metals—Recovery Processes, Current Trends, and Recycling Strategies. *Angew Chemie - Int Ed*. 2017;56(10):2544-2580. doi:10.1002/anie.201605417
3. Bell N, Waugh R, Parker D, Baker K. Magnesium Recycling in the EU. *Oakdene Hollins Research & Consulting*, 2017 (reference: IMA-09 454).
4. Hanko G, Antrekowitsch H, Ebner P. Recycling automotive magnesium scrap. *Jom*. 2002;54(2):51-54. doi:10.1007/BF02701075
5. Eurostat. <http://ec.europa.eu/eurostat/web/waste/key-waste-streams/elvs>. Cited 25.4.2018.
6. Ehrenberger S, Friedrich HE. Life-cycle assessment of the recycling of magnesium vehicle components. *Jom*. 2013;65(10):1303-1309. doi:10.1007/s11837-013-0703-3
7. EU's Climate Action. https://ec.europa.eu/clima/policies/strategies_en. Cited 25.4.2018.

17 NATURAL GRAPHITE

17.1 INTRODUCTION

Natural graphite is a crystalline mineral of pure carbon, which exists in the form of amorphous graphite, flake graphite and crystalline graphite. Natural graphite has important properties, such as chemical inertness, low thermal expansion and lubricity, which make it perfect material for certain uses such as refractories and steelmaking.[1]–[3] Currently, the main use of natural graphite includes refractories (66%), batteries (8%), friction products (5%) and lubricant (5%). In 2016 the global mine production of natural graphite amounts to 1.2 million tons and the production is dominated by China (61%), India (14%) and Brazil (7%), as shown in Error! Reference source not found..[4]

Natural graphite has been classified as a Critical Raw Material for the EU since 2011. [1]

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

17.2 GAPS LIMITING CIRCULAR ECONOMY

17.2.1 PRODUCTION OF NATURAL GRAPHITE

The production of natural graphite is mainly related to the mining, mineral processing and refining. During mining and mineral processing tailings and middling are generated. These materials are normally taken as solid wastes with low added values and the further extraction of natural graphite from these materials has low economic incentive. During the refining process acid leaching and roasting-leaching processes are applied and these processes are normally related to the consumption of acid and alkali, accompanied by the generation of a large quantity of acidic and alkaline waste water.

17.2.2 RECYCLING OF NATURAL GRAPHITE

The use of natural graphite in many products is dissipative and the recycling of natural graphite from the end-of-life product is very rare. The spent refractories are normally used as roadbed materials or sent for landfill, thus these spent refractories are not used as their original purposes or the useful components (e.g. graphite) are not used properly. The spent brake linings are normally disposed as hazardous waste or partially smelted to low quality steel and in this case the graphite is not functionally recycled either. Natural graphite used in the lithium ion batteries accounts for another big share of its usage; however, there is no industrialized process to recycle graphite from the spent lithium batteries at the moment.

17.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

The natural graphite in certain applications is interchangeable with synthetic graphite. Exploring the possibilities to extend the applications of synthetic graphite is important to ensure a circular economy. However, the final solution will still be dependent on the recycling of natural graphite from end-of-life products, especially that from the refractories and batteries.

17.4 ENVIRONMENTAL ISSUES

The graphite is minimally toxic if they are swallowed or drawn onto the skin. However, during the mining, mineral processing and refining solid wastes and waste water is generated and these can pose potential environmental issues.

17.5 SUMMARY

Natural graphite is mainly used to produce refractories, batteries, friction products and lubricant. During mining, mineral processing and refining solid wastes as well as waste water could be generated. The graphite itself is minimally toxic; however, the generated solid wastes and waste water can pose potential environmental

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

problems. The recycling of natural graphite from the end-of-life products is almost zero at the moment. To ensure a circular economy the recycling of natural graphite from refractories and batteries should be explored.

17.6 REFERENCES

- [1] E. Commission, *Study on the review of the list of critical raw materials*, no. June. 2017.
- [2] "Graphite (C) - Classifications, Properties and Applications of Graphite." [Online]. Available: <https://www.azom.com/article.aspx?ArticleID=1630#>.
- [3] W. D. Jackson, G. Christiansen, and Geological Survey (U.S.), "International Strategic Minerals Inventory summary report--Natural Graphite," *U.S. Geol. Surv. Circ. 930-N*, p. vi, 68 p., 1993.
- [4] U.S. Geological Survey, "Mineral Commodity Summaries: Graphite (natural)," 2017.

18 NATURAL RUBBER

18.1 INTRODUCTION

Natural rubber is harvested from rubber tree, mainly grown in Southeast Asia, which is why EU is fully relying on imports. The tyre industry is the largest consumer of natural rubber, accounting for about 75% of the demand in the EU. Therefore, the circular economy of natural rubber is tightly linked with the recycling of tyres.

Other product destinations within the EU can be divided into three categories: industrial products, consumer products, and latex products (such as gloves and condoms). Only approximately 0.9% of the natural rubber from primary resources is currently being replaced by secondary natural rubber. (European Commission 2017)

Although all tyres contain natural rubber, the higher the performance or size required, the larger percentage of natural rubber is needed in comparison to synthetic rubbers. For example, ordinary passenger car tyres contain approximately 40% of natural rubber of their rubber content, whereas truck tyres contain 70–100%, and airplane tyres 100%. (Isayev 2014; Forrest 2014)

Products made of natural rubber are thermosets because they are vulcanised. Vulcanisation means that rubber is cured by cross-linking to achieve a stable three-dimensional molecular network; therefore, vulcanised rubber cannot be reprocessed just by heating. (Isayev 2014)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

18.2 GAPS LIMITING CIRCULAR ECONOMY

18.2.1 TECHNICAL RECYCLABILITY

Technical recyclability is the main obstacle limiting the circular economy of natural rubber. The recycling of natural rubber from EoL products requires devulcanisation as a first step. (Isayev 2014) This means that devulcanisation is the only possibility, if secondary rubber is wanted to replace primary rubber. Mechanical recycling of natural rubber (grinding to granulates or powder) basically means the material is reused in other applications than where virgin natural rubber is used. These applications include acoustic screens and sound barriers, asphalt rubber, athletic tracks, sports areas and playgrounds, equestrian floors and synthetic turf (Scott 2015). Therefore, mechanically recycled natural rubber hardly ever replaces virgin natural rubber, and a closed loop is almost impossible to achieve by this route.

The aim of the devulcanisation process is to break the sulfur-to-sulfur bonds, and some of the sulfur-carbon bonds while leaving intact the molecular carbon-carbon backbone. This transforms the rubber particles back into a reactive polymer, which can be molded to new products. However, as reclaimed rubber has altered properties compared to unvulcanised virgin rubber due to the presence of additives, it is unsuitable for use in many products, such as tyres due to their strict safety regulations. In some products, however, revulcanised rubber can be mixed with virgin material to produce satisfactory physical properties. (New Rubber Technologies 2017; Myhre & MacKillop 2002)

To carry out devulcanization, an addition of chemical agents is often required. This affects the chemical composition of rubbers, which may in some cases limit the use or applications of the recycled rubber. The process conditions of devulcanisation thus need further optimisation to make the rubber industry to approve these technologies. (Isayev 2014)

Currently, industrial devulcanised tyre-derived products exist globally and are used, among other applications, in new tyres, where they substitute a fraction of the virgin rubber compound material. (Genan 2017; Tyromer 2018; TRS 2018)

18.2.2 COMPLEXITY OF MATERIALS

In terms of quantity, end-of-life tyres (ELTs) compose the most attractive source of secondary natural rubber. However, the composition of tyres is highly complex, and not just because of the number of rubber types, but also due to various other material types. For example, an all-season passenger tyre may contain 30 kinds of synthetic rubber, eight kinds of natural rubber, eight kinds of carbon black, steel cords and wires, textile fibres, in addition to other chemical compounds, such as waxes, oils, pigments and minerals. (Evans & Evans 2006) To

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

control their input, the tyre manufacturers would most likely seek only to recycle material from their own products. (Scott 2015)

18.2.3 MARKET PRICE OF RUBBER

One of the major barriers for developing a devulcanisation process, or running a devulcanisation plant on a profitable basis, is the significant fluctuations that can occur to the market price of rubber, including natural rubber. (Forrest 2014)

As a biotic material, the price of natural rubber is affected by more factors than just the fundamental economic factors such as the crude oil price, and supply and demand. The other factors include the number and output of plantations, in addition to possible natural disasters. Past years have seen some main suppliers of natural rubber changing part of land use from natural rubber to other crops, such as palm oil. Moreover, this has coincided with an increase in demand for natural rubber especially from China. Providing for changes in the demand for natural rubber is difficult as it takes around 10 years for a new plantation to reach maturity. (Forrest 2014)

18.2.4 LACK OF STANDARDS

Concerning the mechanical recycling of ELTs, one of the challenges has been the lack of standards for the rubber granulates resulting from ELT size reduction processes. Tyre shredders often work to their own specifications, meaning that they aim their product for energy recovery, which is the cheapest processing option. Anything else they may produce has been poorly standardised. (Scott 2015)

However, the standardisation has been initiated to better respond to the needs of industry using tyre-derived materials (TDMs). This led, in a first stage, to the defining the categories of TDMs obtained from ELTs in relation to their size or impurities. In a second stage, the robustness, reproducibility and repeatability of the test methods proposed in the first stage were assessed in order to turn the technical specification into an EN standard. It was also identified that the determination of specific physical and chemical characteristics needs further regulation, in addition to quality criteria for the selection of which tyres are the most suitable for recovery and recycling processes. (Scott 2015)

18.2.5 THERMAL CONVERSION OF END-OF-LIFE TYRES

With a calorific value equivalent to that of good quality coal, combustion is an attractive EoL treatment option for old tyres. However, as on average only 20% of ELTs is composed of natural rubber, the only renewable material in tyres, the CO₂ released in the combustion of ELTs is mainly of fossil origin. (ETRma 2011a) In Europe, 46% of ELTs are recycled as material and 49% as energy. (5% is considered as residual waste.) (Scott 2015)

Pyrolysis (or thermolysis) conversion has been an emerging recovery route for ELTs in recent years. In pyrolysis, ELTs are thermally decomposed to gas, oil and char. The process also enables an easy separation of steel that is present in tyres (Jung & Bouysset 2015). The char is used to produce carbon black, often referred to as recovered

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

or recycled carbon black (r-CB or reCB). It can potentially be used as a filler for example the rubber industry, paints and coatings, ink production. r-CB is seen as an environmentally friendly option to carbon black obtained from oil-based processes. (ETRma 2011a; Biogreen 2018) r-CB from ELTs entering new tyres can be considered a partial tyre-to-tyre closed loop, but average tyres contain only 6% of carbon black, and it is claimed that only a small percentage of that can be replaced by r-CB. (Scott 2015)

The profitability of the tyre pyrolysis process was earlier questioned (ETRma 2011a), but at the end of 2015, there were eight tyre pyrolysis plants in operation in Europe, having the total treatment capacity to process about 24 000 tonnes of ELTs. In addition, three plants were at a pilot stage. (Jung & Bouysset 2015)

18.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

18.3.1 BUSINESS MODELS PROMOTING THE CE OF TYRES

18.3.1.1 RETREADING OF TYRES

Retreading of used tyres consists of replacing the tread on worn tyres while preserving the structure of the tyre (casing): new tread is vulcanised on top of the casing. After retreading, the tyres are introduced to the distribution circuit of truck tyres. The light vehicle market has too much dimensional variety for retreading processes to be applicable. (Ernst & Young 2016)

Retreading is a relatively wide spread business model in the EU. Retreaded truck tyres had a market share of 30% in the EU5 (France, Italy, Germany, Spain, United Kingdom) in 2015. The corresponding figure for the rest of the EU (+Turkey) was 22% in the same year. The main competitor of the retreaded tyre is the low-end tyre imported from Asia, as these tyres are not retreadable. It has been estimated that the environmental impacts of retreaded tyres, depending on the criteria, are 19–70% lower than those of nonretreadable low-end tyres. (Ernst & Young 2016)

18.3.1.2 LEASING OF TYRES

Tyre manufacturer Michelin pioneered leasing tyres under a pay-per-kilometre business model already in the 1920s. As of 2011, Michelin Fleet Solutions offered tyre management (upgrades, maintenance and replacement) for 290,000 vehicles under leasing contract, to optimise the performance of large truck fleets. In Europe, 50% of large truck fleets externalise their tyre management. (European Commission 2012)

By maintaining control over the tyres throughout their lifetime, Michelin is able to collect them at end of the leases and possibly extend their technical life for instance by retreading. In other cases, it can ensure the proper treatment for the ELTs. (European Commission 2012)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

18.3.2 ELT MANAGEMENT MODELS

The collection rates of used tyres and the ELT management figures are generally high in Europe. In EU28, 95% of used tyres were either directly reused in their original purpose (in other vehicles), retreaded, reused in other purposes (e.g. in civil engineering), recycled as material (after grinding), or recovered as energy. The remaining 5% was either landfilled or the destiny was unknown. (ETRma 2015)

The management figures are calculated by the estimated “used tyres arisings”, which comprise new tyres (replacement market), retreaded tyres (national market), and import of second-hand tyres. (ETRma 2015) The ELT recovery rates by country are presented Figure 18-1.

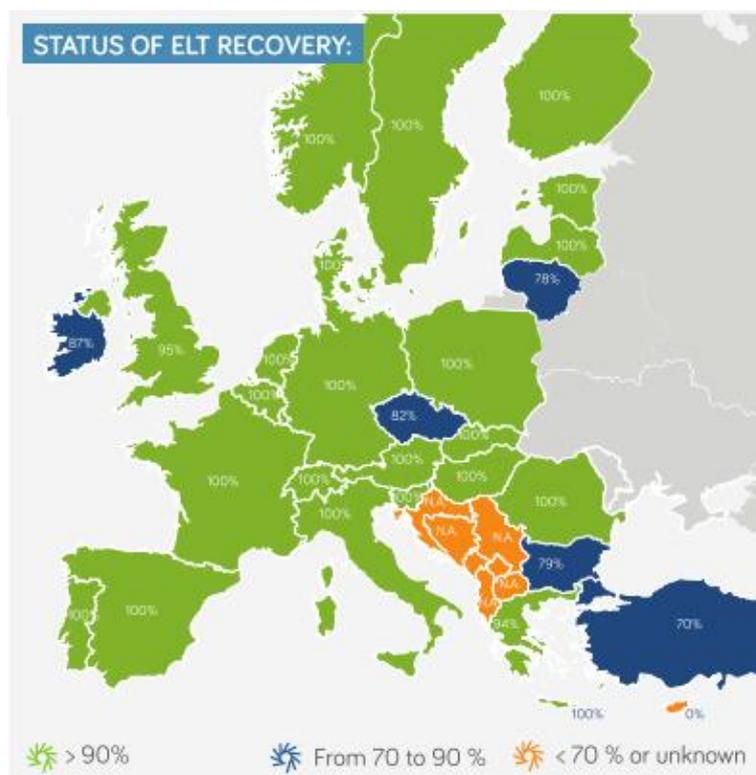


Figure 18-1. ELT recovery rates by European countries in 2013. Adapted from (Scott 2015).

There are three different models for managing ELTs in Europe: extended producer responsibility (EPR), free market, and tax system, where the management is on the government’s responsibility, financed through a tax. (Scott 2015) Figure 18-2 presents the adopted management systems by European countries.

In the EPR system, the original manufacturer has to ensure that the waste from its products is disposed of responsibly and in an environmentally friendly way. The legal framework is defined by law, which assigns the responsibility to the tyre manufacturers and importers to organise the management of ELTs. (Scott 2015)

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

specifications in the quality of latex products. These latex rejects contain only lightly cross-linked rubber, which are available in large quantities. Therefore, these scrap latex rejects are considered as potentially valuable, but currently untapped sources for recycling. (Mathew et al. 2001)

18.4 ENVIRONMENTAL ISSUES

The use of ELTs in civil engineering, where they are brought to contact with soil, has raises questions of possible leaching of toxins into the groundwater. ELTs contain heavy metals and harmful chemicals, posing a risk of a contamination especially in wet soils. However, research has shown that very little leaching occurs when shredded tyres are used as filling material. Nevertheless, in each site should be individually assessed if the product in question is environmentally suitable for the surrounding conditions. (Liu et al. 1998)

The majority of evidence shows that shredded tyres will not cause metals levels to exceed the primary drinking water standards, or the naturally occurring background levels in both above and below water table applications. (Humphrey & Swett 2006)

18.5 SUMMARY

Recycling natural rubber is technically challenging due to the facts that rubber products are vulcanised and contain a variety of additives. In terms of quantity, used automotive tyres compose the most attractive source of secondary natural rubber. In addition, their collection rates are very good in Europe. The collection is mainly organised by the extended producer responsibility (EPR) system. However, due to the complex structure of tyres, and due to the strict safety regulations that control their performance, the material from end-of-life tyres (ELTs) is mostly used in other applications in the form of powder or granulates, than recycled in new tyres.

Because of the challenges in the true material recycling of ELTs, and because of the good calorific value of tyres, 49% of ELTs are currently used in energy recovery in Europe.

There are, however, industrial examples of devulcanising technologies that will possibly enable wider utilisation of ELTs as a raw material for tyre manufacturing in the future.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

18.6 REFERENCES

- Biogreen, 2018. Tire pyrolysis: sustainable waste tires and rubber valorisation. Available at: <http://www.biogreen-energy.com/pyrolysis-applications/tire-pyrolysis/> [Accessed April 22, 2018].
- Ernst & Young, 2016. *The socio-economic impact of truck tyre retreading in Europe - The circular economy of tyres in danger*, Available at: http://www.etrma.org/uploads/Modules/Documentsmanager/201611-ey_retreading_lr.pdf.
- ETRma, 2015. 2015 ELT Management Figures. Available at: http://www.etrma.org/uploads/Modules/Documentsmanager/2017-01-25_2015-elt-data_final.pdf.
- ETRma, 2011a. Energy recovery. *European Tyre and Rubber Manufacturers' Association*. Available at: <http://www.etrma.org/tyres/ELTs/energy-recovery> [Accessed April 21, 2018].
- ETRma, 2011b. Producer Responsibility. *European Tyre & Rubber Manufacturers' association*. Available at: <http://www.etrma.org/tyres/ELTs/ELT-management/producer-responsibility> [Accessed April 23, 2018].
- ETRMA, 2017. Management schemes. *European Tyre & Rubber Manufacturers' association*. Available at: <http://www.etrma.org/tyres/ELTs/ELT-management/ELT-management-schemes> [Accessed April 23, 2018].
- European Commission, 2017. *Study on the review of the list of critical raw materials*, Brussels. Available at: <https://publications.europa.eu/en/publication-detail/-/publication/7345e3e8-98fc-11e7-b92d-01aa75ed71a1/language-en> [Accessed November 30, 2017].
- European Commission, 2012. EUROPEAN RESOURCE EFFICIENCY PLATFORM Working Group I: Circular Economy / Greening the Economy. , (November), pp.1–12.
- Evans, R. & Evans, A., 2006. *The Composition of a Tyre: Typical Components*, WRAP. Available at: http://www2.wrap.org.uk/downloads/2_-_Composition_of_a_Tyre_-_May_2006.0c1f8c06.2856.pdf.
- Forrest, M., 2014. Overview of the World Rubber Recycling Market. In *Recycling and Re-Use of Waste Rubber*. Smithers Rapra Technology, pp. 17–30.
- Genan, 2017. Cradle to Cradle Recycling. Available at: <http://www.genan.eu/about-us/cradle-to-cradle/> [Accessed April 23, 2018].
- Humphrey, D.N. & Swett, M., 2006. Literature Review of the Water Quality Effects of Tire Derived Aggregate and Rubber Modified Asphalt Pavement.
- Isayev, A.I., 2014. Recycling of natural and synthetic isoprene rubbers. In *Chemistry, Manufacture and Applications of Natural Rubber*. Elsevier, pp. 395–435. Available at: <http://linkinghub.elsevier.com/retrieve/pii/B9780857096838500161> [Accessed April 21, 2018].
- Jung, G. & Bouysset, J.-P., 2015. Recoverd Carbon Black from tyre pyrolysis. *4th annual international Recycled Rubber Products (R2P) technology conference 2015*. Available at: <http://www.depotec.eu/wp-content/uploads/2015/12/C-GISELE-JUNG-DEPOTEC-LIFE-25.11.15.pdf>.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- Liu, H.S., Mead, J.L. & Stacer, R.G., 1998. Technical Report #2 Environmental Impacts of Recycled Rubber in Light Fill Applications: Summary & Evaluation of Existing Literature. , (August 1998), p.20.
- Mathew, G. et al., 2001. Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber. *Polymer*, 42, pp.2137–2165.
- Myhre, M. & MacKillop, D.A., 2002. Rubber Recycling. *Rubber Chemistry and Technology*, 75(3), pp.429–474. Available at: <http://rubberchemtechnol.org/doi/abs/10.5254/1.3547678> [Accessed December 15, 2017].
- New Rubber Technologies, 2017. New Rubber Technologies: Devulcanization. Available at: http://www.newrubbertech.com/devulcanization_technology.php [Accessed December 15, 2017].
- Scott, E., 2015. *End-of-life Tyre Report 2015*, ETRma. Available at: <http://www.etrma.org/library-2>.
- TRS, 2018. Biological surface devulcanization for rubber powders. *Tyre Recycling Solutions*. Available at: <http://www.trs-ch.com/> [Accessed April 23, 2018].
- Tyromer, 2018. Tyromer Rubber Devulcanization Technology. Available at: <https://tyromer.com/technology/> [Accessed April 23, 2018].

19 NIOBIUM

19.1 INTRODUCTION

Nb is a soft ductile metal indispensable in many industrial applications thanks to its excellent physico-chemical properties. It has nearly zero electric resistance at low temperatures, high corrosion resistance, shape memory properties and high capacitance (i.e ability to store electric charge) [1]. It belongs to the refractory metal group, which are highly strategic metals due to its properties: high melting point (above 2000°C), high density and inertness [2].

European Commission has declared Nb as critical raw material due to its singular characteristics, growing significance for the EU manufacturers and economy and high risk of supply shortage. Global primary production of Nb is mainly concentrated in Brazil (90%) and Canada (10%), being negligible for EU. Secondary production of Nb takes place in EU but there is not available data about the production from these sources [3].

Nb is mainly used in High Strength Low Alloys Steels (HSLA), which contain at most 0,1% Nb. These steels are used in high-pressure pipeline construction, building sector, and as major components in the automotive industry [4] [5]. Nb is used as standard FeNb in HSLA steels, so standard FeNb represents about 89% of the world production of Nb-containing materials. Standard FeNb contains around 60% Nb). The remaining percentage (11%) is used to produce Nb compounds, alloys, high-purity FeNb, and other Nb-based wares [6]. The use of Nb in superconducting alloys, although also important, is less than for HSLA steels [4], so HSLA steel has been chosen

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

as main application for doing the circular economy analysis of Nb. Nb is mainly imported and exported as FeNb in EU. Total imports of FeNb in EU were 25219 tons in 2015. Total exports accounted for 5658 tons of FeNb in 2015 [7].

19.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

19.2.1 PRODUCTION

19.2.1.1 FROM MINERAL ORE TO FERRONIUBIUM

Nb supply comes mainly from primary sources, with the mineral pyrochlore accounting for more than 95% of the total primary production. Columbo-tantalite minerals are also potential sources of Nb. Concerning secondary sources, Nb is also extracted as a by-product from tin slags and recycling [1]. The main producers of Nb are CBMM in Brazil and Niobec mine in Canada. CBMM sells its products to steel companies (for example Arcelor Mittal in Germany) and major specialty alloy producers such as H.C. Starck (Germany), Treibacher AG (Austria), or Silmet (Estonia), which in turn sell their products to the automotive, manufacturing and construction industries [1].

Pyrochlore mineral ores are the main source of Nb_2O_5 , precursor of FeNb, so this source is considered for the analysis. The formula of pyrochlore is: $(Na,Ca,Th,La)_2(Ti,Nb,Ta)_2O_6(OH,F)$. The content of Nb in pyrochlore is between 50-71,5 % [8].

Pyrochlore ores are usually mined by standard methods, e.g. drill, blast, and muck cycles. After they are comminuted and concentrated by flotation, being first removed the irrecoverable ultrafines to achieve acceptable concentrate grades (generally more than 50% Nb_2O_5) and removal of undesired contaminants. Several flotation stages as well as electrical separation are required. Figure 1 shows the Nb production flowsheet for the Niobec mine in Canada [9].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

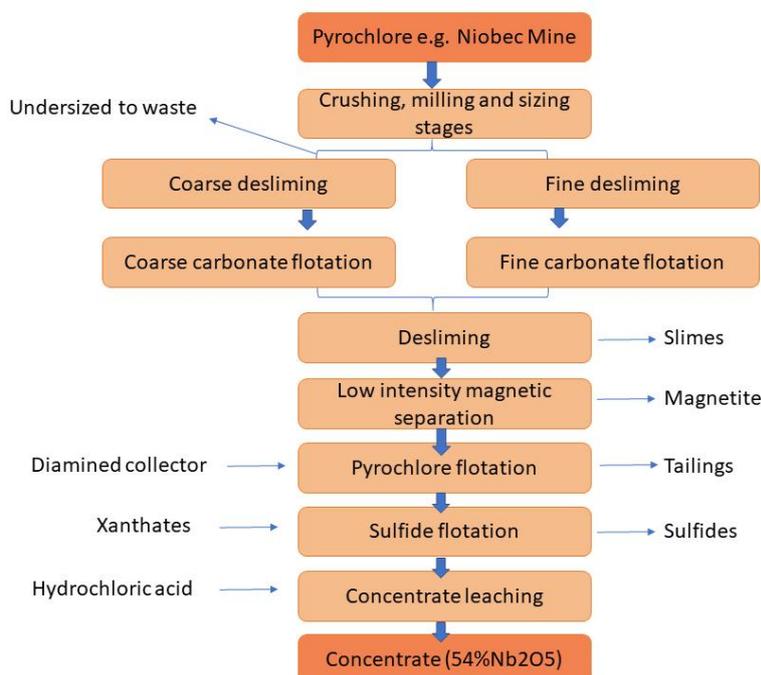


Figure 11 Nb production flowsheet of Niobec Mine [9]

A total of 2,4 kg of Nb_2O_5 are produced per each ton of ore. Nb_2O_5 [10]. The produced concentrate (54% Nb_2O_5) is converted to FeNb by way of thermite reaction, at 2250°C, in 10 minutes. A typical load of 6400 kg of concentrate generates 2400 kg of FeNb. Following a cooling period, the FeNb is crushed to sizes specified by various steel plants (to produce HSLA steels), packaged in 10 to 1500 kg containers and shipped worldwide [10].

Nb can be also extracted as a by-product of tin smelter waste, but Nb produced in this way accounts only for 2% of total Nb production. Low-grade smelter wastes can be upgraded by electrothermic reduction yielding a concentrate with up to 50% Nb_2O_5 [11]. Initially, the conventional methods for extracting Nb from tin slags consist of full dissolution with HF or H_2SO_4 , or smelting in electric furnaces, but these methods are currently limited by economic or environmental considerations [12].

Concerning environmental aspects, pyrochlore ores may contain significant levels of U and Th. This fact is important to be considered during mining and transportation of the concentrate [4]. Environmental precautions in the mining and concentration of the mineral are considered satisfactory. The flotation reagents used in the concentration are biodegradable and as there are not sulphide minerals in the deposits, the tailings ponds do not have acid mine drainage, and therefore are not considered hazardous [9]. The process involves high amount of HF, which is highly toxic and generates a large amount of effluents containing fluoride ions. To avoid this fact,

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Deblonde *et al.* (2016) developed a fluoride-free process for recovery of Niobium from Mabounié mine, with the use of sulfuric acid and water [5].

FeNb production from concentrates does not have either environmental problems, if standard safety procedures occur, but the thorium and uranium contained in the concentrates may reach the FeNb slag. This slag is stored on site [9].

No evidence about the Nb recovery from tailings and residues of the production processes has been found, nor information about the grade of Nb in these outputs.

19.2.1.2 FERRONIBIUM IN HSLA STEEL PRODUCTION

Steel is an alloy of Fe and C, and little quantity of other elements may be present. Rare metals can be added to steel for improving the steel performance: Cr, Co, Cu, Mn, Mo, Nb, Ni, Pb, Sn, V, and W have functional applications in varieties of steel. Current steel production normally proceeds in two ways: by electric arc furnaces and by integrated plants, including blast furnaces and basic oxygen furnaces [13].

Co-outputs of steel production and processing can contain relatively rare metals. Such co-outputs in part consist of scraps, which are divided into home or internal scrap (from metal production) and new or process scrap (from the processing of metal into products). It has been estimated that 24-26% of liquid steel is lost to co-outputs before the product stage. Currently, scraps from the production of steel are usually recycled. Apart from processing residues containing small pieces of steel (Swarf), scraps from steel processing are often recycled to steel production.

Other co-outputs of steel production and processing are residues, which include slags, dusts, scales, spittings, swarf and sludges, with slags dominating residues quantitatively. These residues are an important sink of relatively rare metals. Under oxidizing conditions in a basic oxygen arc furnace most Nb present in hot metal moves to slag in conventional dephosphorization. Recycling Nb from production residues to applications as functional metals in steel is limited [13].

Where strength at high temperature is required in steel, metals such as Mo and V are often used as substitutes for Nb [11].

Steel production consumes much energy and therefore it is associated with resource conservation, energy efficiency, and emissions reduction [14].

19.2.2 USAGE

The use stage of steel may also give rise to losses of relatively rare functional metals. In part such losses come from wear, erosion, abrasion, weathering and corrosion of steel and in part they come from coatings [13].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Nb is recycled when Nb-bearing steels are recycled but specific recovery for Nb from steels do not exist. Statistics for recycled Nb are not available, but this could be as high as 20% of apparent consumption [9].

Because of its durability, steel can be reused or repurposed in many ways, with or without remanufacturing. This already occurs with automotive components, buildings, train rails and many other applications [15].

Reuse is advantageous because few or no energy is required for reprocessing, but initial design based on life cycle thinking is critical if reuse is to succeed [15].

19.2.3 END OF LIFE

The steel recycling is very common, as it takes place since the creation of the steel, due to its 100% of recyclability. It can be recycled many times to create new steel products in a closed material loop, without losing of its inherent properties. The magnetic property of steel ensures easy and affordable recovery for recycling from almost any waste stream while the high value of steel scrap guarantees the economic viability of recycling. Today, steel is the most recycled material in the world, but concrete data about Niobium recycling is not available [15].

Present steel recycling relies on re-melting. The basic oxygen furnaces, which are currently the main suppliers of steel in practice, allow for adding a limited amount of scrap to the input of Fe. Electric arc furnaces for steel production allow for an input of 100% scrap (including scrap for EOL products). A characteristic of re-melting is that rare elements do not partition in the same way to steel and residues such as slags and dusts. Nb separates more in residues. The percentage of Nb that ends in liquid steel in electric arc furnaces is between 1-60% and 40-99% for residues [13].

The end-of-life stage of steel has characteristics that are associated with losses of relatively rare metals. Cooper *et al.* (2014) estimated that about 40% of the demand for steel is used to replace products that have failed due to premature component failure, often leaving much of the steel in the product under exploited. The metal industry has claimed that metals from end-of-life products are widely recycled at high rates and that those metals are recycled repeatedly. For their work it can be concluded that in practice metals present in steel from EOL products are recycled only a small number of times into new steel products [14].

Poor efficiencies in collection for recycling and trends in design which do not allow for easy separation of steel from other substances contribute to limiting the number of times that steel is recycled. Also input requirements of steel producers may matter. For instance, producers of advanced high-strength steels have requirements as to inputs in steel production which are at variance with high levels of recycling. End-of-life steel scrap in part ends up in landfills and in part reaches waste incinerators- Magnetic separation facilities may be present at incineration facilities or landfills to separate the magnetic fraction of steel scrap for further processing, e.g in shredders [13].

Concerning the use of HSLA steels in automotive industry, the development of functional recycling of ELV scarce metals requires knowledge of car metal contents and fates of individual metals in recycling systems. However, available information on both is limited. Regarding fates there are considerable knowledge gaps. Measurements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

of scarce metals in some waste flows exist for certain metals, such as Co and Mn, but no measures about Nb have been found. In EOL vehicles, normally the steel is shredded and sent to steel production [16].

EOL vehicles are presently the most important source of steel containing Nb, since their life span is relatively short, comparing to other applications. A new way to recover more Nb from EoL is to separate exhaust part and suspension parts from the rest of ferrous metals. The steel for exhaust production contains 0,03-0,3% of Nb, while the vehicle body only 0,02-0,05%. Therefore, proper separation can be a successful way to increase recovery rate of Nb [17].

19.2.4 RESIDUE TREATMENT

As said before, when re-melting of the steel, Nb ends majority in the waste stream, but no treatment of these wastes has been found.

19.3 SUMMARY

The Nb market is estimated to grow at a rate of 8% per year driven mainly by higher demand for high-grade steel use in the automotive and construction industries, which are expected to expand as the global economy recovers [1] [7]. The analysis of the Niobium value-chain from production from primary ores to the end-of-life HSLA steel products have revealed that Niobium contained in HSLA steel is recycled when steel is recycled. Also, it seems that Niobium ends more in the wastes of re-melting of steel in electric arc furnaces than in the steel, but no information about the treatment of that wastes have been found. Reuter *et al* (1994) studied Nb distribution between metal melt and slag in an electric arc furnace dependent on temperature, equilibration time and basicity and they concluded that the loss of Nb to dephosphorization slag under oxidizing conditions in basic oxygen furnaces may be reduced by using a highly basic BaO-based slag, while retaining dephosphorization [13].

For reducing the loss of Niobium in steel applications, it could be substituted by Ti, Mo, W and N.

Concerning HSLA steels in EOL pipelines and vehicles it seems that steel is used for new steel production, so again the Nb is recycled but no recovery of Nb metal is occurring.

19.4 REFERENCES

- [1] L. Moreno, «Tantalum and Niobium Primer. Two critical metals,» Jacob Securities Inc, Toronto, 2011.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [2] MSP-REFRAM, «Prometia,» 21 11 2017. [En ligne]. Available: <http://prometia.eu/msp-reframs-project-results-are-now-available/>.
- [3] EC, «European Commission,» 20 November 2017. [En ligne]. Available: http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_es.
- [4] D. A. Mackay, «Geology, Market and Supply Chain of Niobium,» *Miner Deposita*, pp. 1025-1047, 2014.
- [5] G. J. Deblonde, V. Weigel, Q. Bellier, R. Houdard, F. Delvallée, S. Bélair et D. Beltrami, «Selective recovery of Niobium and tantalum from low-grade concentrates using a simple and fluoride-free process,» *Separation and Purification Technology*, pp. 180-187, 2016.
- [6] E. Nikishina, D. Drobot et E. Lebedeva, «Niobium and Tantalum: State of the World Market, Fields of Application, and Raw Sources. Part I,» *Metallurgy of rare and noble metals*, pp. 28-34, 2013.
- [7] D. Hartmann, Y. X. Sheng, S. Casanovas, R. B. García et M. Gonzalez Moya, «Report on current and future needs of selected refractory metals in EU,» 2016. [En ligne]. Available: <http://prometia.eu/deliverables/>.
- [8] E. Nikishina, D. Drobot et E. Lebedeva, «Niobium and Tantalum: State of the World Market, Application Fields, and Sources of Raw Materials. Part 2',» *Metallurgy of rare and noble metals*, pp. 29-41, 2014.
- [9] R. Linnen, D. Trueman et R. Burt, «Tantalum and Niobium,» British Geological Survey, 2014.
- [10] Niobec, «Niobec,» 21 11 2017. [En ligne]. Available: <http://niobec.com/en/about/process/>.
- [11] MineralsUK, «British Geological Survey,» 21 11 2017. [En ligne]. Available: <http://www.bgs.ac.uk/mineralsuk/statistics/mineralProfiles.html>.
- [12] J. Odo, W. Okafor, S. Ekpe et C. Nwogbu, «Extraction of Niobium from Tin Slag,» *International Journal of Scientific and Research Publications*, pp. 2250-3153, 2014.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [13] L. Reijnders, «Conserving functionality of relatively rare metals associated with steel life cycles: a review,» *Journal of Cleaner Production*, vol. 131, pp. 76-96, 2016.
- [14] G. M. Olmez, F. B. Dilek, T. Karanfil et U. Yetis, «The environmental impacts of iron and steel industry: a life cycle,» *Journal of Cleaner Production*, vol. 130, pp. 195-201, 2016.
- [15] W. Association, «Steel in the circular economy. A life cycle perspective,» World Steel Association, Brussels, 2015.
- [16] M. Andersson, M. L. Söderman et B. A. Sandén, «Are scarce metals in cars functionally recycled?,» *Waste management*, vol. 60, pp. 407-416, 2017.

20 PLATINUM-GROUP METALS (PGM)

20.1 INTRODUCTION

Platinum group metals (PGMs), are six metals (platinum, palladium, rhodium, iridium, ruthenium, osmium) used in a wide variety of technologies: catalysts in chemical processes (especially oil refineries) and in hydrogen fuel cells, catalytic converters for exhaust control in transport vehicles, as well as in electronic components, jewellery and glassmaking. (Hagelüken 2012; Glaister & Mudd 2010) Given the urge to expand almost all of these uses to meet both environmental challenges and consumer needs, the growth of demand for PGMs can be expected to be steady in the future (Glaister & Mudd 2010).

Figure 20-1 presents a conventional lifecycle of PGMs from ores to disposal or recycling. The main gaps limiting the circular economy of PGMs lie in the collection systems for various PGM-containing consumer products, but small improvements can be done throughout the chain. The losses identified in the figure provide an opportunity for making improvements to the processes or for creating incentives that promote recycling to take place. (Hagelüken 2012)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

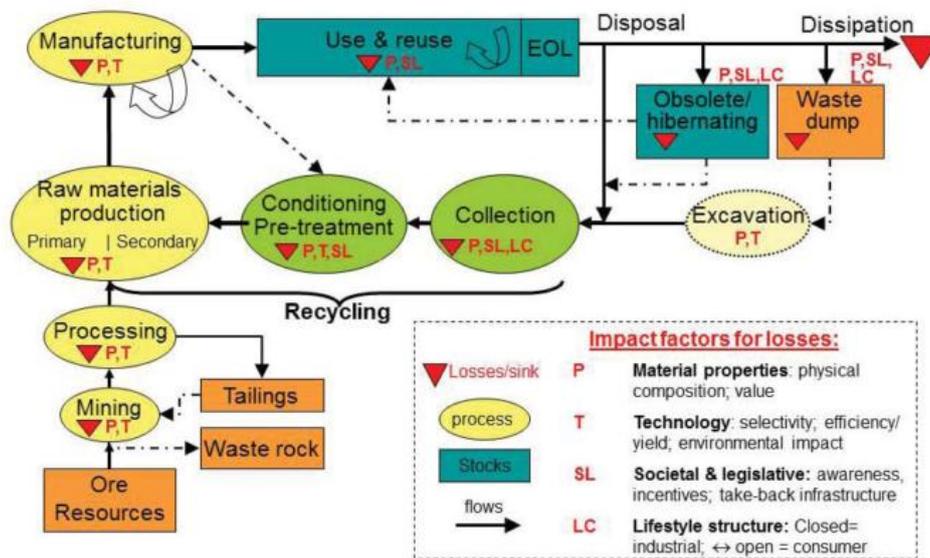


Figure 20-1. Lifecycle for a typical PGM-containing product, highlighting the various points at which losses of precious metal can occur. Derived from (Hagelüken 2012).

Recycling of PGMs plays an important role in cutting the environmental burden of the global PGM production. The environmental advantage of secondary PGMs, such as lower energy consumption, largely arises from the much higher concentration they appear in compared to primary PGM sources. In addition, the high value of PGMs promotes the recycling of other metals present in PGM-containing products, which might not otherwise be recovered due to their lower price. (IPA 2017)

20.2 GAPS LIMITING CIRCULAR ECONOMY

20.2.1 ACCESSIBILITY OF THE METALS

There are only minor technical challenges concerning the recycling of PGMs. These challenges exist especially with complex products such as vehicles and electronics, and are mainly related to the accessibility of the metals in an application. An example of such applications are circuit boards used in car electronics. However, as long as the circuit boards are separated or dismantled before the vehicle is scrapped, the precious metals they contain are easily recyclable. (Hagelüken 2012)

20.2.2 PROFITABILITY

The high price of PGMs makes their recovery usually attractive from an economic point of view. However, the economic viability of PGM recycling is evidently very application dependent: the lower the concentration of

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

precious metals, the smaller the profitability. Consumer components for electronics, such as computer motherboards contain around 80 g/t of palladium, mobile phone handsets up to 130 g/t of palladium, and automotive catalytic converters up to 2000 g/t of PGMs in the active part of the converter. This is significantly higher than the PGM content in primary ores, which is less than 10 g/t (Panda et al. 2018). Consequently, a dismantled PC motherboard has a positive net value when PGMs are recovered from it. Even more valuable for recycling are PGMs used in jewellery, as PGMs in these items are typically concentrated at an even higher level. In contrast, a dismantled ultra-thin PGM-coated PC hard disk usually has a negative net value due to the cost of processing it. (Hagelüken 2012)

20.2.3 COLLECTION MECHANISMS

The major defects of the recycling chain of PGMs are related to the collection of consumer goods and handling of them within the recycling chain. This is due to the fundamentally different life cycle structure of PGM-containing consumer products compared to that of industrial PGM products. In the case of industrial goods, such as process catalysts, the ownership usually remains with an industrial user, with the result that the product location is well known and handling throughout the life cycle is conducted in a well-defined way. This is an example of a closed loop recycling system. (Hagelüken 2012)

In contrast to the industrial products containing PGMs, the ownership of consumer goods tends to change frequently when products, such as mobile phones, and vehicles are transferred around the world. Manufacturers lose track of their items and the flow of products becomes impossible to record. This flow creates an open loop where recycling cannot be guaranteed. (Hagelüken 2012)

Insufficient collection of consumer electronics waste forms a significant leakage of PGM containing applications, as less than 15% of PGMs carried by WEEE (waste electrical and electronic equipment) is recycled (Hagelüken et al. 2016). Items such as old PCs or mobile phones may end up being stored in households or discarded into the municipal solid waste (MSW), ending up in landfill or municipal incineration. Only about 35 wt% of WEEE was officially collected in the EU in 2012. This leads to a situation where precious metals are lost from the recycling chain. (Huisman et al. 2015; Hagelüken 2012)

After the products have entered into the recycling chain, the next step is to ensure the goods will also remain there. The goods, such as items of WEEE or end-of-life vehicles (ELVs) may exit the recycling chain if they are shipped, either legally or illegally, to countries that lack a proper infrastructure for recycling. (Hagelüken 2012) It has been estimated that, of the 9.45 Mt of WEEE generated in the EU (in 2012), 2.25 Mt of WEEE was shipped outside the EU (Huisman et al. 2015).

Even though well-organised recycling chains already exist in Europe, it is important to ensure that items such as PCs or mobile phones are not mixed with other low-grade electronic waste where they are channelled into a shredder process without prior removal of the precious metal-containing circuit boards. The same applies to the PGM-containing catalyst in a car or fuel cell. (Hagelüken 2012)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

20.2.4 CAPACITY

The final gap possibly limiting a comprehensive recycling of PGMs is the amount of capacity to process the volume of material available for recycling. Precious metal refiners are willing to invest in building up sufficient capacities provided there is sufficient reliability of the feed later on. The proper functioning of collection mechanisms is thus crucial to trigger timely investments in a principally growing market of PGM recycling. (Hagelüken 2012)

Moreover, if applications containing PGMs are dumped or treated by sub-standard methods, the result is not only a negative impact on human health and the environment, but also a significant pressure on recycling prices and a disturbance on the recycling market, as such operations externalize environmental and social costs. This makes it difficult for state-of-the-art recyclers to achieve a stable capacity utilization and to invest in new processes or capacity expansion. This may compromise the medium- and long-term harvesting of the EU's potential on secondary raw materials. (Hagelüken et al. 2016)

20.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

20.3.1 "METAL SCAVENGERS"

So called metal scavengers are developed to recover precious metals from liquid solutions, used in chemical processes or produced as effluents from chemical wastewater treatments. A commercial example of a metal scavenger goes under tradename Smopex, which can be used to remove PGMs from the solution down to parts per billion (ppb) levels. Smopex is a fibrous material with a polypropylene or viscose backbone grafted with functional groups that are highly selective for PGMs. (Phillips & Kauppinen 2010)

Metal scavengers are especially beneficial when used *in situ* to avoid shipping large quantities of very dilute solutions to secondary PGM refiners. (Frankham & Kauppinen 2010) The fibres in Smopex can carry a metal loading of up to 10 wt%, and after the refinement of the solution the loaded fibres can be sent for traditional refining to recover the precious metals. (Phillips & Kauppinen 2010) The use of metal scavengers benefits both economic and environmental objectives because, the solutions may contain so small amounts of PGMs in such large volumes that the cost of transporting them as such is higher than the economic benefit achieved from the recovery. (Frankham & Kauppinen 2010)

20.3.2 DESIGN FOR DISASSEMBLY

Product design is an important stage in the lifecycle of a product, as the material choices and the selection of connection methods between components and parts are carried out in this stage. Since different types of connection methods perform differently in the recycling systems, improvements in the recycling efficiency can be made by taking this into consideration. However, the selections should be carried out without losing the functionality of the object, as well as taking into account aspects such as appearance. (Bachér et al. 2017)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Active dismantling or disassembly has gained attention in the recent years. Active dismantling or disassembly is a concept, which enables the separation of components from products for recycling through the use of smart materials or structures in the product design. The detachment or loosening function is activated through a single or a combination of external triggers. As an example, if products are designed with shape memory snap fits, the disassembly is initiated when product is heated. Upon heating, all snap fits are deformed, thus releasing the individual components and consequently the products are dismantled. Beside thermal triggers, a number of other triggers have been identified. (Bachér et al. 2017) Possible triggering methods are presented in Table 20-1.

Table 20-1. Possible triggering methods that can be used in the product design of electronic devices to ease their disassembly. Adapted from (Bachér et al. 2017)

Trigger mechanism	Implementation
Mechanical force	<ul style="list-style-type: none"> • Centrifugal force • Acceleration • Water jet
Vibration	<ul style="list-style-type: none"> • Mechanical vibration • Sound waves • Water waves
Pressure	<ul style="list-style-type: none"> • Pressure variation (air/water)
Electrical	<ul style="list-style-type: none"> • Electric current
Chemical reaction	<ul style="list-style-type: none"> • Reagent in surrounding atmosphere (pH-level, hydrogen, H₂O, ...) • Submerging in reagent
Thermal reaction	<ul style="list-style-type: none"> • Joule effect • Radiation (laser, infrared rays, ...) • Microwaves • Submerging in hot water tubs
Magnetic field	<ul style="list-style-type: none"> • Presence of electromagnet (Magnetising vs. Demagnetising) • Magnetic Ray Interference (MRI)
Light radiation	<ul style="list-style-type: none"> • UV-radiation
Biological action	<ul style="list-style-type: none"> • Presence of bacteria • Enzymes inducing chemical reactions • Bionically designed systems

20.3.3 BUSINESS TO BUSINESS (B2B) CYCLES

As discussed in section 20.2.3, the recycling of PGMs is functioning in the most efficient way when the ownership of the PGM-containing materials remains within the industrial users. Industrial applications such as catalysts used by chemical industry and PGM equipment used in the glass industry are the current benchmark for PGM recycling, with recycling rates of 80–90%. Recycling in these cases is heavily market driven due to the price of

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

PGMs and forms an integral part of the product life cycle. The recycling reduces the need for primary metal supply for these industries, which is required to cover the small lifecycle losses and enable market growth and new applications. (Hagelüken 2012)

On the contrary, in a business-to-consumer (B2C) environment metal losses are significantly higher, but not because of technical restraints in the recycling process. In B2C applications, ownership of the metals changes each time a transaction occurs, transparency is low and tracking of items is challenging. To improve overall recycling rates, a gradual shift towards more industrial style practices is needed, through frame conditions contributing the move from open B2C business models towards closed business-to-business (B2B) models. (Hagelüken et al. 2016)

The main idea in B2B models is to create strong incentives for returning products at their end of life. Examples are deposit fees on new products and product service systems, such as leasing. For emerging technologies, such as fuel cells and photovoltaics aimed at consumer sector, setting up closed loop models from the beginning will be essential. Manufacturers setting up successful B2B models for their products can better secure their supply of PGMs for the future. (Hagelüken 2012)

20.3.4 LEGISLATION

20.3.4.1 WASTE SHIPMENT REGULATION

A considerable number of ELVs are exported illegally from the EU predominantly to Africa. These countries usually lack an appropriate recycling chain, which would result even higher PGM losses without the excellent recyclability of the PGMs and the economic attractiveness of automotive catalyst recycling. Better enforcement of Waste Shipment Regulation No 1013/2006 to limit the export of ELVs could improve the recycling rates in Europe. The Regulation includes a ban on the export of hazardous wastes to non-OECD countries as well as a ban on the export of waste for disposal. (Schneider et al. 2010; Hagelüken 2012; European Commission 2018)

However, an important factor affecting the issue is the differentiation between ELVs and used cars. The question is ultimately, when a used car ceases to be product and becomes waste, and EU member states may answer this question differently. As a consequence, the question if Waste Shipment Regulation should be applied to a transboundary shipment of a vehicle is answered differently in individual cases. (Schneider et al. 2010)

As a one measure to tackle the problem of identifying waste crossing illegally EU borders as non-waste, EU launched a tool for customs officials in 2016. The tool, which can be applied to goods that can be correlated with a waste code, serves as an alert for customs that waste may be crossing EU borders illegally. This measure is expected to help resolving the problem of illegal exports of waste, which prevents the leakage of valuable raw materials out of the EU. (European Commission 2018)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

20.3.4.2 WEEE DIRECTIVE

Recycling rates of PGMs are currently only 5–10% in electronic applications. The main driver for recycling is legislation, such as the WEEE Directive 2012/19/EU. (Hagelüken 2012) The Directive enabled the creation of collection systems where consumers could return their WEEE free of charge. The collection of WEEE from collection facilities, the treatment, recovery and disposal of WEEE is to be financed by the producers. (European Parliament 2012)

The WEEE Directive helps to stimulate recycling of electrical and electronic products but its enforcement is currently weak. More transparency (cf. B2B models) and better monitoring of EoL products would improve the rates of recycling. In addition, a shift of focus of the current, quite generic legislation, towards a more pragmatic approach by the introduction of treatment standards and certification systems along the recycling chain would improve the recycling rates of PGMs. (Hagelüken 2012)

20.4 ENVIRONMENTAL ISSUES

No environmental issues were identified related to secondary PGM production that would not occur in the primary PGM production, as the technical recovery is similar in both cases. The main difference in their processing arises from the higher concentration of valuable metals in secondary sources, which reduces the environmental footprint of secondary PGM production compared to that of primary PGM production from ores. (IPA 2017)

As the environmental issues of PGM production are mainly associated with the primary PGM production, the geographical distribution of the environmental burden of the total PGM production is concentrated to the areas where the primary production occurs, particularly in South Africa and Russia. The environmental impacts include mining waste and sulphur dioxide emissions, in addition to the side effects of the used power source (e.g. coal). As a consequence, the development of cleaner technologies (e.g. catalytic converters, fuel cells) in the more wealthier parts of the world can be thought to be responsible for the concentration of the environmental burden in the countries of primary production. (Saurat 2006)

20.5 SUMMARY

Over 95% recovery rate is technically achievable for the PGMs in a state-of-the-art refining facility. Although some minor technical challenges still exist, the main barriers to the recycling of PGMs lie in the collection of scrap and in the capacity and technical capabilities of recycling chains around the world. Economic and legislative drivers have a significant role in the circular economy of PGMs, but legislation needs better enforcement and a more pragmatic approach, for example through an introduction of treatment standards. Technical recyclability, which is mainly limited by the accessibility of the PGMs in an application, could be further improved by eco-design principles, such as design for disassembly.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

20.6 REFERENCES

- Bachér, J. et al., 2017. *Future trends in WEEE composition and treatment - A review report*, CLIC Innovation Ltd. Available at: <http://arvifinalreport.fi/files/D2.3-2 and D4.2-6 Review report on WEEE composition and treatment.pdf>.
- European Commission, 2018. EU Framework legislation: Shipment of waste. Available at: <http://ec.europa.eu/environment/waste/shipments/index.htm> [Accessed April 16, 2018].
- European Parliament, 2012. *Directive 2012/19/EU of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE)*, Available at: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2003:037:0024:0038:en:PDF>.
- Frankham, J. & Kauppinen, P., 2010. The use of metal scavengers for recovery of precious, base and heavy metals from waste streams. *Platinum Metals Review*, 54(3), pp.200–202.
- Glaister, B.J. & Mudd, G.M., 2010. The environmental costs of platinum-PGM mining and sustainability: Is the glass half-full or half-empty? *Minerals Engineering*, 23(5), pp.438–450. Available at: <http://dx.doi.org/10.1016/j.mineng.2009.12.007>.
- Hagelüken, C., 2012. Recycling the Platinum Group Metals: A European Perspective. *Platin. Met. Rev.*, 56(1), pp.29–35.
- Hagelüken, C. et al., 2016. The EU Circular Economy and Its Relevance to Metal Recycling. *Recycling*, 1(2), pp.242–253. Available at: <http://www.mdpi.com/2313-4321/1/2/242> [Accessed April 15, 2018].
- Huisman, J. et al., 2015. *Countering WEEE Illegal Trade Summary Report, Market Assessment, Legal Analysis, Crime Analysis and Recommendations Roadmap*, Lyon, France. Available at: <http://www.cwitproject.eu/wp-content/uploads/2015/08/CWIT-Final-Summary1.pdf>.
- IPA, 2017. The Secondary Production and Recycling of Platinum Group Metals (PGMs). Available at: http://www.ipa-news.com/assets/sustainability/Secondary Production Fact Sheet_LR.pdf.
- Panda, R., Jha, M.K. & Pathak, D.D., 2018. Commercial Processes for the Extraction of Platinum Group Metals (PGMs). In Springer, Cham, pp. 119–130. Available at: http://link.springer.com/10.1007/978-3-319-72350-1_11 [Accessed April 15, 2018].
- Phillips, S. & Kauppinen, P., 2010. The use of metal scavengers for recovery of palladium catalyst from solution. *Platinum Metals Review*, 54(1), pp.69–70.
- Saurat, M., 2006. Material Flow Analysis and Environmental Impact Assessment Related to Current and Future use of PGM in Europe. , p.229.
- Schneider, J. et al., 2010. *End of life vehicles: Legal aspects, national practices and recommendations for future research*, European Parliament, Policy Department A: Economic and Scientific Policy.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

21 PHOSPHATE ROCK AND WHITE PHOSPHORUS

21.1 INTRODUCTION

Phosphate rock, $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ is the main source of phosphorous (P) from the earth's crust being vital part of plant and animal nourishment. The major end-user for phosphate rock in the EU are mineral fertilizer (86%), food additives (10%) and fireworks and detergents (4%) (European Commission 2017). Approximately 90-95 % of world phosphate rock goes to agriculture, around 85 % to fertilizers and 5-10 % to animal feed. Phosphate rock is however, also essential for a wide range of industrial applications including (Potočník 2016):

- Electronics - production of microchips
- Fire safety - replacing halogenated flame retardants
- Pharmaceuticals, Medical applications, Agrochemicals
- Food additives for example nontoxic food preservatives
- Catalyst and Chemicals
- Other new innovative applications with high potential for society, such as new compounds for batteries, safer than lithium ion.

Figure 1 presents phosphate rock value chain with its main applications:



Figure 2. Phosphate rock value chain (Deloitte 2015).

White phosphorus, P_4 , is an elemental form of phosphorus, produced from phosphate rock. There are various allotropic forms of elemental phosphorus but only two forms have commercial significance - white and red phosphorus - and white phosphorus, P_4 , is the most commercially important, accounting for 99% of demand worldwide. White Phosphorus major end-user are in chemical industry applications (90%), electronics (5%) and in metal products (5%). (European Commission 2017) A wide range of the phosphorus-based products used in chemical industry can today only be produced via white phosphorus P_4 shown in figure 2 (Schipper 2016).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

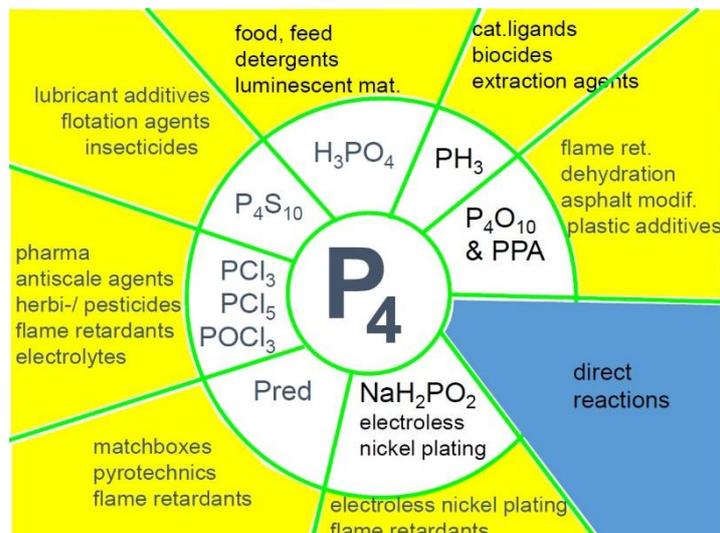


Figure 2. White phosphorous containing chemicals and applications (Schipper 2016)

21.2 GAPS LIMITING CIRCULAR ECONOMY

21.2.1 MARKET AND DEMAND

The food system and especially agriculture are the most important drivers and actors in the phosphorus import demand and Europe's dependency on primary phosphate rock. As Europe has no significant phosphate mines, it is highly dependent on the import of phosphate ore. The increasing popularity of meat and dairy products in developing economies and phosphorus demand for non-food uses, may further increase global demand. Moreover, the challenges related to increasing urbanization and changes in diets are putting further pressure on the phosphorus demand, as agricultural production will have to increase further to meet food demand. Meanwhile, the burgeoning bio based economy and growing demand for bio-energy are increasingly competing with the food production sector for scarce land, fresh water, and other natural resources. (Schoumans et al. 2015).

21.2.2 LOSSES IN FLOWS

Figure 3 shows simplified Sankey diagram for phosphate rock (Deloitte 2015). It shows that phosphorus is lost (1 550kt/ year of P content) to the environment due to dissipative use or to landfill. Secondary materials flow result mostly from post-consumer recycling (around 180 kt/year of P content).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

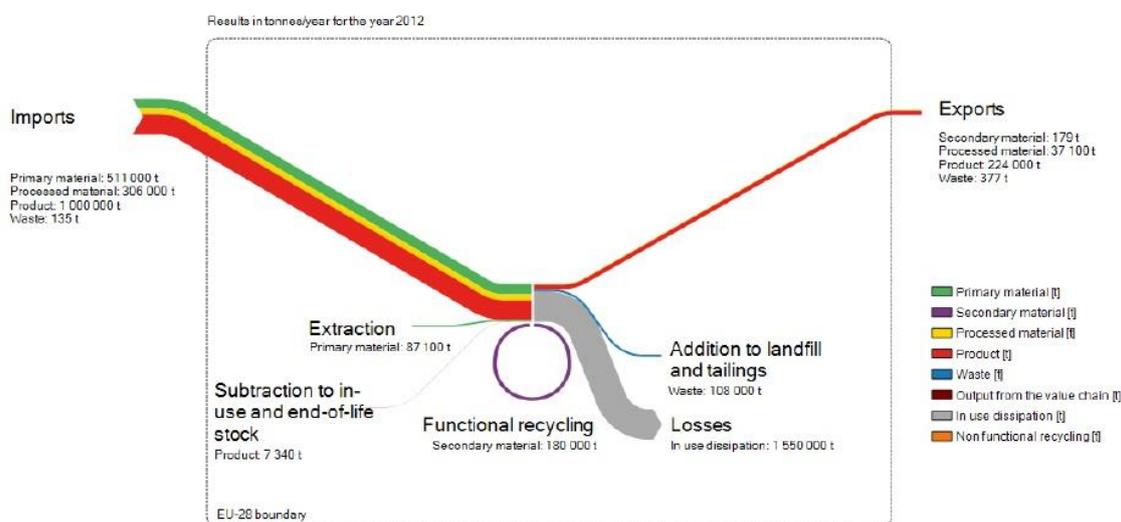


Figure 3. Simplified Sankey diagram for phosphate rock. (Deloitte 2015)

Losses of phosphorus occur along the whole phosphorus chain in all stages including mining losses, losses due to soil erosion, crop losses as well as food losses. In the waste sector losses occur e.g. when phosphorus-rich materials end up in landfill or in sewage sludge. Further losses can occur if manure is not used appropriately for crop production. Also accumulation of phosphorus in agricultural soils is also one factor causing the losses. (van Dijk et al. 2016) (Schröder et al. 2010)

Van Dijk et al. (2016) suggest that more than half of the EU system input phosphorus is lost in 2005. 54% was lost from consumption in diverse waste flows, 28% from food processing, mainly by sequestration of phosphorus in ashes of incinerated slaughter residues (e.g. bones), and the remaining losses were shared almost equally between crop production, animal production and non-food production. Among the total consumption losses, the largest shares are 55%, lost via the wastewater system; followed by 27%, lost with food waste in municipal solid waste (MSW) originating from households, retail and food services; and 11%, lost in pet excreta accumulating in public spaces and gardens but also via MSW. The emissions of phosphorus to the hydrosphere are at least 17% of the total system losses identified. These phosphorus releases are a major cause of eutrophication with large negative effects on water quality and biodiversity.

Phosphate rock is further processed into phosphate products either via the acid route (for fertilizer production), thermal route (for industrial and feed phosphates) or for direct application as fertilizer. In the acid route, sulphuric acid is reacted with phosphate rock to yield phosphoric acid when the product losses predominantly in the form of phosphogypsum. Losses occur also during the thermal route as sludge and slag. Erosion is probably contributing most to the worldwide loss of phosphorus and subsequent soil degradation. Phosphorus can also be made agronomical ineffective via accumulation in soils beyond justifiable levels. The accumulation of phosphorus is usually caused by high livestock densities leading to regional phosphorus surpluses, and

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

subsequently to excessive phosphorus inputs from manure in the surrounding. Phosphorus is also lost in the form of organic waste or losses which are related to the extra cycle which occurs when producing animal products from feed. Losses in the food commodity chain include crop storage, processing and trade, bulk food storage, processing and trade, food retailing and food storage, preparation and consumption. (Cordell et al., 2009) (Schröder et al., 2010) Table 1 gathers the types of losses and the circular economy response strategies presented by Schröder et al. (2010) and Abdulai et al. (2015).

Table 2. Phosphorous losses and suggested strategies for circular economy (Schröder et al. 2010) (Abdulai et al. 2015).

LOSS TYPE		EXAMPLES	CE RESPONSE STRATEGY
PERMANENT LOSSES (from the food production and consumption system)	LOSSES TO ENVIRONMENT	<ul style="list-style-type: none"> • Mining losses • Losses in P extraction 	<ul style="list-style-type: none"> • Reduce spillages, wastage • Development of more efficient recovery techniques
		<ul style="list-style-type: none"> • Losses in fertilizer production • Phosphogypsum stockpiles • Spillage during storage, transport 	<ul style="list-style-type: none"> • Process improvements • New recovery techniques • Reduce spillage, wastage
		<ul style="list-style-type: none"> • Erosion, run-off, leaching 	<ul style="list-style-type: none"> • Improving the soil infiltration capacity • Discouragement of erosion sensitive crops
TEMPORARY LOSSES (within the food production and consumption system) (i.e. potentially recoverable)	ACCUMULATION in agricultural soil	Excess P in soils due to: <ul style="list-style-type: none"> • Abundant fertilization 	<ul style="list-style-type: none"> • Soil testing and management • Better utilization of soil P preserves • Fertilizer placement • Mycorrhizal fungi
		<ul style="list-style-type: none"> • Local excess of manure due to the concentration of livestock 	<ul style="list-style-type: none"> • Policies aiming at lives-tock production • Manure processing and export of nutrients from surplus areas • Using low P feed

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

	<p>ORGANIC WASTE</p> <p>BY-PRODUCTS</p> <p>losses (due to inefficient use, unnecessary waste production or suboptimal recycling)</p>	<ul style="list-style-type: none"> • Slaughterhouse waste • Crops used for non-food purposes • Crop residues • Organic waste from food and feed industry • Food preparation & consumption waste • Manure, human excreta 	<ul style="list-style-type: none"> • Improve reuse in agriculture • Prioritize P use for food security • Improve reuse to conserve nutrients • Composting with other organic rest streams • Collect organic household waste followed by e.g. bio-gas production • Source separation and re-use in agriculture • Sewage sludge reuse
--	--	---	--

21.2.3 LOW RECYCLING RATE

Phosphate rock itself is not recyclable. On the other hand, phosphorus as an element is recyclable to some extent, and therefore refining phosphorus from secondary resources reduces the demand of virgin phosphate rock. According to European Commission (2017) End-Of-Life recycling Input Rate (EOL-RIR) is 17% for phosphate rock in mineral fertilizers and food additives and 0% in chemical industry applications. Phosphate rock can be replaced by secondary sources of phosphorus from the recycling of biogenic wastes (e.g. manure or other animal by-products, bio- and food wastes, wastewater) for which recycling is considered as functional because it replaces primary phosphorus. (European Commission 2017, 2018) (Deloitte 2015)

van Dijk et al. (2016) suggested the phosphorus recycling rates as fractions of the total input of the sectors were 73% in animal production, 29% in food processing, 21% in consumption and nearly 0% in non-food production. Many waste flows contain high concentrations of phosphorus, which provides opportunities for efficient and effective recycling. Alternatively, waste flows sent to landfills and pet excretion in gardens and parks can be potential stocks of phosphorus for future recycling. For recycling, the concentration, quality and spatial location of stocks are important limiting factors, as well as economic considerations (Good management and innovations) will determine future recycling options.

Schipper (2016) showed product routes for white phosphorus P₄ indicating that P₄ derivatives P ends up in five broad categories. Phosphorous essential use is in agriculture and only 2% of P is used in true P₄ chemistry. When considering cradle-to-cradle design for P chemicals (e.g. recycle flame retarded plastics as such they suggested that a limit on non-agricultural uses of P does not seem needed at this point.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

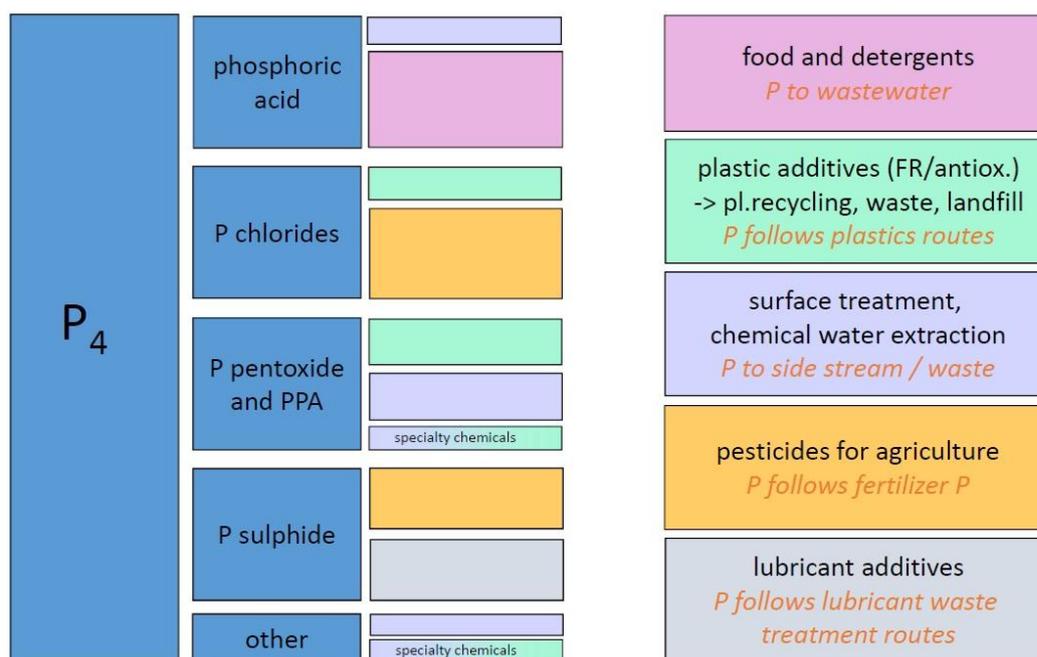


Figure 4. P4 product routes (Schipper 2016)

21.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

According to Schröder et al. (2010) and Cordell et al. (2010) the key drivers for the recovery and reuse of phosphorus are mainly the following:

- Minimizing onsite environmental and social impacts (e.g. pollution prevention - reducing phosphorus from effluent reaching water bodies where it can lead to eutrophication and in turn algal blooms). The recycling of phosphorus rich wastes can also help prevent water eutrophication.
- Fertilizer value; recovered phosphorus can substitute scarce mineral phosphates from phosphate rock.
- Industrial phosphorus value; recovered phosphorus can also be utilized in industrial applications, assuming sufficient quality
- Improved wastewater treatment
- Substitutability; investing in renewable, recovery based sources of phosphorus

Schoumans et al. (2015) suggested that the import of phosphorus can easily be reduced by (i) applying P fertilizers only where required, (ii) taking into account the amount of P forms in the soil (fast and slow release), and (iii) by reducing the P content in feed to meet the actual dietary requirements of the animals. The biggest reductions can be obtained by reducing or even stopping the import of chemical phosphorus fertilizers by recovering

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

phosphorus from waste streams and manure and by cost-efficiently transporting the resulting fertilizer products to regions with less phosphorus.

21.3.1 5R STRATEGY

Withers et al. (2015) proposed the 5R strategy intended to close the phosphorus cycle in Europe. The five Rs are: Realign P inputs, Reduce P losses to waters, Recycle P in bio-resources, Recover P from waste, and finally if necessary Redefine our food system.

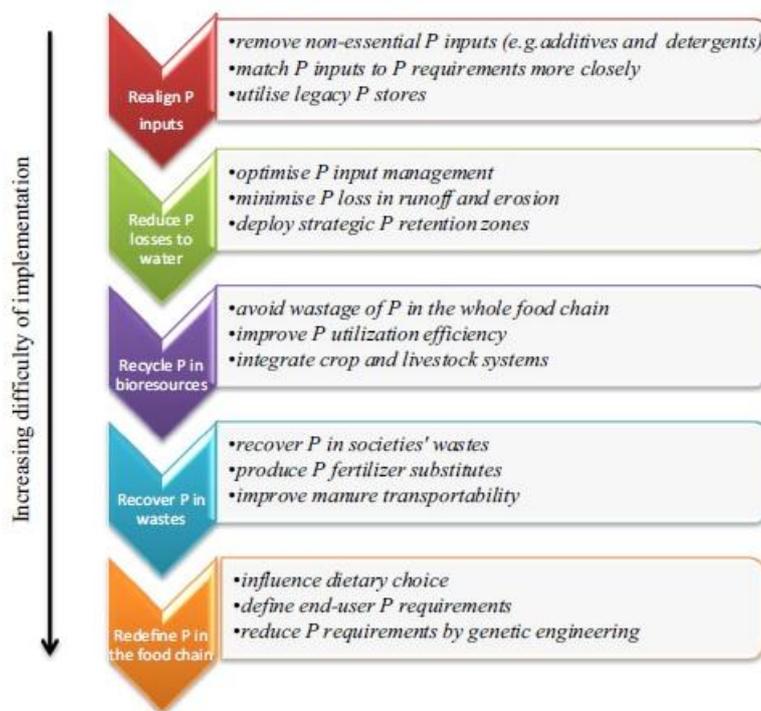


Figure 5. The 5R strategies to reduce Europe's dependency on phosphate rock-derived P (Withers et al., 2015)

21.3.2 RECYCLING POTENTIAL

In general, the recycling potential of phosphorus is large. However, some important barriers have to be overcome before P recycling can be implemented, such as developing technology, governmental regulation, financial investments, and social acceptance. One of the key factors in the recycling of waste flows is their quality since the final recycled end products must be accepted by end users. (van Dijk et al., 2016) There are many options to

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

recover phosphorus, but many techniques still have to be tested in practice at pilot and full scale, especially those for recovering phosphorus from manure. (Schoumans et al. 2015)

According to van Dijk et al. (2016) the highest recycling potential is in wastewater and biodegradable solid waste such as food waste and pet excreta. In the wastewater system P can be recycled via struvite precipitation at WWTPs (max 20% of influent) or via the ashes of incinerated sludge (max. 80% of influent). In the solid waste system, recycling of P in organic waste can be enhanced by reducing food waste in retail, households and food service. Additionally, better organic waste separation from MSW together with improved collection can lead to more high quality compost, suitable for agricultural use. In non-food production, the efficiency can be increased by more and better recycling of P in incinerated wood ashes from the bioenergy sector to forestry and (potentially) agricultural soils. (van Dijk et al., 2016)

21.4 ENVIRONMENTAL ISSUES

There are both direct and indirect environmental impacts of phosphorus use resulting from the consumption of resources (such as water, energy, phosphate rock), mismanagement and the generation of waste either in large volumes or with high toxicity, which can in turn pollute receiving environments and damage ecosystems. Environmental impact of phosphate tends to concentrate two aspects. Firstly, there are localized impacts during the mining and processing of phosphate rock (such as water pollution). Secondly, ecological impact of phosphorus leakage from agricultural soils to aquatic ecosystems. Phosphorus lost from the recycling chain is not only a question of resource efficiency, but also an environmental issue in the regions where it exists in excess. In aquatic ecosystems, excess phosphorus loads can lead to eutrophication that results in oxygen-depleted conditions, where economically important fishes and other aquatic organisms cannot survive. Also drinking water supplies are endangered when algal bloom, deriving nutrition from excess phosphorus, release a toxic substance called algal toxin. (Schröder et al. 2010)

White phosphorus is the probably most dangerous form of phosphorus being highly reactive and poisonous and significant exposure can be fatal. For this reason, white phosphorus P_4 is usually reacted immediately on production to other "holding derivatives" (usually PCl_4), these derivatives can then be transported and used to produce the different phosphorus chemicals for which P_4 is a necessary raw material. (European Commission 2017)

21.5 SUMMARY

Phosphate rock is the main source of phosphorous from the earth's crust being vital part of plant and animal nourishment. Approximately 90-95 % of world phosphate rock goes to agriculture, around 85 % to fertilizers and 5-10 % to animal feed . The remaining is used in a wide range of industrial applications. White phosphorus is an

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

elemental form of phosphorus, produced from phosphate rock. White Phosphorus major end-user are in chemical industry applications.

Food production in Europe is dependent on imported phosphorus, but phosphorus use is inefficient and losses to the environment are high. In addition, the excessive use of phosphorus leads to deterioration of the water quality, eutrophication, and loss of biodiversity. Because the global phosphate rock reserves are limited, there is a pressure for Europe for closing the phosphorus cycle. There exist opportunities to recover phosphorus, but many techniques still have to be tested in practice at pilot and full scale. Strategic frameworks are proposed to help identify and deliver a range of integrated, cost-effective, and feasible technological innovations to improve phosphorus use efficiency in society and finally reduce Europe's dependence on phosphorus import.

21.6 REFERENCES

Abdulai, M., Kuokkanen, A., Plank, B. Virtanen, E. Zha, G. 2015. Circular Economy of Phosphorus Flow. HENVI Workshop 2015: Circular Economy and Sustainable Food Systems

Cordell, D., Drangert, J.-O., White, S. 2009. The story of phosphorus: Global food security and food for thought. *Global Environmental Change* 19 (2009) 292–305

Deloitte 2015. Study on Data for a Raw Material System Analysis: Roadmap and Test of the Fully Operational MSA for Raw Materials Final Report. Available: <https://ec.europa.eu/jrc/en/scientific-tool/msa>

European Commission 2017. Study on the review of the list of Critical Raw Materials. Critical Raw Materials Factsheets. European Commission (EC), Brussels, Belgium

European Commission 2018. COMMISSION STAFF WORKING DOCUMENT. Report on Critical Raw Materials and the Circular Economy. European Commission (EC), Brussels, Belgium (http://ec.europa.eu/enterprise/policies/raw-materials/documents/index_en.htm).

Potočník, J. 2016. Phosphorus: global resources perspective. Presentation ESPP conference Phosphorus stewardship in industrial applications 01-12-2016. <https://www.phosphorusplatform.eu/links-and-resources/downloads>

Schipper, W. 2016. Phosphorus in industry and society Presentations ESPP conference Phosphorus stewardship in industrial applications 01-12-2016. <https://www.phosphorusplatform.eu/links-and-resources/downloads>

Schoumans, O. F., Al Bouraoui, F., Kabbe, C., Oenema, O., van Dijk, K. C. Phosphorus management in Europe in a changing world. *AMBIO* 2015, 44(Suppl. 2):S180–S192

Schröder, J.J., Cordell, D., Smit, A.L., Rosemarin, A., 2010. Sustainable Use of Phosphorus (European Union Tender Project ENV.B.1/ETU/2009/0025). Plant Research International, Wageningen University and Research Centre, Wageningen, The Netherlands, p. 122.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

van Dijk, K.C., Lesschen, J.P., Oenema, O. 2016. Phosphorus flows and balances of the European Union Member States. *Science of the Total Environment* 542 (2016) 1078–1093

Withers, P. J. A., van Dijk, K. C., Neset, T-S. S., Nesme, Thomas, Oenema, O., Rubæk, G.H., Schoumans, O. F., Smit, B, Pellerin, S. Stewardship to tackle global phosphorus inefficiency: The case of Europe. *AMBIO* 2015, 44(Suppl. 2):S193–S206

22 RARE EARTH ELEMENTS

23 CERIUM

23.1 INTRODUCTION

Cerium is the second element of lanthanide series. It is a soft, ductile and silvery-white metal (luster and hardness similar to that of silver) that tarnishes when exposed to air. Its melting point is at 795 °C. Cerium often shows the +3 oxidation state as a rare earth element while it also exceptionally has a stable +4 state that does not oxidize water. Cerium is the 26th most abundant element, with up to 66 ppm of the Earth's crust, while it has no biological role and toxicity [1].

Cerium, as a rare earth element, has been classified as critical raw metals by the EU Commission taking into account its; chemical properties, geological availability, and supply demands. Cerium is produced under strong monopoly conditions (as China produces the 90% of the global REE amount), while they present a high supply risk [2].

Metallic cerium is the major component for the production of the mischmetal alloy, which usually contains: about 50% of cerium, 25% of cerium, 18% of neodymium, 5% of praseodymium and 2% other rare earths. Mischmetal alloy is added in small quantities to other metal alloys such as magnesium, aluminum and nickel as it significantly increase their strength at high temperature, hardness and oxidation resistance. Mischmetal-iron (70-30 % w/w) alloy is also used for the construction of cigarette lighters [3].

Cerium oxide has a wide range of applications. A complex mixture of cerium oxide and other rare earths is used a catalyst for cracking petroleum, waterproofing agent and fungicide in textile manufacturing. CeO₂ is an

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

excellent polish material for optical glasses. It is added as a component in specific type of glasses because it decreases the rate of discoloration in glass, primarily by preventing divalent iron from forming, i.e. oxidizes Fe(II) to Fe(III). Cerium dioxide consists of a crucial material for TV tubes, where electron radiation could cause glass discoloring that downgrades TV picture. It is also used to photochromic glasses, ceramic coatings, refractory oxides, phosphorus, cathodes, capacitors and semiconductors. Cerium dioxide is used as diluent in uranium, plutonium or thorium oxide nuclear fuels due to its low nuclear cross section. Cerium oxide under Ce_2O_3 form is a catalytic converter for the oxidation of CO and NO_x emissions in the exhaust gases from motor vehicles. Cerium(IV) sulfate is used as an oxidising agent in quantitative analysis [4,5].

23.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

21.2.1 PRODUCTION

23.2.1.1 FROM MONAZITE TO CERIUM OXIDE

Monazite $(Ce, La, Y, Th)PO_4$ and bastnäsité $(La, Ce)FCO_3$ are the two major mineral sources of cerium. It is also contained as trace element in a number of ores such as bauxite, laterite and zinc sulfides. Monazite deposits are mainly exist in India, Malaysia, Australia, Brazil, China, South Africa, Sri Lanka, Thailand, and the United States, while bastnäsité deposits, which constitutes the larger portion of world's rare earth resources, occurs mainly in China and Australia. Monazite is frequently found in association with heavy minerals like ilmenite, rutile, zircon which should be removed prior to the main metallurgical route. Secondary non commercial minerals of cerium are loparite, parasite and allanite. The main La sources, monazite and bastnäsité are mined in open pits and in situ mining [6].

Figure 1 presents the flowsheet of the metallurgical processing of monazite from Moemeik Myitsone deposit. The ore contains about 13% w/w cerium oxide along with other notable metals such as Ce, Sm, Pr and Nd. The first step include the digestion of the ore with with caustic soda for 3 h at 140 °C. In hydrochloric acid dissolution, 1.5 kg acid per kg. Subsequently, solid product is leached with dense hydrochloric acid. The precipitation is carried out three times using ammonium hydroxide. After 3rd precipitation, 96.0% cerium oxide is obtained. Alternatively, synergistic separation of cerium and neodymium derived from using organophosphorus reagents namely trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TRPO) in kerosene [6].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

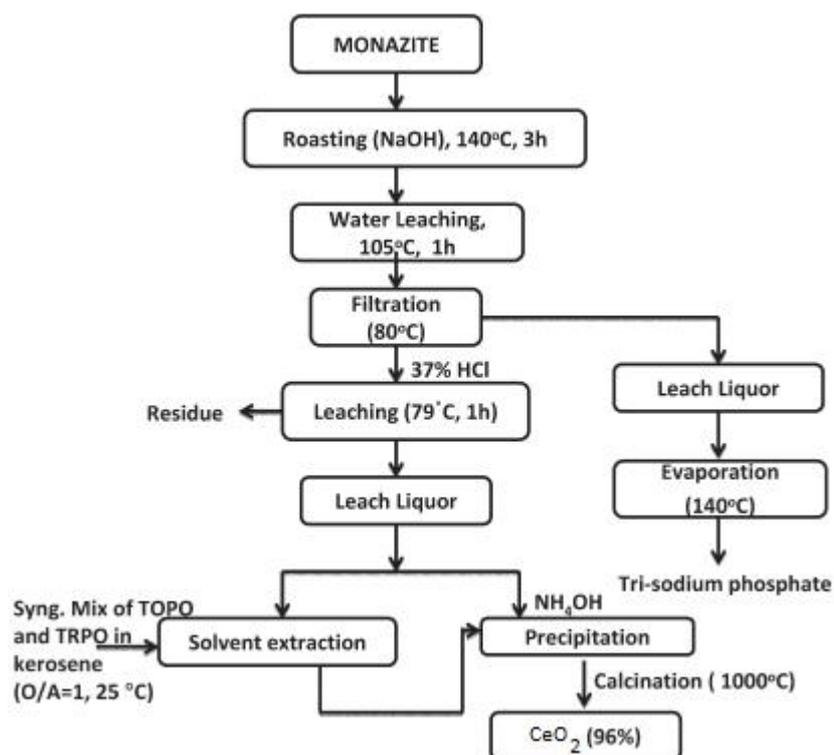


Figure 1. Flowsheet of cerium oxide production from monazite [6].

Concerning the environmental impact that created during Ce production and Ce-rich materials processing, recent studies have shown that a major source of CeO₂ nanoparticles from industrial processing plants (e.g., electronics and optics manufactures) is likely to be deposited in landfills and soils [7]. It has been proved that aquatic and terrestrial organisms have been exposed to CeO₂ NPs, potentially yielding in negative impact on human and ecosystem health. Figure 2 presents the environmental fate and the main sources of cerium exposure. Cerium oxide particles are found in a wide range of industrial wastes related with glass, pharmaceuticals, alloys processing and chemical industries. A specific mention should be done concerning cerium exposure by internal combustion engines. Cerium is added in diesel fuel as it drastically decrease emissions in automobile exhaust, up to 90%. Some Ce escaping in the emissions could accumulate in soils. Exhaust particulate matter exists as very fine particles, normally < 1 μm, leading to extremely diffuse pollution through air exposure. Cerium is also introduced to landfills as solid wastes of electronics, soils via recycling of sewage sludge, and the aquatic environment via wastewater discharge from ceramic manufacturing plants [7].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

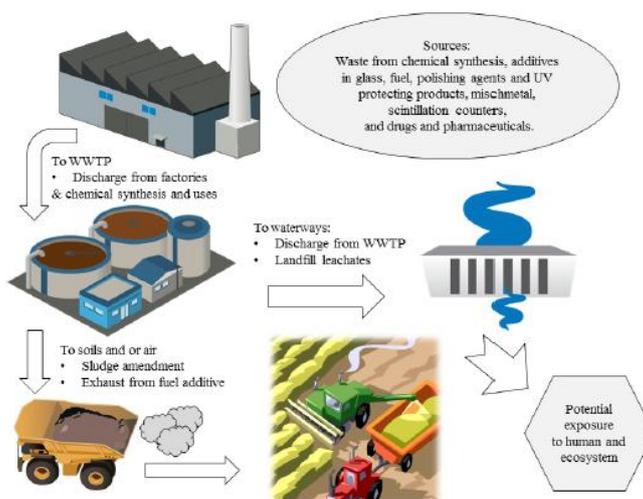
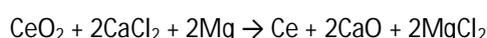


Figure 2. Environmental fate and main sources of cerium oxide nanoparticles exposure to the environment [7].

23.2.1.2 CERIM OXIDE FOR THE PRODUCTION OF VARIOUS ALLOYS

Mischmetal is an alloy of rare earth elements in various occurring proportions. Monazite-derived Mischmetal typically is about 48% cerium, 25% ceriumnum, 17% neodymium, and 5% praseodymium, while bastnasite derived Mischmetall is higher in ceriumnum and lower in neodymium. Mischmetal is the lowest priced rare earth metal because it is produced directly from REE oxides without their separation. Cerium oxide in a mixture with other rare earth oxides is dissolved in an electrolyte consisting of alkali fluorides (to improve conductivity), alkaline earth fluorides (to reduce melting point), and rare earth fluorides (to improve the solubility of rare earth oxides) and reduced electrolytically to the rare earth metals. The electrolytic cell consists of a graphite crucible with graphite anode and molybdenum cathode, working under an inert gas atmosphere to prevent oxidation. Electrolyte and electrodeposited rare earth metals are kept liquid by the joule heat. An electrolytic cell produces about 500 kg of REE metal alloy per day [8,9].

Metallothermic reduction of cerium oxide, aiming to the production of mischmetal alloys, is carried out by using metallic calcium as a reducing agent into a cerium oxide- F_3 melt (calciothermic process). Metallothermic process offers a high recovery yield (reach 90%), however, on the other hand, it presents a number of disadvantages in comparison to electrolysis process such as a high energy consumption that is requires for the maintenance of non-oxidizing environment. Metallothermic reduction is mainly used for the production of aluminium-cerium alloys (Al-4% w/w Ce) for automotive and aerospace industries. Metallic cerium is has been also produced by injecting CeO_2 powder into an Al-Mg alloy and by metallothermic reduction using alkaline earth metal ("Ames process") [9]. The following reaction describes the metallothermic reduction with magnesium in the presence of $CaCl_2$ as flux:



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

21.2.2 USAGE

In general, mischmetal is soft and brittle. However, because rare earths readily oxidize and absorb hydrogen and nitrogen, it is extremely difficult to produce a sufficiently pure sample of mischmetal with excellent mechanical and electrical properties. However, it has been proved that it significantly improves the castability and the mechanical properties in certain alloys. Mischmetal is not traded as a commodity on major exchanges, but is consumed through multiple channels of industry. Mischmetal is directly used (self-contained or as an additive) as an oxygen getter in vacuum tube manufacturing, for production of NiMH batteries, as a spark source to start fires and flames, as well as in movie special effects. Mischmetal alloy is added in small quantities in nodular pig iron, stainless and tool steel and specific vacuum/heat resistant alloys. It is also additive for Ferro Silicon Magnesium (FeSiMg or MgFeSi) and Zinc-Aluminium alloy named Zinc-5 % Aluminum-Mischmetal (Zn-5Al-MM), having a 95% Zn - 5% Al and traces of mischmetal (cerium, ceriumnum). Finally it is used as a steel coating which to enhance the product life for certain applications [10,11].

21.2.3 END OF LIFE

The recovery of Ce from mischmetal alloys contained in NiMH batteries (Ce content about 2% w/w) has been performed at laboratory scale. Negative electrode powder (in which Ce is contained) is treated by a leaching step with HCl. Ce with other REEs is received from the leachate through solvent extraction with ammonium and phosphonium ionic liquids. Additionally, a pyrometallurgical method has been developed which involves the reductive smelting of negative electrode scrap. The metal phase rich in nickel and other minor metallic compounds is obtained, while Ce and other REEs concentrate in the slag phase as oxides. The concentration of Ce in the slag is enriched using molten salt processes. It should be noted that despite the progress in NiMH batteries recycling, a completed route that leads to recovery of metallic Ce has not so far be developed [12].

In addition to mischmetal alloys, the recovery of Ce has been attempted in a number of other industrial wastes.

Recycling of vehicle converters consists of a promising secondary cerium resource. CeO₂ is contained as a ceramic material in converters substrate both with platinum metals such as palladium (Figure 2). Recently, has been developed a novel hydrometallurgical process for the simultaneous recovery of cerium and platinum metals (Figure 3). The process is based on the leaching of the substrate with hydrochloric acid while H₂O₂ is added as oxidant. During dissolution soluble chlorocomplexes are formed as following [13]:



Soluble cerium chloro-complexes therefore can be found in the pregnant solution after the filtration step Ce can be obtained through solvent extraction or precipitation techniques.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

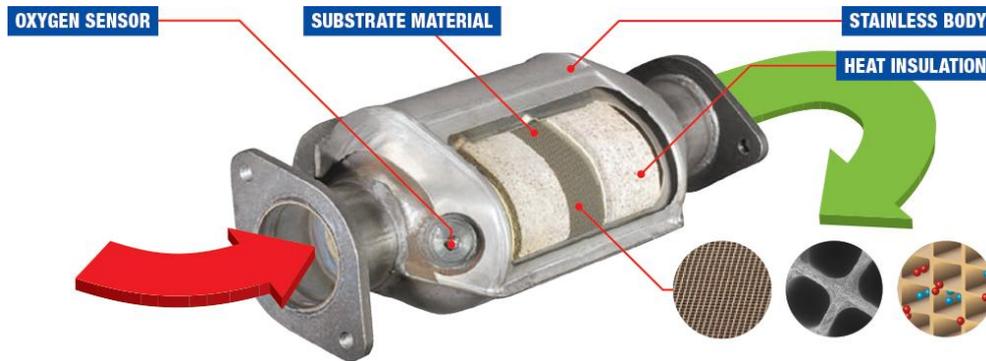


Figure 2. A typical vehicle converter [<http://www.autobend.co.nz/exhaust-products/emissions-control.html>].

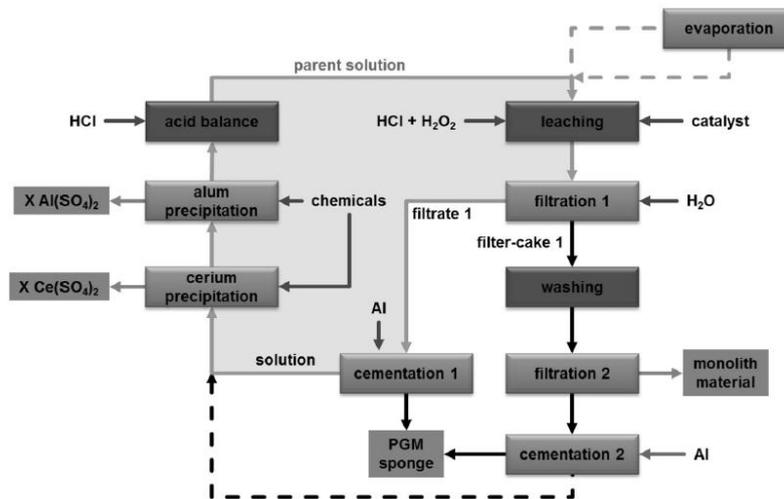


Figure 3. Recycling process of vehicle converters.

The recovery of cerium from e-wastes has been studied also. Two waste residues have been proposed as potential source of REEs (cerium, europium, terbium, yttrium, gadolinium) and cerium: spent lamp phosphors and cathode ray tube (CRT) phosphors. The cerium content in this kind of scraps is ranged between 0.7 and 2% w/w. Cerium (and REEs) recovery from the e-waste residues has been performed through a combination of different hydrometallurgical techniques. More specifically:

REEs recovery from the lamp phosphor waste is performed by leaching with H_2SO_4 followed by precipitation with oxalic acid. The received product is a mixed REE oxalate which can be further treated by calcination to obtain a mixed REE oxide. The recovery of REEs from CRT phosphors is also performed by acid leaching and precipitation with oxalic acid, however, in this case a thermal pre-treatment will here be considered to oxidise the ZnS contained in the CRT powder [12].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

21.2.4 RESIDUE TREATMENT

The recovery of cerium by automotive industry scrap (NiMH batteries, vehicle catalytic converters) involves in all cases a hydrometallurgical treatment. Therefore, significant quantities of acidic liquid wastes are produced. The environmental impact of the recycling processes has not so far been quantified.

23.3 SUMMARY

Cerium is a relatively common rare earth element which is used in a wide range of applications in elemental or oxide form. It is extracted, along with other REEs, mainly from monazite and bastnäsite. The general metallurgical route for the cerium oxide production comprises the acidic leaching followed by selective precipitation or solvent extraction. Cerium oxide price is expected to be stabilized below 3500 \$ per ton between 2020-2015 [13]. However, this balance may be perturbed due to the high dependence by China which it's the major REEs and cerium producer [14]. A potential of minimizing the supply risk by recovery of cerium from secondary resources instead of importing from China have been described by USGS [15]. NiMH batteries and vehicle catalytic converters are the most promising secondary resources of cerium. Extraction tests have been attempted at laboratory scale showing that the sustainability of the techniques is possible as other precious metals can be simultaneously recovered. Life cycle analysis focused on the environmental impact of Ce extraction from primary and secondary sources should be performed improving the benefit of cerium recovery by specific scraps (NiMH batteries and vehicle catalytic converters) of automotive industry.

23.4 REFERENCES

- [1] Lide, D. R., ed. (2005). CRC Handbook of Chemistry and Physics (86th ed.). Boca Raton (FL): CRC Press.
- [2] European Commission, 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials.
- [3] Klaus Reinhardt and Herwig Winkler in "Cerium Mischmetal, Cerium Alloys, and Cerium Compounds" in Ullmann's Encyclopedia of Industrial Chemistry 2000, Wiley-VCH, Weinheim
- [4] <http://nautilus.fis.uc.pt/st2.5/scenes-e/elem/e05830.html>
- [5] Arenas, L.F.; Ponce de León, C.; Walsh, F.C. (2016). "Electrochemical redox processes involving soluble cerium species". *Electrochimica Acta*. 205: 226–247
- [6] S. S. Abhilash, P. Meshram. B. D. Pandey, 2016. Metallurgical process for the recovery and recycling of cerium from various resources-A review, Hydrometallurgy 16, pp. 47-59.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [7] J. T. Dahle, Y. Arai, 2015. Environmental geochemistry of cerium: applications and toxicology of cerium oxide nanoparticles, *International Journal of Environmental Research and Public Health*, 12, pp. 1253-1278.
- [8] F. Habashi, 2013, Extractive metallurgy of rare earths, *Canadian Metallurgical Quarterly*, 52(3), pp. 2224-233.
- [9] S. Nuryadi, 2015. Preparation of metallic cerium by metallothermic reduction using cerium oxide as a raw material, *Indonesian Mining Journal*, 18 (2), pp. 82 – 91.
- [10] <https://www.thebalance.com/what-is-mischmetal-2340178>
- [11] <http://mbrmetals.com/products/mischmetal.html>
- [12] L. Yurramend, F. Forte, C. Del-Rio, R. Lagioia, T. Muller, S. Sgarioto, K. Binnemans, 2017. Recovery of rare earths from e-waste residues for production of high-performance REE-Mg alloys, *ERES2017: 2nd European Rare Earth Resources Conference*, Santorini, Greece.
- [13] S. Steinlechner, J. Antrekowitsch, 2015. Potential of a hydrometallurgical recycling process for catalysts to cover the demand for critical metals, like PGMs and cerium, *The Journal of The Minerals, Metals & Materials Society*, 67 (2), pp. 406-411.
- [13] <https://www.statista.com/statistics/450146/global-reo-cerium-oxide-price-forecast/>
- [14] <https://www.statista.com/statistics/268011/top-countries-in-rare-earth-mine-production/>
- [15] D.I. Bliewas, 2013. Potential for recovery of cerium contained in automotive catalytic converters (Reston, VA: U.S. Geological Survey)

24 ERBIUM

24.1 INTRODUCTION

Erbium (Er), with atomic number 68, is a trivalent member of lanthanides. Elemental pure erbium is malleable (or easily shaped), soft yet stable in air, and does not oxidize as quickly as some other rare-earth metals. Its salts are rose-coloured, and the element has characteristic sharp absorption spectra bands in visible light, ultraviolet, and near infrared [1].

Like other rare earths, Er is never found as a free element in nature. The principal commercial sources of erbium are the minerals species xenotime and euxenite, and most recently, the ion adsorption clays of southern China where vast deposits exist. China is the leader global supplier of this element [2].

Erbium is a critical raw material due to its unique properties and the lack of alternative materials for its applications in modern technologies. According to European Commission forecasts concerning the market

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

situation of Heavy Rare Earths metals, among them Er, the average growth demand to 2020 will be highly increased (8% per year) while the supply will appear small deficit. [3]

Erbium is used for glass colouring, as an amplifier in fibre optics, and in lasers for medical and dental purposes. The erbium (+3) ion has a very narrow absorption band colouring erbium salts pink. It is therefore used in eyewear and decorative glassware. It can neutralize discolouring impurities such as ferric ions and produce a neutral grey shade. Furthermore, it is particularly useful as an amplifier for fibre optic data transfer [4]. Lasers based on erbium-doped yttrium aluminium garnet laser, erbium YAG laser ($\text{Er:Y}_3\text{Al}_5\text{O}_{12}$) are ideally suited for surgical applications because of its ability to deliver energy without thermal build-up in tissue [5]. In addition, Er is added in vanadium alloys lowering the hardness and improving the workability [6].

24.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

23.2.1 PRODUCTION

24.2.1.1 23.1.1 FROM MINERAL ORE TO ERBIUM OXIDE

Erbium is extracted from monazite, bastnasite, xenotime and euxenite ores. Crushed minerals are leached by hydrochloric or sulfuric acid transforming insoluble rare-earth oxides into soluble chlorides or sulphates. The acidic filtrates are partially neutralized with caustic soda (sodium hydroxide) to pH 3–4. Thorium, which is a radionuclide, precipitates out of solution as hydroxide and is removed. Subsequently, the solution is treated with ammonium oxalate to convert rare earths into their insoluble oxalates. The oxalates are converted to oxides by annealing. The oxides are dissolved in nitric acid that excludes one of the main components, cerium, whose oxide is insoluble in HNO_3 . The solution is treated with magnesium nitrate to produce a crystallized mixture of double salts of rare-earth metals. The salts are separated by ion exchange. Following this process, rare-earth ions are sorbed onto suitable ion-exchange resin by exchange with hydrogen, ammonium or cupric ions present in the resin. Suitable complexing agent then selectively washes out the rare earth ions [7].

The environmental impact generated by the processing of erbium-rich ores is mainly related with the radioactivity of these ores. Especially, it has been found that monazite presents the higher radionuclide concentrations. It is expected that the cost and space to dispose of the radioactive waste products originated by monazite ore will rise and remain a problem to be tackled as this can result in limiting of the use of this mineral. High radionuclide concentrations have been reported also to other erbium rich ores such as in bastnasite from California and ion adsorption clays from Southern China [8].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

24.2.1.2 ERBIUM OXIDE IN ER-DOPED FIBRE

Erbium oxide, also called erbia, is an important colourant in glasses and porcelain enamel glazes. High purity erbium oxide is widely applied as dopant in making optical fibre and amplifier. It is particularly effective as an amplifier in fibre optic data transfers. Erbium oxide has a pink colour, and is sometimes used as a colorant for glass, cubic zirconia and porcelain. These glasses are widely used in sunglasses and cheap jewellery. Erbium-doped fibre has become the main component of almost all optical amplifiers including repeaters, power amplifiers, preamplifiers, and distributed amplifiers [9]. MCVD (modified chemical vapour deposition), VAD (vapour axial deposition), and OVPO (outside vapour-phase oxidation) are among the main techniques for the fabrication of silica optical fibres. The VAD method is below described. According to the vapour axial deposition, the porous material is processed in the rare earth chloride vapour. The rare earth chloride is adsorbed on the surface of the glass particles composing the porous material. The porous preform processed by adsorption is placed in high-temperature surroundings and the rare earth chloride is oxidized. At this point, the doping concentration can be controlled by the concentration of the rare earth chloride vapour in time of the adsorption, the time duration and the density of the porous preform. In order to increase the preform density, the maximum of rare earth doping concentration must be reduced. A vertical electric furnace composed by a SIC heater, a silica glass tube, and a uniform heating zone is used. Water-free pure ErCl_3 (99.9-percent purity) is used as the Er source material. The porous preform is aligned to the uniform zone of the vertical furnace and He gas is pumped into the reaction chamber as the ambient material. The adsorption process, under the pressure of ErCl_3 , is carried out for 2 hr. After the adsorption, the porous core material again is heated up to 1500°C in the vertical furnace to make it a transparent glass [10].

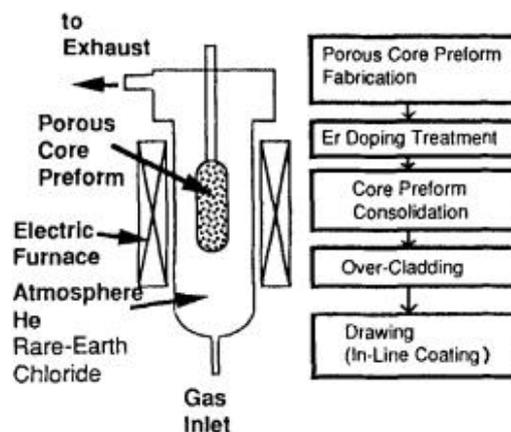


Figure 1: Fabrication process for rare-earth doped silica fibres [10].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

23.2.2 USAGE

High silica based optical fibres are established as the most efficient interconnection media for optical telecommunication networks. The fibres are used to guide optical signals over long distances. The doping of silica optical fibres with rare-earth element ions generates an optical activation due to characteristic emission of the REEs when pumped at suitable wavelengths. REEs doped fibres have shown great potential for use as active devices for photonic applications like optical amplifiers and fibre lasers at various wavelengths. In Erbium Doped Fibre Amplifier (EDFA) the core of a silica fibre is doped with trivalent erbium ions and can be efficiently pumped with a laser at a wavelength of 980 nm or 1,480 nm, and exhibits gain in the 1,550 nm region. This high-powered light beam excites the erbium ions to their higher-energy state. The broad gain-bandwidth of fibre amplifiers make them particularly useful in wavelength-division multiplexed communications systems as a single amplifier can be utilized to amplify all signals being carried on a fibre and whose wavelengths fall within the gain window [11,12].

23.2.3 END OF LIFE

Bibliographic data don't mention a process for the recovery of erbium from secondary resources (electronic wastes), however it is possible that recycling is taking place at a limited scale by some companies. A preliminary study for the identification of erbium content in electronic devices should be performed. The results will prove whether the extraction of erbium from scrap deserved to be realized.

23.2.4 RESIDUE TREATMENT

There are no data concerning the residues that generated by the extraction of Er from secondary resources.

24.3 SUMMARY

Erbium is a rare earth elements which is produced in relative small amounts (500 tonnes annually) and has a limited number of applications. China is the major producer of the metal, therefore its relative supply risk is high. The price of Er is estimated at about 150 \$ per kg while it is expected that its price will present a slight decreasing until 2025 [13]. Erbium is produced mainly by euxenite and xenotime ores via a process which comprises acid leaching, selective precipitation and ion exchange for its separation from the other REEs. The recovery of Er from electronic wastes is not mentioned in the bibliography. Erbium is mainly used for the construction of laser diodes working at the near at 1550 nm wavelength.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

24.4 REFERENCES

- [1] E. John, 2001. *Nature's Building Blocks: An A-Z Guide to the Elements*, Oxford, England: Oxford University Press.
- [2] F.H. Spedding, J.E. Powell, 1954. A practical separation of yttrium group rare earths from gadolinite by ion-exchange.
- [3] E. Commission, 2014. Report on critical raw materials for the EU: Report of the Ad hoc Working Group on defining critical raw materials.
- [4] P. Becker, A. Olsson, J. Simpson, 1999. *Erbium-Doped Fibre Amplifiers, Fundamentals and Technology*.
- [5] G. Teikemeier, D.J. Goldberg DJ, 1997. Skin resurfacing with the erbium: YAG laser. *Dermatologic Surgery*, 23, pp. 685-687.
- [6] C. R. Hammond, 2000. The Elements, in *Handbook of Chemistry and Physics 81st edition*, CRC press.
- [7] P. Patnaik, 2002. *Handbook of Inorganic*, McGraw-Hill.
- [8] C. K. Gupta, N. Krishnamurthy, 2005. *Extractive Metallurgy of Rare Earths*, CRC Press.
- [9] B. J. Ainsle, 1991. A review of the Fabrication and Properties of Erbium-Doped Fibres for Optical Amplifiers.
- [10] M. Shimizu, M. Yamada, M. Horiguchi, 1992. Fabrication and Characterisation of Erbium-Doped Silica Single-Mode Fibres, *Electronics and Communications*, pp. 545-551.
- [11] E.J. Graeber, G.H. Conrad, S.F. Duliere, 1966, Crystallographic data for solvated rare earth chlorides, *Acta Crystallographica*, 121, pp. 1012-1013.
- [12] X. Song, M-H. Chang, M. Pecht, 2013. Rare-Earth Elements in Lighting and Optical Applications and Their Recycling, *JOM*, 65, pp. 1276–1282.
- [13] <https://www.statista.com/statistics/450172/global-reo-erbium-oxide-price-forecast/>

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

25 EUROPIUM

25.1 INTRODUCTION

Eu is widely applied in modern technologies. It is a typical member of the lanthanide series and is the most chemically reactive of the rare earth elements. It is a moderately hard, silvery metal, which readily oxidizes in air and water and burns at about 150 to 180 °C. Europium usually exists at the oxidation state +3, however the oxidation state +2 is also common. Natural europium contains two stable isotopes, while 35 other radioactive isotopes and isomers are known [1].

Europium is one of the less abundant rare-earth elements: it is almost as abundant as tin. It is never found in nature under element form, but there are many mineral species containing europium. The most important sources are bastnäsite, monazite, xenotime and loparite-(Ce). Main mining areas are China and USA. Reserves of europium are estimated to be around 150.000 tonnes and world production of the pure metal is around 100 tonnes per year [2].

It is recognized that demand for europium is partly driven by the adoption of high efficiency fluorescent lighting technologies including compact fluorescent bulbs and T5 long tube lamps [3]. Europium oxide is widely used as a phosphor activator and europium-activated yttrium vanadate is commercially used as the red phosphor in colour TV tubes. Europium-doped plastics are used as a laser material. With the development of ion-exchange techniques the cost of the metal has been greatly reduced in recent years [4]. The use of Europium, for anti-counterfeiting has a great potential. The Euro banknotes that came out in 2002 relied on the emission from Eu^{2+} and Eu^{3+} under UV excitation [5]. Europium isotopes are good neutron absorbers and are being studied for their future application in nuclear control applications. Europium is one of the rarest and most costly of the rare-earth metals. It is priced at about \$50/g (99.9% pure) [4].

25.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

24.2.1 PRODUCTION

24.2.1.1 FROM MINERAL ORE TO EUROPIUM OXIDE

Bastnäsite ore is typically used to produce rare-earth metals. The following steps are describing the rare-earth-metal extraction process from the ore:

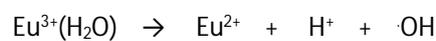
After extraction, bastnäsite ore is typically contains an average of 7% REO (rare-earth oxides), the ore goes through comminution using rod mills, ball mills, or autogenous mills. Steam is consistently used to remove the ground ore, along with soda ash fluosilicate. This is done to coat the various types of rare earth metals with either

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

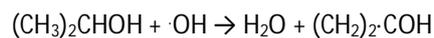
flocculent collectors or modifiers for easier separation in the next step. Subsequently, separation of the gangue from the rare-earth metals is becoming with flotation process using the previous chemicals.

The next stage comprises the dissolution of the concentrate using HCl solution that reduces the pH to < 5. This enables europium to become soluble. Subsequently, oxidizing roasting further concentrates the solution to approximately 85% REO. This is done at ~100 °C or higher if necessary.

Samarium, europium, and ytterbium can be easily separated from the trivalent rare earths mixture after reducing them to a divalent state. The first application of selective reduction for the separation of a rare earth was by Yntema on 1930 using a mercury cathode he electrolytically reduced Eu(III) to Eu(II). Lithium amalgam electrodes were used for separation of Sm from Eu, and Yb by selective reduction. Recently, europium can be separated from other rare earths by a photochemical reduction to the divalent stage followed by precipitation of the divalent europium as sulphate or chloride (Figure 1).



The OH radical is scavenged by isopropanol as:



While, Eu is received as EuSO_4 precipitate that is formed homogeneously during the photolysis [8].

Eu_2O_3 oxide is finally received after dissolution of europium sulphate with hydrochloric acid followed by precipitation (Figure 1).

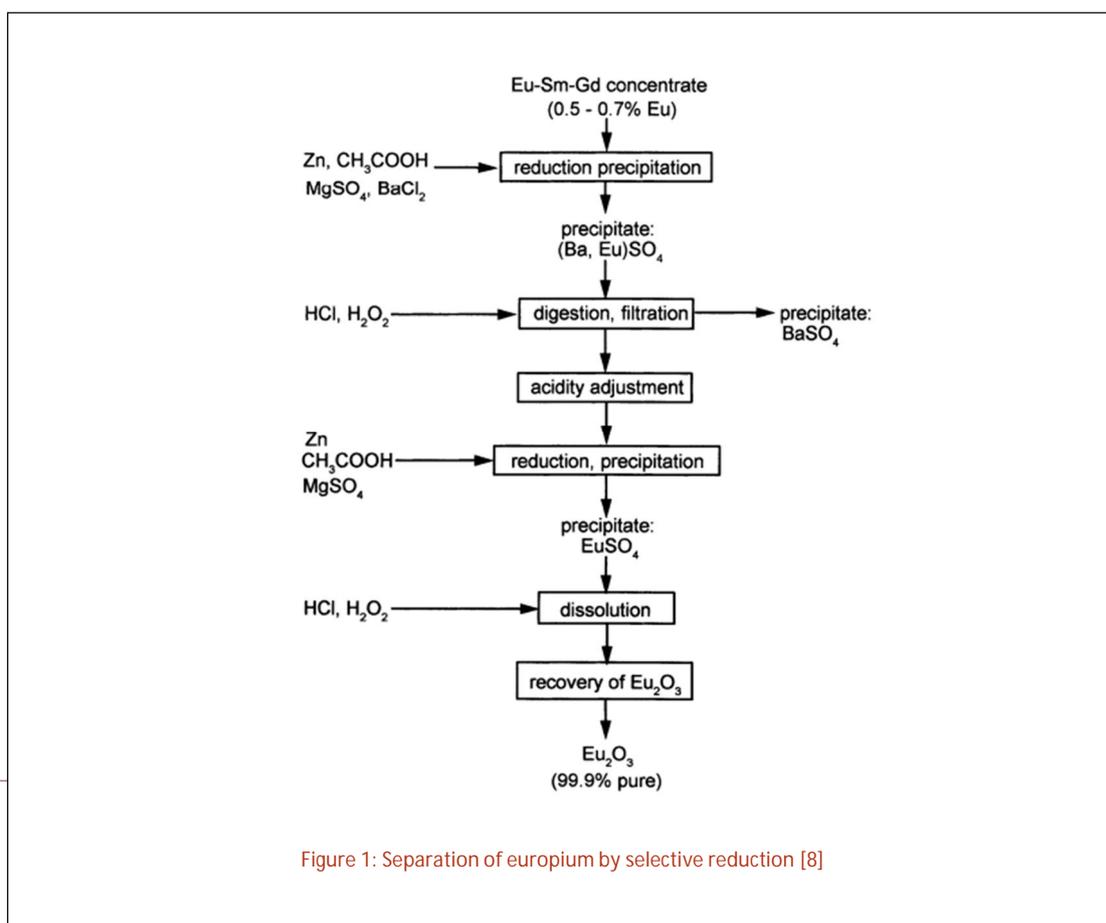


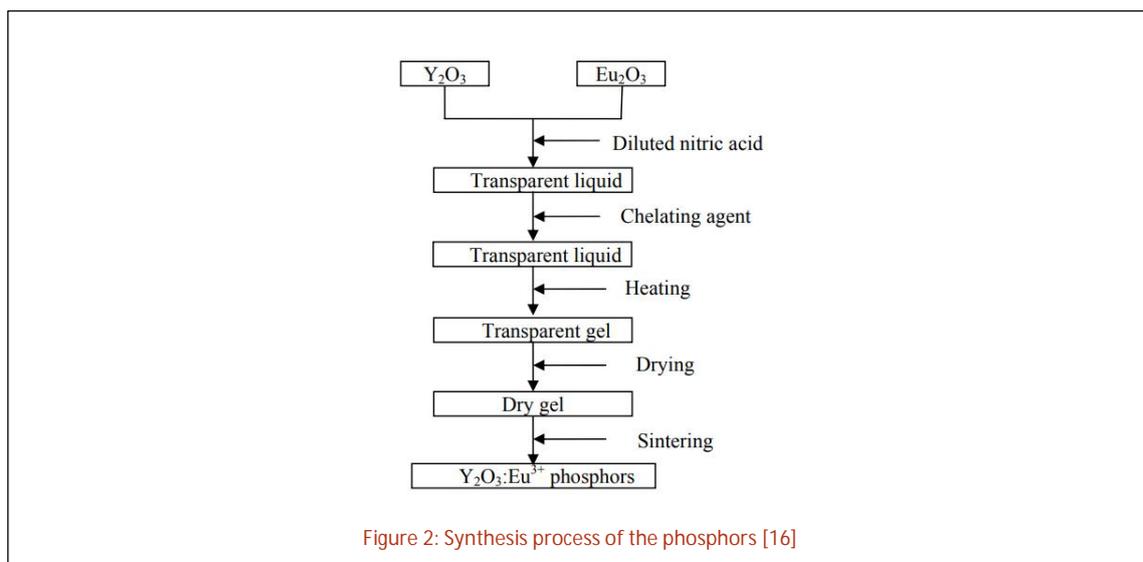
Figure 1: Separation of europium by selective reduction [8]

25.2.1.2 EUROPIUM OXIDE TO $Y_2O_3:Eu^{3+}$ PHOSPHORS

The red phosphor $Y_2O_3:Eu^{3+}$ has been studied and widely applied in fluorescent lamps because of its high quantum efficiency. Especially, it can be effectively excited by 254 nm radiation displaying a stronger emission to those of mercury vapour. While in many applications, such as fluorescent lamps (FL), cathode ray tubes (CRT), plasma display panels (PDP), particle size of the phosphor is in the range of several micrometres, nanoscaled $Y_2O_3:Eu^{3+}$ has been indicated to be one of the most promising red phosphors for field emission displays (FED). $Y_2O_3:Eu^{3+}$ has been prepared by various methods. Vu et al. [9] used combustion reaction to synthesize the phosphor with the particle size estimated in the range of 10 to 20 nm. Nanocrystalline cubic $Y_2O_3:Eu^{3+}$ with an average particle size of only 10 nm was fabricated using chemical vapour technique by Konrad et al. [10]. A laser-heated gas condensation technique has been employed to prepare nanocrystalline $Y_2O_3:Eu^{3+}$ with monoclinic crystal structure [11], while prepared similar material, with average size between of 0.5 and 2 μm , has been synthesized by sol-gel method employing citric acid as a chelating agent [12]). Several researchers have investigated the luminescent properties of bulk and nanocrystalline cubic yttrium oxide prepared by chemical vapour synthesis [[10], [13]], combustion synthesis [[11], [14]], and fast thermal decomposition of metal nitrate solution [[12], [15]].

In the Figure 2, the nanophosphors synthesis by sol-gel process is presented. Citric acid and tartaric acid are employed as chelating agents in making sol.

The initial rare earth oxides Y_2O_3 and Eu_2O_3 are dissolved in a definite amount of diluted nitric acid and stirred to obtain a transparent liquid. Next, chelating agent was fed on. The solution is stirred for 12 hours and after heated at 80°C and a transparent sol was formed. During the heating process, the condensation reaction between –COOH groups occurred and led to the formation of water. Further heating causes the combustion of the gel and the powder with a brownish colour is obtained, which is called dry gel. The dry gel is then sintered at different temperatures to obtain the phosphors [16].



programme under grant agreement No 730227

24.2.2 USAGE

Oxide phosphors have recently gained much attention for applications such as screens in plasma display panels and field emission displays and for white colour light emitting diodes because of their higher chemical stability in comparison to the conventional sulphide phosphors. Over the last decade, many oxide based phosphors were synthesized to improve luminescent performance, including colour purity, emission intensity and quantum efficiency. Many efforts have been made to discover host materials as well as activators with high performance for phosphor applications. [17]

24.2.3 END OF LIFE

An innovative process for the recovery of Eu from secondary sources, such as fluorescent lamps, has been developed (Figure 3). Waste phosphor powder from recycled lamps is retorted, sieved, and leached to produce a europium/yttrium leach solution. The separation of europium and yttrium from the pregnant leach solution is conducted by selectively reducing Eu(III) to Eu(II) via zinc powder and precipitating europium (II) sulphate from solution using sulfuric acid as the precipitating agent. After selective reduction and precipitation, the purity and recovery of europium (II) sulphate was greater than 95% and 80%, respectively [18].

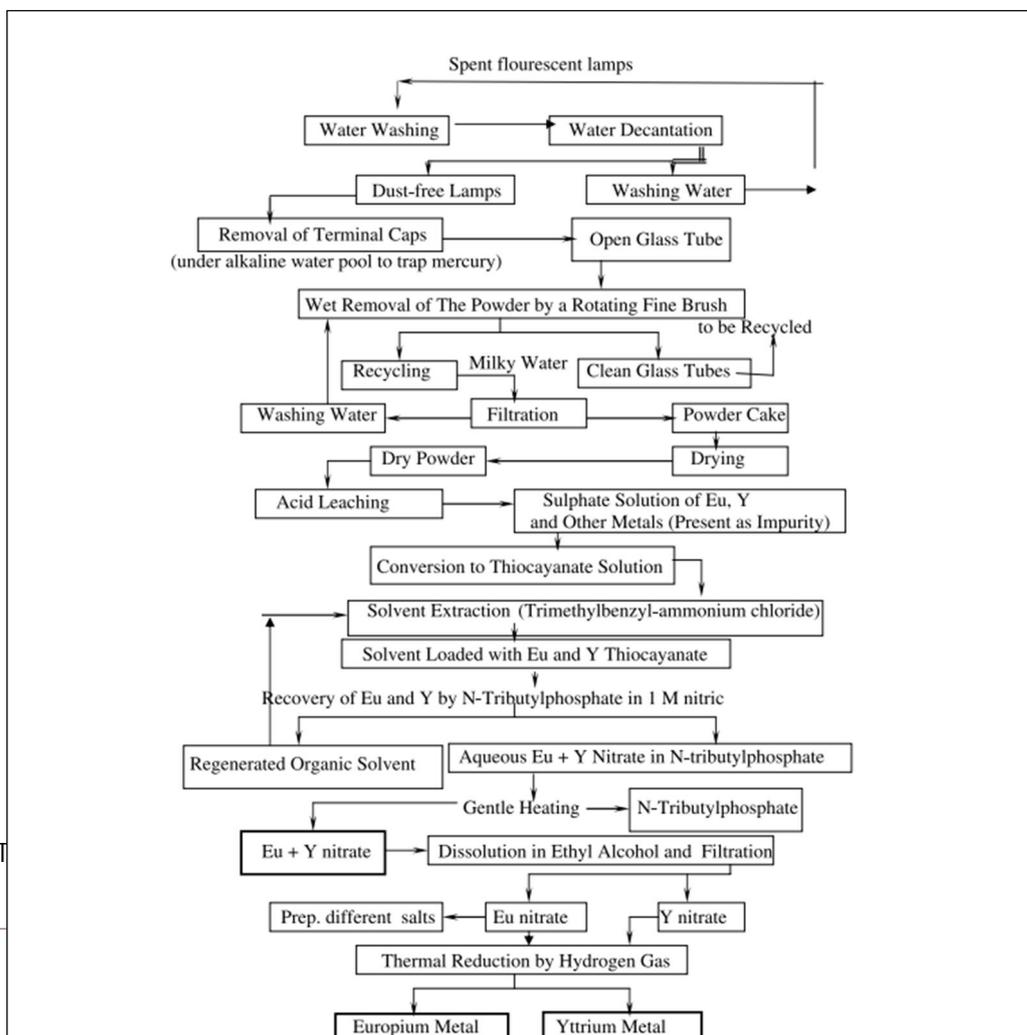


Figure 3: A conceptual flow sheet for the recovery of europium, yttrium metals and some salts from spent fluorescent lamps. [22]

According to 2007 data, about 8000 tons of phosphor dust are annually discarded into landfills. Based a conservation calculation of concentration of 0.3% europium in the discarded dust, there is a potential to recover 240 tons per year. However, the concentration of europium in the dust will increase due to fewer halophosphate based T12 lamps being recycled and a greater ratio of newer T8 lamps being recycled [19].

24.2.4 RESIDUE TREATMENT

There are no available data concerning the environmental impact that is created by the recovery of Eu by secondary sources so far. This issue consist a crucial research subject as the recycling process, as it was previously described, is complex involving the use of several chemical reagents.

25.3 SUMMARY

Europium is a rare earth metal which oxidizes readily in presence of air and water. It is generally present in oxide form and has applications in automobiles, catalysts, consumer electronics, flat panel displays, metallurgy and fluorescent lamps and as a dopant of glass in lasers and optoelectronic devices. Europium is extracted, among other REEs, from Bastnäs site ore while its separation is performed via photochemical reduction technique. A recycling process for the recovery of Eu from secondary sources, such as fluorescent lamps, has been developed.

Eu doped yttrium vanadate ($YVO_4:Eu^{3+}$) as red phosphor in colour television picture tubes, replacing the previously used Ag activated CdS red phosphor, was one of the first cutting-edge application in which the use of REEs was involved taking place on 1965.

China is the largest producer of europium and its related complex materials, while Asia Pacific region is the largest consumer of the metal. The basic availability of europium oxide is sufficient in short term period and likely adequate in the medium term. An extra Eu demand will be possibility arose by the flat panel displays and LEDs markets in Asia Pacific in near future [20].

25.4 REFERENCES

- [1] N. N. Greenwood et A. Earnshaw, Chemistry of Elements (2nd ed.), Butterworth-Heinemann, 1997.
- [2] P. Maestro, 'Lanthanides' Kirk- Othmer of Chemical Technology. 14. pp. 1096-1120.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

-
- [3] Alexander H. King et Roderick G. Eggert, Critical Materials Institute, USA.
- [4] T. Folger, «The Secret Ingredients of Everything», *National Geographic*. pp. 136-145, June 2011.
- [5] A. J. Meijerink, 'Europium beveiligd de Euro', 2002: *Chemisch 2 Weekblad* 4.
- [6] Long, Keith R., Bradley S. Van Gosen, Nora K. Foley et Daniel Cordier, Scientific Investigations Report 2010-5220. The Principal Rare Earth Elements Deposits of the US-A summary of Domestic deposits and a Global Perspective, 3 Mar. 2014.
- [7] M. Roderick, Knaefield Project-Major Technical Breakthrouh, Greenland Minerals and Energy LTD, Web Mar.2014.
- [8] C.K.Gupta et N.Krishnamurthy, *Extractive metallurgy of Rear Earths*, CRC Press, 2005.
- [9] Vu N., Anh T. K., Yi G. C. et Strek W., *Lumin.*122-123 77, 2007.
- [10] Konrad A., Fries T., Gahn A., Kummer F., Herr U., Tidecks R. et Samwer K., *Appl. Phys.* 86 3129, 1999.
- [11] Eilers H. et Tissue B. M., *Chem. Phys. Lett* 251 74, 1996.
- [12] Zhang J., Zhang Z., Tang Z., Lin Y. et Zheng Z., *J. Mater. Pro. tech.* 121 265, 2002.
- [13] Konrad A., Herr U., Tidecks R., Kummer F. et Samwer K., *J. Appl. Phys.* 90 3516, 2001.
- [14] Fu Z., Zhou S., Pan T. et Zhang S., *J. Lumin.* 124 213, 2007.
- [15] Jia M et al., *Chem. Phys. Lett.* 384 193, 2004.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [16] Bui Van Hao, Pham Thanh Huy, Tran Ngoc Khiem, Nguyen Thi Thanh Ngan et Pham Hong Duong, Synthesis of Y₂O₃:Eu²⁺ micro and nanophosphors by sol-gel process, J. Phys. :Conf. ser 187 012074, 2009.
- [17] Yee- shin Chang, Hui-Jan Lin, Yin-Lai Chai et Yu-Chun Li, Preparation and luminescent properties of europium-activated YInGe₂O₇ phosphors, 2008.
- [18] Mark L. Strauss, Brajendra Mishra et Gerald P. Martins, Selective Reduction and Separation of europium from Mixed Rare Earth Oxides from Waste Fluorescent Lamp Phosphors, 2017.
- [19] P.M. Eduafo et M. Strauss, «Experimental investigation of recycling rare earth metals from waste fluorescent lamp phosphors,» Rare Met. Technol. 253-259, 2015.
- [20] Baolu Zhou, Zhongxue Li et Congcong Chen, «Global Potential of Rare earth Resources and Rare Earth Demand from Clean Technologies,» 2017.

26 GADOLINIUM

26.1 INTRODUCTION

Gadolinium Gd, with atomic number 64, is a silvery-white, malleable, and ductile rare earth metal. It is found in nature only in oxidized form, and even when separated, it usually has impurities of the other rare earth elements [1]. The isotope gadolinium 157 has the highest thermal-neutron capture cross-section among any stable nuclide: about 259,000 barns [2]. Gadolinium is ferromagnetic at temperatures below 20 °C, while it is strongly paramagnetic above this temperature [3]. In contrary to the other rare-earth elements, metallic gadolinium is relatively stable in dry air. Furthermore it is a strong reducing agent [4].

As the majority of rare earth elements, gadolinium is found in the ores monazite and bastnasite, although at minor quantities. The main source of gadolinium is from China's inner Mongolian mines. World production of gadolinium is about 7,500 mt per year. Although China is the main producer country, gadolinium is also found in countries such as the USA, Brazil, India, Australia, Greenland and Tanzania. Global reserves of gadolinium have been estimated at about 1 million tonnes [5-7].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Due to its unique magnetic properties, gadolinium presents a number of specialized applications. It is mainly used for magnetic refrigeration purposes. Magnetic refrigeration is a cooling technology based on the magnetocaloric effect which consists a magneto-thermodynamic phenomenon. The temperature change of magnetic refrigeration susceptible materials caused by the exposure of these materials to a changing magnetic field. It has been found that the effect is extremely stronger in case of gadolinium alloy $Gd_5Si_2Ge_2$ [3]. Optical lenses containing gadolinium are used for magneto-optical and electro-optical systems. In medicine, gadolinium is used in MRIs to provide better imaging of tumours [8]. It is also used in electronic ceramics, glasses, lasers, magnetic recording and crystal scintillators [9]. Gadolinium is used with yttrium to synthesize garnets that have microwave applications. It can also be alloyed with certain metals, such as iron and chromium, to improve their workability and resistance to high temperatures and oxidation. Gadolinium compounds are also used to make phosphors in televisions.

Gadolinium, as a heavy rare earth elements, have been classified as critical raw metals by the EU Commission taking into account their; chemical properties, geological availability, supply demands and cutting edge applications. Gadolinium produced under strong monopoly conditions (as China produces the 90% of the global REE amount), therefore it presents a high supply risk [10].

26.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

25.2.1 PRODUCTION

26.2.1.1 FROM MINERAL ORE TO GD

The ion adsorption type ores in several major deposits of southern Jiangxi and western Fujian provinces are the main resources for the production of gadolinium. These deposits are characterized by low cerium and high neodymium, samarium, europium, gadolinium, and terbium. Additionally, gadolinium is contained in bastansite, xenotime and gadolinite minerals. Gadolinium is extracted through the Goldschmidt high temperature direct chlorination process to directly obtain an anhydrous rare earth trichloride product. The flowsheet of the method can be seen in Figure 1 as it is used in case of bastansite ore [11].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

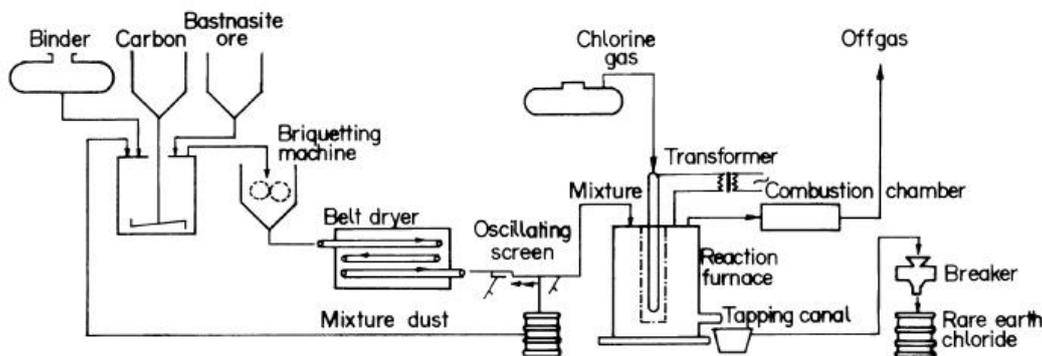


Figure 1. Goldschmidt process for bastnasite or gadolinite chlorination [11].

After the Goldschmidt process gadolinium is received via fractional crystallization. According to the method (Figure 2), a part of the salt in solution is precipitated by a change in temperature or by evaporation of a saturated solution [11]. If the solubility of various components in the solution differ, the composition of the crystal crop will be different from that of the original solution. While the crystal crop becomes enriched in the less soluble component, simultaneously, the more soluble components will be enriched in the liquor. This method has been considered as the best of the classical separation procedures for producing individual elements in high purity. The most suitable compounds that are used are the double ammonium nitrates.

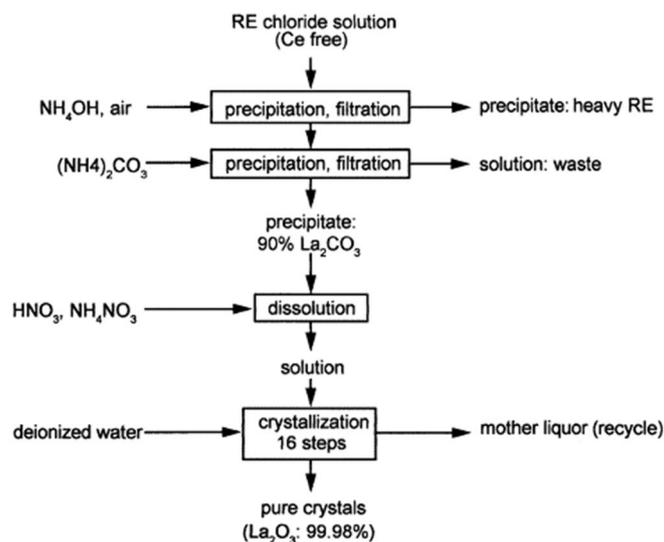


Figure 2. Separation process of REEs. The method is used also for the separation of gadolinium [11].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

26.2.1.2 GD IN $Gd_5 Ge_2 Si_2$ ALLOY PRODUCTION

As previously mentioned the $Gd_5 Si_2 Ge_2$ alloy synthesis for magneto-caloric effect (GMCE) purposes in the main application of gadolinium. In order to get the so-called giant magneto-caloric effect (GMCE) the alloy must have a stoichiometry of $Gd_5 (Si_x Ge_{1-x})_4$ where $0.24 \leq x \leq 0.5$, and the monoclinically distorted derivative of the orthorhombic $Sm_5 Ge_4$ -type structure be present. This is a difficult task, as the gadolinium itself is a very reactive element, so the conventional synthesis by melting in a crucible is not an option. Therefore, arc melting is employed in an inert atmosphere of argon using a pure copper hearth as the mould. This method proved to be very effective in terms of negligible mass losses of the charge material.

Pure gadolinium (99.99 %), silicon (99.9995 %) and germanium (99.9999 %) are used to produce fine pellets of Gd-Ge-Si alloys. An arc melting facility is used that allows the internal atmosphere to be removed and replaced by pure argon (Figure 3). Prior to introducing the argon into the arc melter a small amount of pure titanium is ignited in order to remove any remaining oxygen. The charge material consisted of small pieces of gadolinium, germanium and silicon, and is placed on the water-cooled copper hearth. Then the charge material is remelted for four times where DC electric current of 90 A was used. The synthesised pellets are then received at they are characterized by scanning electron microscopy.



Figure 3: The melting facility with a watercooled copper mould at the bottom and the tungsten tip used to produce the electric arc [12].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

25.2.2 USAGE

The giant magnetocaloric material $Gd_5(Si_xGe_{1-x})_4$ is useful for various types of refrigeration applications, from liquifaction of helium (4K) to room temperature air conditioning and climate control. Magnetic refrigeration materials are the key issues for the application of the magnetic refrigerating technique. Magnetic refrigeration technology is considered to have great potential to be developed as a green refrigeration technology in the 21st century to replace the traditional refrigeration technology since it has the advantages of high efficiency, energy-saving, limited noise and no greenhouse effect. The main advantage of magnetocaloric refrigeration compared to well-established vapour compression technologies is that the former is based on internally-reversible thermodynamic cycles, while the latter are based on an internally irreversible cycle (Reversed Rankine cycle) [13-15]. The discovery of $Gd_5(Si_xGe_{1-x})_4(0.24 \leq x \leq 0.5)$ alloys in general is the most important breakthrough in the fields of magnetic refrigerating materials. The $Gd_5(Si_xGe_{1-x})_4$ series alloys have giant magnetocaloric effect, its Curie temperature may be adjusted among in the range from 30 K to 300 K by tuning the ratio of Si/Ge, which makes the magnetic refrigeration technology have the possibility to come true.

25.2.3 END OF LIFE

Recycling processes of scrap rich in Gd have not been reported due to the limited applications of the metal. Moreover, most of Gd applications are still at the research/investigation stage.

25.2.4 RESIDUE TREATMENT

Treatment processes of the wastes generated by Gd secondary resources have not been described.

26.3 SUMMARY

Gadolinium is a REE with specific physicochemical properties. In contrary to the other REEs is stable in air atmosphere while the gadolinium alloy $Gd_5Si_2Ge_2$ has magneto-thermodynamic properties favouring its magnetic refrigeration. The price of gadolinium is about 55\$ per kg in case of a 99.5% purity while China is the major producer of the metal. Gd is produced via chlorination method while subsequently the metal is separated by other REEs through fractional crystallization. The demand of the metal is expected to be dramatically increased due its use in magnetic refrigeration, however it cannot be predicted when exactly this technology be applied at wide scale.

26.4 REFERENCES

- [1] N. Greenwood, A. Earnshaw, 1997. Chemistry of the Elements (2nd ed.). Butterworth-Heinemann.
- [2]"Gadolinium". Neutron News. NIST. 3 (3): 29. 1992.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [3] D. R. Lide, 2005. CRC Handbook of Chemistry and Physics (86th ed.). Boca Raton (FL): CRC Press.
- [4] Chemical reactions of Gadolinium. 2009. Webelements.
- [5] J. Emsley, 2011. Nature's Building Blocks, An A-Z Guide to the Elements, New Edition, Oxford University Press.
- [6] T. Gray, 2009. The Elements, A Visual Exploration of Every Known Atom in the Universe, Black Dog & Leventhal Publishers.
- [7] A. Stwertka, 2012. A Guide to the Elements, 3rd Edition, Oxford University Press, 2012
- [8] K.N. Raymond, V.C Pierre, 2005. Next Generation, High Relaxivity Gadolinium MRI Agents. Bioconjugate Chemistry, 16, pp. 3–8.
- [9] V.D. Ryzhikov et al., 2005. Use of gadolinium oxyorthosilicate scintillators in x-ray radiometers. Optical Engineering. 44.
- [10] European Commission, 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials.
- [11] C. K. Gupta, N. Krishnamurthy, 2005. Extractive Metallurgy of Rare Earths, CRC Press.
- [12] B. Markoli, P. J. McGuinness, B. Podmiljšak, I. Škulj, S. Kobe, 2009. The synthesis of a magneto-caloric Gd₅(GeSi)₄ alloy using arc melting procedure, RMZ – Materials and Geoenvironment, 56, pp. 1–8.
- [13] R.D. Shull, R.D. McMichael, J.J. Ritter, 1993. Magnetic nanocomposites for magnetic refrigeration, Nanostructured Materials, 2, pp. 205-211.
- [14] H.S. Liu et al., 2009. More accurate calculations of magnetic entropy change, Journal of Magnetism and Magnetic Materials, 321, pp. 3221–3224.
- [15] X.L. Hou et al., 2011. Effect of B alloying on magnetocaloric effect of Gd₅.1Si₂Ge₂ alloy in low magnetic field, Materials International 21, pp. 413-417.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

27 OTHERS (HOLMIUM, LUTETIUM, YTTERBIUM, THULIUM)

27.1 INTRODUCTION

Holmium (Ho), Thulium (Tm), Ytterbium (Yb) and lutetium (Lu) are Heavy Rare Earth Elements (HREE) that have not been exploited in significant quantities, but which are now attracting new interest because of likely new sources and potential use in new technologies. Like the other lanthanides, the most common oxidation state of these elements is +3, seen in its oxide, halides and other compounds. They are silvery white metal easily oxidized in air atmosphere [1].

Holmium

It occurs in combination with other elements in gadolinite, monazite and other rare-earth minerals. No holmium-dominant mineral has yet been found. The main mining areas are China, United States, Brazil, India, Sri Lanka, and Australia with reserves of holmium estimated as 400,000 tonnes. Holmium has concentration up to 1 part per million in the soils and 400 parts per quadrillion in seawater. Holmium obeys the Oddo–Harkins rule: as an odd-numbered element, it is less abundant than its immediate even-numbered neighbours, dysprosium and erbium. The principal current source of Ho are some of the ion-adsorption clays of southern China. Holmium is relatively inexpensive for a rare-earth metal with the price about 1000 USD/kg. Holmium has the highest magnetic strength of any element, and therefore is used to create the strongest artificially generated magnetic fields, when placed within high-strength magnets. Therefore, it is applied in the construction of motors that used in hybrid vehicles and wind energy turbines. It is also used in nuclear reactors since it can absorb nuclear fission-bred neutrons. Furthermore Ho is applied in glass making as a colourant in glass and enamels, and also as a calibration standard for optical spectrophotometers [1-3].

Thulium

Thulium is often found with minerals containing yttrium and gadolinium and more specifically, thulium occurs in the mineral gadolinite. However, it also occurs in the minerals monazite, xenotime, and euxenite. Its abundance in the Earth's crust is 0.5 mg/kg by weight while it contained in sea water in concentrations about 250 parts per quadrillion of seawater. Thulium ore occurs most commonly in China. However, Australia, Brazil, Greenland, India, Tanzania, and the United States also have large reserves of thulium. Total reserves of thulium are approximately 100,000 tonnes. Thulium is the least abundant lanthanide on earth except for promethium. Holmium-chromium-thulium triple-doped yttrium aluminum garnet is an active laser medium material with high efficiency producing activation at 2080 nm and is widely used in military applications, medicine, and meteorology. It is also used a radiation source in X-ray machines (particularly portable X-ray machines). It is also applied for banknote purposes because it fluoresces with a blue colour in ultraviolet light. It is currently added to euro banknotes as a measure against counterfeiting [1-3].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Ytterbium

Ytterbium is found with other rare earth elements in several rare minerals. It is usually recovered commercially from monazite sand (0.03% ytterbium). The element is also contained in euxenite and xenotime. The main mining areas are China, the United States, Brazil, India, Sri Lanka, and Australia. Several ytterbium compounds are rare and have not yet been well characterized. The abundance of ytterbium in the Earth's crust is about 3 mg/kg, while the world production of ytterbium is only about 50 tonnes per year, indicating that it has few commercial applications, most of them are extremely specificity. Ytterbium is mainly used in portable X-ray machines, requiring lower energies than other sources. It is also used for the production of stable atomic clocks developed at the National Institute of Standards and Technology (NIST). Other applications comprising its use; in long life lasers in which Yb generates short pulses, in earthquake monitors (Ytterbium metal increases its electrical resistivity when under high stress and is used in earthquake detectors), in flares replacing magnesium as it has higher emissions in the infra-red range [1-3].

Lutetium

It is recovered as a by-product from the processing of the rare earth phosphate mineral monazite (Ce,La,...)PO₄, which has concentrations of about 0.0001% of the element, not much higher than the abundance of lutetium in the Earth crust of about 0.5 mg/kg. The main mining areas are China, United States, Brazil, India, Sri Lanka and Australia. The world production of lutetium (in the form of oxide) is about 10 tonnes per year. It is one of the rarest and most expensive of the rare earth metals with the price about US\$10,000 per kilogram. It is used for the construction of detectors in positron emission tomography (PET), as a phosphor in LED light bulbs and for the construction of high refractive index lenses. It is also used a catalyst for petroleum cracking and alkylation, hydrogenation, and polymerization purposes [1-3].

Holmium, thulium, ytterbium and lutetium, as a heavy rare earth elements, have been classified as critical raw metals by the EU Commission taking into account their; chemical properties, geological availability, supply demands and cutting edge applications. Holmium, thulium, ytterbium and lutetium are produced under strong monopoly conditions (as China produces the 90% of the global REE amount), therefore it presents a high supply risk [4].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

27.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

26.2.1 PRODUCTION

27.2.1.1 FROM MONAZITE TO HEAVY RARE EARTH ELEMENTS

The heavy rare earth elements holmium, thulium, ytterbium and lutetium are mainly produced by monazite ore in China through a complex process which comprises many steps, especially at the element separation step. In Figure 1 the processing of monazite ore in the Shanghai Yue Long Chemical Plant is described [5,6]. Monazite is initially digested with NaOH, filtrated while the residue is leached with HCl. The resulting rare earth chloride solution is extracted with D2EHPA and the rare earths are split into three groups, from which mixed and pure oxides, carbonate, or chlorides are produced. The ion-adsorption type rare earth ores are first leached with HCl or H₂SO₄. Cation exchange extractants, such as HEHHP and naphthenic acid, are frequently used to extract rare earths elements from the leachate, since these ores have high levels of heavy rare earths, which have a strong affinity for acidic extractants. Heavy rare earth elements holmium, thulium, ytterbium and lutetium are recovered with yttrium in the last stage of solvent extraction. Alternatively to monazite, bastnesite ore, which is the main rare earth resource in China, is used for the production of HREEs. The ore concentrate is typically roasted with H₂SO₄, followed by leaching with water or dilute sulfuric acid. Rare earths are recovered from the leachate by solvent extraction with (D2EHPA). Preferential stripping is used to divide the rare earths elements [6].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

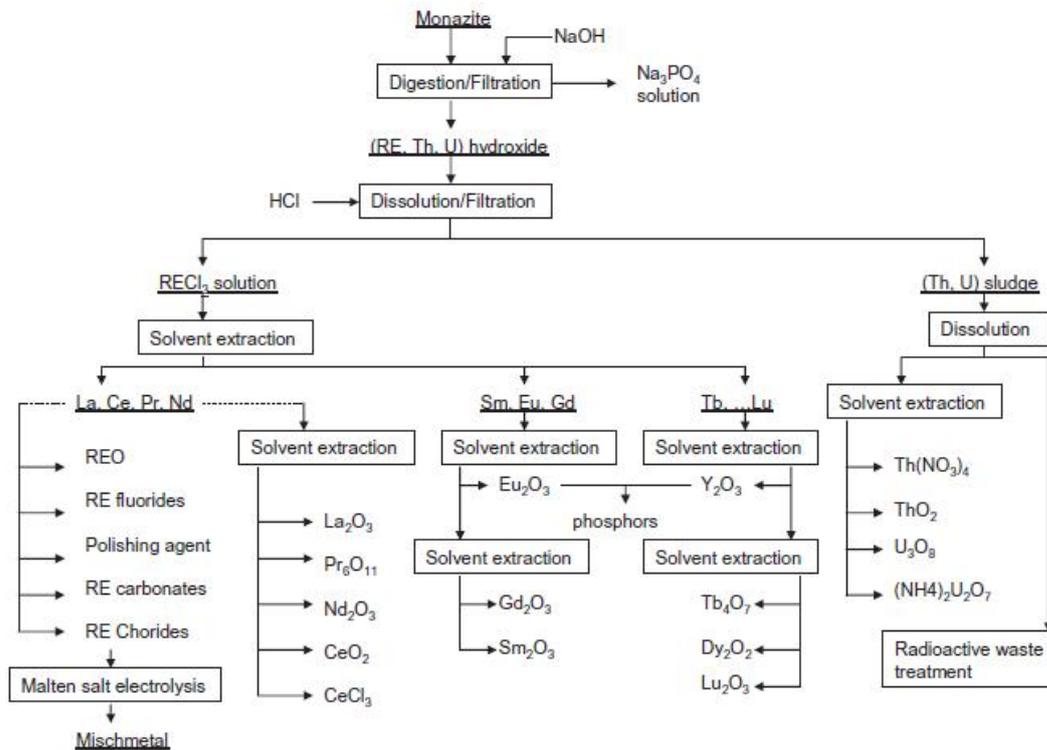


Figure 1. Simplified flowsheet of the Shanghai Yue Long Chemical Plant where heavy rare earth elements are produced [6].

There is not currently available a detailed life cycle analysis and environmental impact analysis concerning HREEs and especially holmium, thulium, ytterbium and lutetium. However, some general information about the environmental impact of REEs production can be mentioned. The REE processing is characterized by high levels of water consumption, energy inputs, and chemicals use. The land allocation can be also significant for both mining and processing operations, as well as for the tailings dams, and long-term storages of the radioactive waste materials [7]. The concentration of radioactive elements rises significantly during beneficiation. This could be of serious concern for the waste by-product, emissions or tailings after the cracking stage in the processing of rare earths bearing minerals. Thorium is the most common natural occurring radionuclide which is exposed during the mining and metallurgical processing. Its market is currently very limited and most of it has to end up either at the long-term storage or permanent disposal. The separation, treatment and disposal of thorium therefore creates a significant additional cost, as well as high human health and environmental risks. Recently, the environmental pollution of rare earth elements (REE) has increased dramatically as a result of wide application of REEs in agricultural production as microelement fertilizers as well as in industry. Therefore, the biogeochemical cycling of REEs and their ecological and environmental effect is highly increasing [7].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

27.2.1.2 PRODUCTION OF HO(III) DOPED IRON OXIDE NANOPARTICLES

The use of holmium, thulium, ytterbium and lutetium HREEs are very limited in specific advanced applications. Below, a new method for the synthesis of holmium incorporated iron oxide nanoparticles is shortly described. The material can be used as drug delivery, biosensing, magnetic separation, magnetic resonance imaging and contrast reagent.

The Ho(III) doped iron oxide nanoparticles are synthesized using Fe and Ho oleates (an ester of oleic acid). Sodium oleate, Fe(III) and Ho(III) oxide powder and chloride hexahydrate are dissolved in a mixture ethanol and heptane. This mixture refluxes at 70 °C for 4 h. Afterwards, the upper heptane layer, which contains the iron and holmium oleates, is separated using a separatory funnel. At the final step, the heptane is evaporated using a rotavapour, resulting in a dark brown waxy solid. The Ho(III) doped iron oxide material is heated further to 320 °C and kept at that temperature for 30 min. The presence of holmium in the nanoparticles can be easily proved by further by total reflection X-ray fluorescence (TXRF), which also allows to determine the exact concentration of the dopant. The magnetic and magneto-optical properties of the holmium incorporated iron oxide nanoparticles were investigated by vibrating sample magnetometry and Faraday rotation measurements. The results indicate that the material has excellent magnetic susceptibility and photoluminescence properties.

26.2.2 USAGE

Iron doped nanoparticles present a great potential for several bio-applications. Molecular imaging is one of the most promising applications of targeted doped iron oxide nanoparticles. Various tests have been evaluated in Vitro and in animal experiments. It has been proved that these kind of nano materials can be used efficiently for the imaging of liver as well as used as blood pool agents (magnetic resonance angiography contrast agents) taking advantage of their high molecular weight and relaxivity [9]. Iron doped nanoparticles can also be used for drug delivery purposes. Nano particles with a diameter ranging from 10 to 100 nm are optimal for intravenous injection and have the most prolonged blood circulation times. These particles are small enough to penetrate small capillaries of the tissues and offer the most effective distribution in targeted tissues. Magnetic drug targeting employing nanoparticles as carriers is a promising cancer treatment avoiding the side effects of conventional chemotherapy. Iron oxide nanoparticles covered by starch derivatives with phosphate groups, which bound mitoxantrone, have been used as chemotherapy [9]. Doped iron oxide nanoparticles can also be used also for therapeutic purposes. Their applications for hyperthermia treatment were first envisaged in 90es. Several studies prove the high efficiency of a superparamagnetic crystal suspension to absorb the energy of an oscillating magnetic field and convert it into heat. This property can be used in ViVo to increase the temperature of tumour tissue and to destroy the pathological cells by hyperthermia [9].

26.2.3 END OF LIFE

The recovery of Holmium (Ho), Thulium (Tm), Ytterbium (Yb) and lutetium (Lu) by secondary resources can be described as an “uncharted field” as the applications of these elements are very limited and their annual

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

produced amounts very small. According to the bibliography, only the recycling of lutetium has been examined at laboratory scale. Lutetium, as has been previously mentioned, is used as a component in positron emission tomography (PET) medical test devices. More specifically, lutetium is used for the synthesis of the lutetium yttrium silicate scintillation (LYSO) crystals of PETs. The waste management of LYSO scraps consists a very interesting topic as Lu is one of the most expensive of the lanthanides because of its low-abundance and the high-cost of the extraction process, therefore a process for recycling of the waste containing expensive Lu is a new priority.

A recent study proposes the recycling of Lu by LYSO scraps through a hydrometallurgical route [10] which can be seen in Figure 2. At the first stage, the scrap material is leached by the 5 M HCl solution while microwave digestion conditions provide the heating of the solution at 180 °C for 2 hours. Subsequently, the valuable metals are recovered using functional resin separation. This technology is very efficient for the separation and recycling of REEs and precious metals due to its simple operation high performance, and cost-effectiveness. The resins consist of a typical macroporous hydrophobic material, which can load various metal-extractants using the solvent impregnation method. In case of the lutetium recovery, a novel green ionic liquid (IL) -mediated resin system that contains CHON-type extractant and green hydrophobic ILs has been developed. The developed process has a number of advantages such as high recovery of Lu (>98% at pH=2.8) and simple flowsheet, while it is environmentally friendly. Additionally, the recovery of a mix of Lu and Y can be reused by LYSO company.

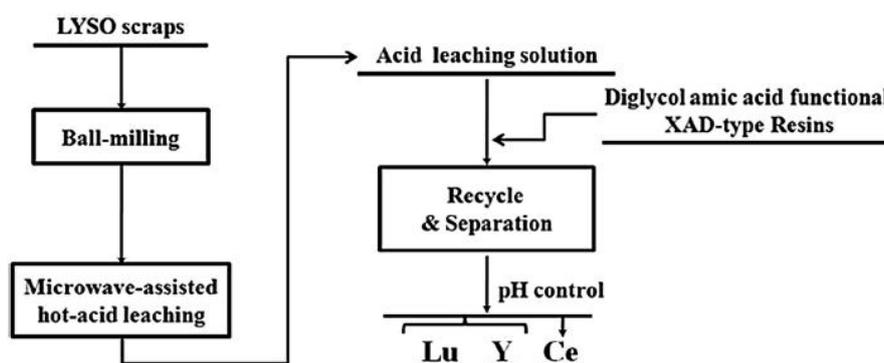


Figure 2. The recycling process for the recovery of Lu by lutetium yttrium silicate scintillation crystals [10].

26.2.4 RESIDUE TREATMENT

There is a lack of available data concerning the environmental impact which is generated by the recovery of Holmium (Ho), Thulium (Tm), Ytterbium (Yb) and lutetium (Lu) from secondary resources. Some limited data exist in case of the laboratory tested recycling process of the lutetium yttrium silicate scintillation (LYSO) crystals. It has been reported the high consumption of electric energy as the leaching is efficient in case of microwave-assisted heating. Furthermore, the use liquors with high acidity (such as sulphuric acid), as well as, the storage

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

of the ionic liquids, that are used in the separation step, are issues in which an increased attention should be given.

27.3 SUMMARY

Holmium (Ho), Thulium (Tm), Ytterbium (Yb) and lutetium (Lu) are heavy rare earth elements that produced at small amounts globally and used in a limited number of cutting edge applications. China is the major exporter of these elements which their price is ranged between 1000 and 10000 \$ per kilogram (lutetium is one of the highest priced REEs). Holmium, due to each magnetic properties, is a component in specific magnets, thulium is a source of X-rays, ytterbium is used in earthquake monitors and lutetium is applied in positron emission tomography. Holmium (Ho), Thulium (Tm), Ytterbium (Yb) and lutetium (Lu) are produced as a mixture of their oxides with yttrium oxide after the hydrometallurgical processing of monazite. The elements are separated via solvent extraction process. The medium-term demand in these metals is possible to be increased due to new application that will be arisen. As an example, the potential use of holmium as an imaging agent and magnetic drug in medicine, can be mentioned.

27.4 REFERENCES

- [1] J. Emsley, 2003. Nature's building blocks: an A-Z guide to the elements. Oxford University Press. pp. 492–494.
- [2] P. Walker, W. Tarn, 2010. CRC Handbook of Metal Etchants. CRC Press.
- [3] Heavy Rare Earth Elements (HREE) opportunities in Queensland, 2014. Department of Natural Resources and Mines Geological Survey of Queensland.
- [4] European Commission, 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials.
- [5] B.Z. Zhang, K.Y. Lu, K.C. King, W.C. Wei, W.C. Wang, 1982. Rare earth industry in China. Hydrometallurgy 9, 205–210.
- [6] F. Xie, T. An Zhang, D. Dreisinger, F. Doyle, 2014. A critical review on solvent extraction of rare earths from aqueous Solutions, Minerals Engineering 56, pp. 10–28.
- [7] G. Charalampides, K. Vatalis, V. Karayannis and A. Baklavariadis, 2016. Environmental defects and economic impact on global market of rare earth metals, IOP Conf. Series: Materials Science and Engineering 161.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [8] M. Bloemen, S. Vandendriessche, V. Goovaerts, W. Brullot, M. Vanbel, S. Carron, N. Geukens, T. Parac-Vogt, T. Verbiest, 2014. Synthesis and characterization of holmium-doped iron oxide nanoparticles, *Materials*, 7, pp. 1155-1164.
- [9] S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. V. Elst, R. N. Muller, 2008. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications, *Chemical Reviews*, 108, pp. 2064–2110.
- [10] P. Chen, F. Yang, Q. Liao, Z. Zhao, Y. Zhang, P. Zhao, W. Guo, R. Bai, 2017. Recycling and separation of rare earth resources lutetium from LYSO scraps using the diglycol amic acid functional XAD-type resin, *Waste Management*, 62, pp. 222-228.

28 LANTHANUM

28.1 INTRODUCTION

Lanthanum is the first element and prototype of the lanthanide series. It is a soft, ductile, silvery-white metal that tarnishes rapidly when exposed to air and is soft enough to be cut with a knife. Lanthanum usually occurs together with cerium and the other rare earth elements. It has second-lowest (after cerium) melting point among all the lanthanides: 920 °C. It presents a relatively high resistivity of 615 nΩm at room temperature; in comparison, the value for the good conductor aluminium is only 26.50 nΩm [1]

Lanthanum, as a rare earth element, has been classified as critical raw metals by the EU Commission taking into account its chemical properties, geological availability, and supply demands. Lanthanum is produced under strong monopoly conditions (as China produces the 90% of the global REE amount), while they present a high supply risk [2].

Elemental lanthanum has not commercial properties, however its alloys and lanthanum oxides are used in a wide range of applications. $\text{La}(\text{Ni}_{3.3}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.7})$ alloy used for anodic material in nickel-metal hydride batteries while lanthanum-nickel alloys are used to store hydrogen gas for use in hydrogen-powered vehicles. Lanthanum is a classic component (25-45% w/w) in pyrophoric (mischmetal) alloys for lighter flints. Lanthanum (III) oxide consists of a component in special optical glasses, as it improves the optical properties and alkali resistance of

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

the glass. Lanthanum salts are good catalysts for the petroleum refining industry. La_2O_3 and LaF_3 are necessary compounds in carbon arc lamps. LaF_3 is also an essential components of the heavy glass named ZBLAN which presents superior transmittance in the infrared range and used in fiber-optical communication systems. The ion La^{3+} is used as a biological tracer for Ca^{2+} , and radioactive lanthanum has been tested for use in treating cancer [1] [3], [4].

28.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

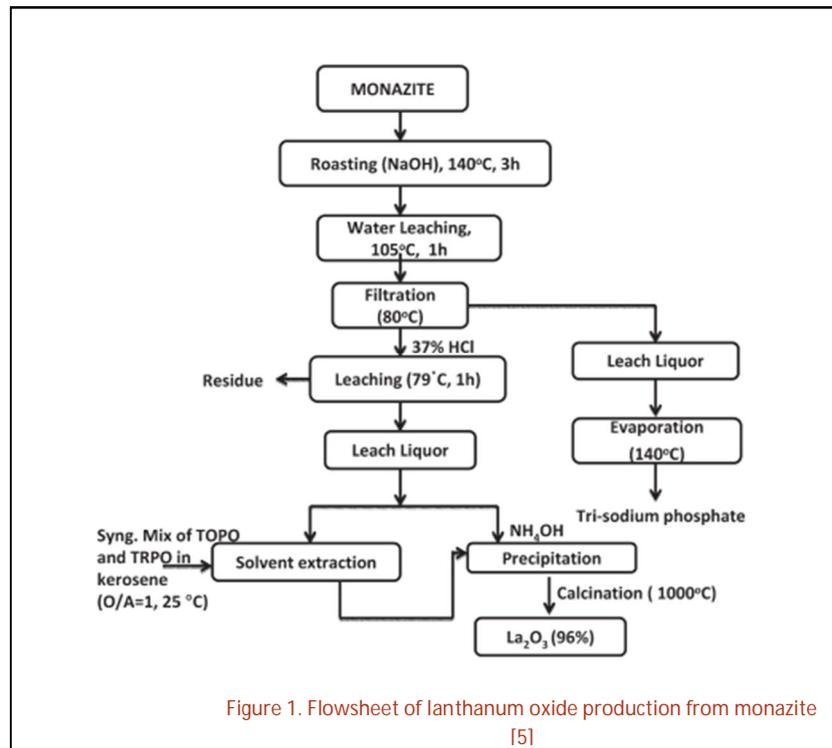
27.2.1 PRODUCTION

28.2.1.1 FROM MONAZITE TO LANTHANUM OXIDE

Monazite $(\text{Ce, La, Y, Th})\text{PO}_4$ and bastnäsite $(\text{La, Ce})\text{FCO}_3$ are the two major mineral sources of lanthanum. It is also contained as trace element in a number of ores such as bauxite, laterite and zinc sulphides. Monazite deposits are mainly exist in India, Malaysia, Australia, Brazil, China, South Africa, Sri Lanka, Thailand, and the United States, while bastnäsite deposits, which constitutes the larger portion of world's rare earth resources, occur mainly in China and Australia. Monazite is frequently found in association with heavy minerals like ilmenite, rutile, zircon which should be removed prior to the main metallurgical route. Secondary, non-commercial minerals of lanthanum are loparite, parasite and allanite. The main La sources, monazite and bastnäsite are mined in open pits and in situ mining [5].

Figure 1 presents the flowsheet of the metallurgical processing of monazite from Moemeik Myitsone deposit. The ore contains about 13% w/w lanthanum oxide along with other notable metals such as Ce, Sm, Pr and Nd. The first step includes the digestion of the ore with caustic soda for 3 h at 140 °C. Subsequently, the solid product of digestion is leached with dense hydrochloric acid. The precipitation is carried out three times using ammonium hydroxide. After the 3rd precipitation, 96.0% lanthanum oxide is obtained. Alternatively, synergistic separation of lanthanum and neodymium derived from using organophosphorus reagents namely trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TRPO) in kerosene [5]

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227



Lanthanum oxide is directly used as a component in a specific type of glasses. Furthermore, La_2O_3 consists of the base material for the production of mischmetal alloys La-Mg-Ni alloy for hydride batteries applications.

The main environmental hazards that are correlated with the production of rare earth oxides, among them lanthanum oxide, are summarized in Table 1. During the mining process, the environmental impact should be focused on the release of fine particle minerals rich in radionuclides. These secondary mineral phases, such as columbite, are frequently contained in monazite and bastnäsite ores. The metallurgical processing involves hydrometallurgical routes and the generation of liquid wastes with high acidity, as acids such as hydrochloric and sulphuric, which are used for the ores leaching. Recycling of industrial wastes (batteries, alloys etc.) which contain lanthanum results to the generation of various residues such as organic materials, dioxins, heavy metals, dust etc.) [6], [7].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Table 1. Than main sources of environmental impacts during the extraction of REEs [6]

Activity	Emission Source (s)	Primary Pollutants of Concern
Mining (aboveground and underground methods)	Overburden Waste Rock Sub-ore Stockpile ▪ Ore Stockpile	Radiologicals Metals Mine Influenced Waters/Acid Mine Drainage/Alkaline or neutral mine drainage Dust and Associated Pollutants
Processing	▪ Grinding / Crushing	▪ Dust
	▪ Tailings ▪ Tailings Impoundment ▪ Liquid Waste from Processing	▪ Radiologicals ▪ Metals ▪ Turbidity ▪ Organics ▪ Dust and Associated Pollutants
Recycling	▪ Collection	▪ Transportation Pollutants
	▪ Dismantling and Separation ▪ Scrap Waste ▪ Landfill	▪ Dust and Associated Pollutants ▪ VOCs ▪ Metals ▪ Organics
	▪ Processing	▪ Dust and Associated Pollutants ▪ VOCs ▪ Dioxins ▪ Metals ▪ Organics

28.2.1.2 LANTANUM OXIDE FOR LANTANUM-MAGNESIUM-NICKEL-COBALT ALLOY PRODUCTION

La-Mg-Ni alloys present specific physicochemical properties, such as reversible hydrogen absorption and desorption and high discharge capacity, and they are considered as promising materials for the construction of negative electrode in nickel hydrogen batteries (Ni-MH type). Especially, $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ alloy present the maximum discharge capacity of 410 mAh/g [8]. Currently, their applicability is limited by the difficulty in their synthesis as magnesium when melted under negative pressure volatilizes in a great quantity while the volatilized amount is unable to be predicted and controlled leading to the instability of alloying component. However, in response to this obstacle, an electro-deoxidation technique has been developed called “FFC Cambridge Process”. The technique is based on the reduction of metal oxides cathodically to the respective metals or alloys. The process typically takes place between 900 and 1100 °C, with an anode (typically carbon) and a cathode (oxide being reduced) in a bath of molten CaCl_2 while a voltage is imposed between the anode and cathode. Metal oxides are negatively polarised and resealing oxygen ions into the CaCl_2 salt and CO or CO_2 being evolved at the carbon anode. In case of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$, prior to electro-deoxidation La_2O_3 , MgO, NiO and CoO powders were mixed homogeneously in anhydrous ethanol and after drying at room temperature, powder is compressed. The oxide mixture pellets of $\text{La}_2\text{O}_3 + \text{MgO} + \text{NiO} + \text{CoO}$ were then sintered at 1200 °C for 2 h. The electro-deoxidation is performed in a quartz cell which is located inside an electrical furnace while the quartz cell is continuously purged with Ar gas [8], [9]. The production of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ via electro-deoxidation has so far been achieved at laboratory scale, however efficiency results are encouraging for the upscaling of the process.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

27.2.2 USAGE

Ni-MH batteries production presents a significant increase the last years which is attributed to the growth of the market of portable digital devices such as digital still cameras and higher-capacity batteries. Market's trend is mainly focused on the production of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ hydrogen-absorbing alloy with superlattice structure that can be used in the electrodes of extra high-capacity batteries [10].

$\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ exhibits approximately 30% higher electrochemical capacity than LaNi_5 -based alloys with CaCu_5 structure and good cycle life for the first few tens cycles in a three-electrode cell. However, no detailed and completed reports have been published at the moment on the performance of the La-Mg-Ni alloys in Ni-MH batteries.

27.2.3 END OF LIFE

As previously has been mentioned, lanthanum is used exclusively as a component in complex alloys, salts and oxide form. In some cases, La is contained in materials which present a high environmental impact. Ni-MH Batteries could be mentioned as an example. Their production requires a high energy consumption, while their burying in the landfill results of acid drainage influencing the human health and the ecosystem. The last years an important effort has been attempted concerning La-containing wastes recycling, however these technologies are still limited at laboratory level. Below some of the most encouraging studies are mentioned for La recovery from wastes:

a) Phosphogypsum

Phosphogypsum is the main by-product of the production of phosphoric acid and it is formed by the acidic digestion of phosphate rocks. Lanthanum is contained in phosphogypsum at significant concentrations (0.4-0.8% w/w). La has been recovered by the leaching of the waste at ambient temperature with 0.1–0.5 M H_2SO_4 solution in a solid-to-liquid ratio of 1:10. The leaching efficiencies can be increased by the mechanical activation of the waste. Subsequently, lanthanum is received from the leaching solution by precipitation as lanthanum double sulphate [11].

b) Iron slags containing La

Lanthanum rich slags are originated by the reduction of iron ores (magnetite), containing also monazite, in arc furnace at 1500 °C for iron extraction. The total content of REE is about 9% w/w while the lanthanum content about 2.8% w/w. Extraction of La is realized via hydrometallurgical route using H_2SO_4 acid at 30–80 °C for 5 h [12].

c) Glass wastes

Lanthanum oxide is contained at high concentrations (about 40% w/w) in specific glasses with high refractive index and a low dispersion that used many applications, such as in optical lenses, microscopes and binoculars.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

The global production of these glasses approaches 20.000 t/year and their recycling presents a high interest. Furthermore about 3000 t/y of optical glasses are lost during cutting processes. The recovery of La from optical glasses has been attempted by their dissolving with sodium hydroxide solution (55 wt %) at 413 K, followed by leaching using 6 M HCl. During this process, lanthanum in the glass is recovered as an aqueous solution of lanthanum chlorides containing 36.5 g/L La with recovery of 99.4% La [13].

d) Ni-MH batteries scrap

Hydrometallurgical routes are the basis of processing spent Ni-MH batteries for recovering lanthanum and other precious metals. Batteries scrap is submitted to leaching with HCl or H₂SO₄ while the leachate is submitted to a number of various separation techniques. Lanthanum has been successfully received as NaLa(SO₄)₂·H₂O via a precipitation process with NaOH. Lanthanum has been also obtained (with a yield reaching 98%) after the leaching of NiCd and NiMH batteries using the synthetic adsorbent LDH + Cyanex 272 [14], [15].

27.2.4 RESIDUE TREATMENT

The recovery of La by metallurgical wastes (slags, phosphogypsum) and industrial materials scrap (batteries, glasses etc.) involves in all cases a hydrometallurgical treatment. Therefore, significant quantities of acidic liquid wastes are produced. The environmental impact of the recycling processes has not so far been quantified.

28.3 SUMMARY

Lanthanum oxide production and price globally is estimated to remain stable until 2025 [16]. However, this trend could be changed in case that cutting edge applications, such as La-Mg-Ni hydride batteries where La is involved, be extended. Several studies that examine the lanthanum production chain from REE ores to lanthanum oxide or lanthanum alloys materials, reveal that recycling of the metal and its recovery from secondary sources is so far limited due to the complexity of the recycling processes and the generation of acidic liquid wastes. Furthermore, it should be noted that La is a relatively abundant rare earth metal with a low market price (around 7800 \$US per metric ton). Phosphogypsum and hydride batteries scrap are two potential future secondary La sources. Phosphogypsum recycling can be economically sustainable because a variety of metals (and especially Sc) can be extracted. On the other hand, the recycling of hydride batteries can be reinforced due to its environmental benefits.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

28.4 REFERENCES

- [1] Lide, D. R., ed. CRC Handbook of Chemistry and Physics (86th ed.) Boca Raton (FL) : CRC Press
- [2] E. Commission, «Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials,» 2014.
- [3] P. Bauerlein, C. Antonius, J. Löffler et J. Kumpers, «"Progress in high-power nickel-metal hydride batteries",» Journal of Power Sources. 176 (2): 547.
- [4] H. Uchida, «'Hydrogen solubility in rare earth based hydrogen storage alloys',» International Journal of Hydrogen Energy. 24 (9): 871.
- [5] S. S. Abhilash, P. Meshram. B. D. Pandey. Metallurgical process for the recovery and recycling of lanthanum from various resources-A review, Hydrometallurgy 16-, pp. 47-59, 2016.
- [6] «Rare Earth Elements Review, Section 6,» Human Health and Environmental Risks, [En ligne]. Available: <https://www.ecologistasenaccion.org/IMG/pdf/p100eubc-chapter-6.pdf>.
- [7] Y. Yu, B. Chen. K. Huang. X. Wang. D. Wang. «Environmental Impact Assessment and End-of-Life Treatment Policy Analysis for Li-Ion Batteries,,» International Journal of Environmental Research and Public Health, vol. 11, pp. 3185-3198, 2014.
- [8] Z. Shengqiang, W. Dahui. H. Xingang. H. Xiuyang. S. Leilei., «Research on a New Synthesis Technology of La-Mg-Ni System Alloys and microstructure of La_{0.67}MgO_{0.33}Ni_{3.0} alloys,» chez Rare Metals Materials and Engineering, 2012, pp. 2075-2080.
- [9] A. B. Aybar, M. Anik., «Direct synthesis of La-Mg-Ni-Co type hydrogen storage alloys from oxide mixtures,» Journal of Energy Chemistry , vol. 26, pp. 719-723, 2017.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [10] S. Yasuoka, Y. Magaria. T. Murata. T. Tanara. J. Ishisa. H. Nakamura. T. Nohma. M. Kihara. Y. Baba. H. Teraoka. «Development of high-capacity nickel-metal hydride batteries using superlattice hydrogen-absorbing alloys,» *Journal of Power Sources*, vol. 156, pp. 662-666, 2006.
- [11] . E.P. Lokshin, O. A. Tareeva «Recovery of lanthanides from extraction phosphoric acid produced by the dihydrate process,» *Russian Journal of Applied Chemistry*, vol. 83 (6), pp. 951-957, 2010.
- [12] C.J. Kim H.S.Yoon K.W. Chung J.Y. Lee, S.D. Kim, S.M.Shin Kim, «Leaching kinetics of lanthanum in sulfuric acid from rare earth element (REE) slag,» *Hydrometallurgy*, 2014, pp. 146, 133-137.
- [13] Y. Jiang, A. Shibayama. K. Liu. T. Fujita. «Recovery of rare earths from the spent optical glass by hydrometallurgical process,» *Canadian Metallurgical Quarterly*, 2004, pp. 43 (4) 431-438.
- [14] .L. Pietrilli, B. Bellomo. D. Fontana. M. R.Montereali, «Rare earths recovery from NiMH spent batteries.,» *Hydrometallurgy*, 2002, pp. 66 (1), 135-139.
- [15] L. Li, S. Xu. Z. Ju. F. Wu., «Recovery of Ni, Co and rare earths from spent Ni-metal hydride batteries and preparation of spherical Ni(OH)₂,» *Hydrometallurgy*, 2009, pp. 100 (1), 41-46.
- [16] <https://www.statista.com/statistics/450139/global-reo-lanthanum-oxide-price-forecast/>.

29 NEODYMIUM, PRASEODYMIUM, DYSPROSIUM

29.1 INTRODUCTION

Neodymium (Nd) is one of the most abundant among rare-earth elements (REEs). It is a soft, silvery metal that is mined as a by-product in following minerals: bastnäsite, monazite, and ion-adsorption clays. Neodymium represents 6.4% of total amount of REEs used in EU, which gives a consumption of around 571 t of Nd per year. It is mostly used in NdFeB permanent magnets, that are part of industrial motors, hard disk drives, automobiles and wind turbines. Other applications include blue pigment in ceramics, cathodes in NiMH batteries, manufacturing of metals, catalysts, glass, laser and other.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Praseodymium (Pr) has similar characteristics to Nd and has good magnetic, electrical, chemical and optical properties. Main application is in NdFeB magnets, but it is also used in ceramic tiles as a yellow pigment, batteries, metals manufacturing, catalysts, polishing powders and glass.

Dysprosium (Dy) in contrast with Nd and Pr is a heavy rare earth element and is found almost exclusively in minerals xenotime and ion-adsorption clays. It is a very hard, silvery material, which becomes oxidized in air very slowly. Dysprosium is used almost solely in permanent magnets, where it aims to increase the temperature resistance up to 200°C. main final applications of Dy-bearing magnets are wind turbines and industrial motors.

The supply of all REEs for Europe is completely reliant on import in form of metal oxides and compounds, mostly from China (European Commission, 2017).

29.2 GAPS LIMITING CIRCULAR ECONOMY

29.2.1 RECYCLING

Recycling activities of rare earths are at an early stage of development. Currently all three REEs are not being functionally recycled on industrial scale due to very little quantities used in final products and issues with separation of individual metals from other components. REEs are usually recycled non-functionally using techniques for standard metals, which lead to losing specific properties of rare metals. In the case of neodymium, the main issue with its recovery from hard disc drives is the liberation of the magnet. The current recycling technologies are based on the already separated NdFeB magnet from other components (Ueberschaar, 2017). The efficient liberation technology required more research and development.

One of the other issues is low collection rates and export of WEEE outside of the EU, where metals may not be completely recovered or inappropriately disposed. Several applications characterise long life span and are not available for recycling yet, for example wind turbines containing REEs in permanent magnets. Other waste products do not reach the recycling stage because of the dissipative content of rare metals that makes them impossible to be recovered (Remeur, 2013). There is often lack of information on the REE concentration in specific product, that makes it difficult to perform economically attractive metal recovery. Moreover, specialists suggest, that reduction of products' size, increased material complexity and shorter life span create recovery challenges and contribute to lower recovery rates (Tsamis & Coyne, 2015).

29.2.2 SUPPLY AND DEMAND (MARKET)

The limitation of reliable supply of all REEs is the fact that EU rely solely on import. There are no mining activities of rare elements in Europe and 95% of the total production takes place in China. Secondary production is not able to supply enough of raw material since the end of life recycling rate for most REEs is around 1%, except praseodymium which recycling rate is estimated as 10%. However, some parts of supply chain take place in Europe. Enterprises located in Estonia and France are capable of separating individual rare earth oxides. Estonian

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

company Silmet is producing neodymium metal in quantities 300-400 tones per year. Moreover, there are few companies that use REEs for manufacturing of alloys and magnets, located in UK, Germany and Slovenia (European Commission, 2017).

Supply and demand for REEs in general is subject to changes and it is difficult to predict the future market for those metals. The future demand is driven by the efforts to substitute or eliminate REEs from supply chain, and by the anticipated growth of green transportation and green energy technologies. The demand for praseodymium is expected to grow by 6% per year (European Commission, 2017).

29.2.3 PRICES

Low prices of REEs are believed to be the main factor influencing low recycling rates of REE-bearing products (Wall, 2014). Price of Nd was fluctuating greatly in the recent years. The highest increase was observed in 2011, when the price reached 467 \$/kg from previous level of 7 \$/kg in 2002. After that peak price, the value of neodymium stabilised and reached 80 \$/kg in 2014 and 53 \$/kg in 2015. Similarly, prices of praseodymium varied between 2010-2014. The price increased from 6 \$/kg in 2002 to 281 \$/kg in 2011 and stabilised at 90 \$/kg in 2015. Even higher variations experienced prices of Dysprosium. From 30 \$/kg in 2002 they dramatically increased to 3400 \$/kg in 2011 due to reduction of quotas in China and rapid increase in demand for permanent magnets. Since then price has decreased to 190 \$/kg in 2017 (European Commission, 2017). The monopoly of China in REE mining, processing and metals alloying can jeopardize supply of those metals to other countries by production and export limits or high prices. Figures 1 and 2 show the history of price fluctuations for selected light and heavy REEs. Presented prices are Free on Board in China, which means that the seller is responsible for cost of delivery to the ship and buyer – for the transportation costs from that point onwards (Wall, 2014).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

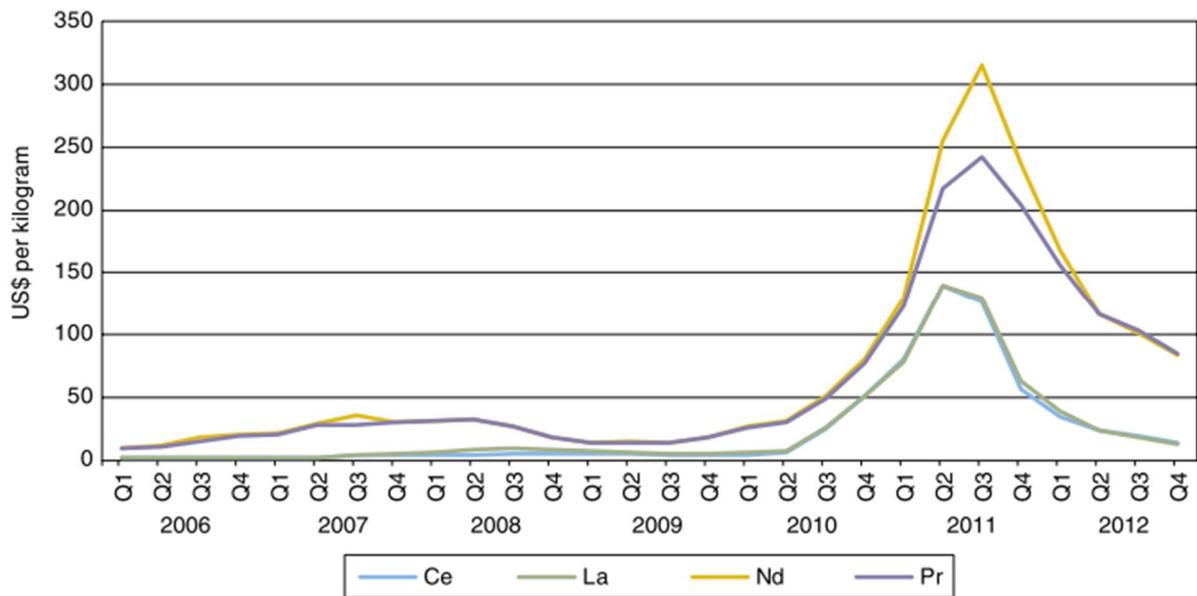


Figure 1. Quarterly average prices for selected light REEs (Wall, 2014)

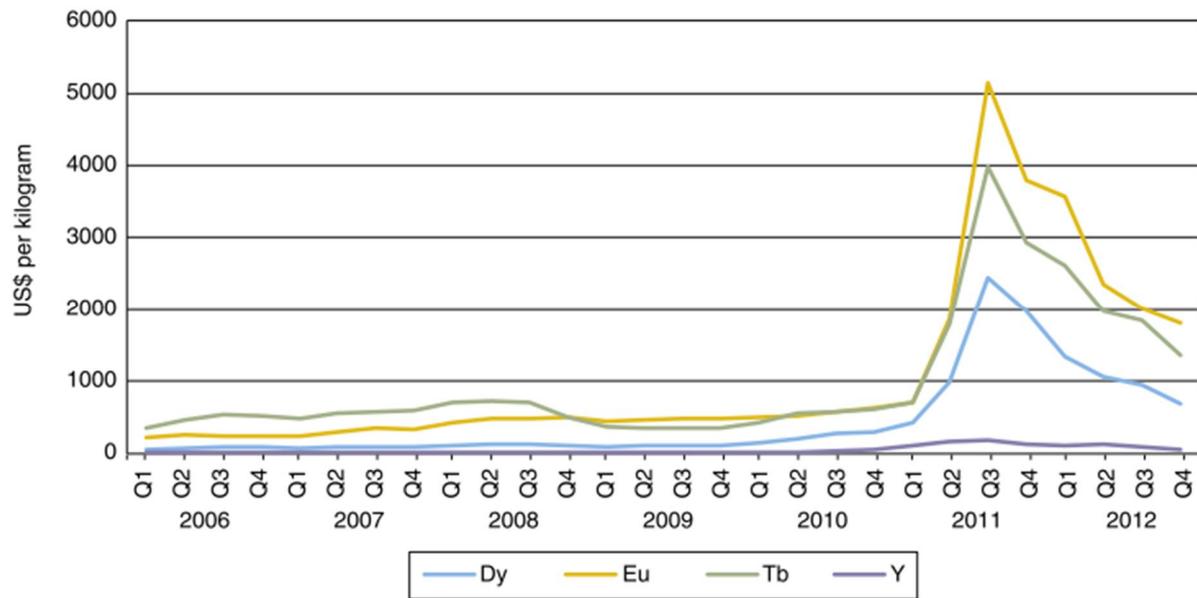


Figure 2. Quarterly average prices for selected heavy REEs (Wall, 2014)

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

Economic aspects are very often drivers for circular economy. The price of a critical metal can be either limitation or an incentive for recycling activities. If the price of metal from primary source is high enough, then secondary raw material can be recovered at lower cost. Consequently, lower price of mined minerals restrains recycling practices, since acquiring primary metal is more economically attractive for producers. The current REE economic market uncertainty does not support investments in the recovery on a large scale. At the current price levels the recycling of REEs is not economically feasible, which could change however if the prices of rare metals would increase. (Tsamis & Coyne, 2015)

29.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

29.3.1 SUBSTITUTION

Material substitution aim at ensuring long-term availability and to reduce the effect of price volatility. It is possible to substitute neodymium only in magnets and batteries, since in different applications substitution is problematic. In case of magnets there are two routes, either replace the neodymium with other material or apply different magnet technology. Nd can be substituted with praseodymium in NdFeB magnets. In practice those two metals are used interchangeably depending on the availability and price. Yet, this solution does not solve the issue of using rare earth minerals in magnets. Technology substitution for Nd-bearing magnets can be implemented by using ferrite magnets. This technology is already used for electric motors and captors. However, ferrite magnets have lower performance than NdFeB and are not used in high technology applications. NiMH batteries containing neodymium are gradually substituted with Li-ion batteries (European Commission, 2017; Remeur, 2013).

Praseodymium can be replaced in three main applications: magnets, batteries and metallurgical applications. In case of magnets, substitution possibilities are the same as for neodymium since they can be used indifferently. In batteries, similarly to neodymium, Pr can be found in NiMH cells, which are being replaced by Li-ion equivalents. In metallurgy Pr is used in alloyed steel to improve its characteristics. In this application praseodymium can be replaced with another rare earth metal gadolinium assuring similar performance. This solution may not be ideal, since it still requires the use of rare elements.

Magnet manufacturers are looking for ways to minimise or eliminate use of dysprosium in permanent magnets, due to high price and supply uncertainty. One of alternatives propose using positioning of Dy atoms at the grain boundaries of NdFeB alloys, which uses less dysprosium to achieve similar performance. It is expected that the content of Dy in permanent NdFeB magnets will be reduced from 2.3% in 2014 to 1.9% in 2020. There are also attempts to eliminate the metals in wind turbines by applying a cooling system to reduce the temperature at which magnet is working (European Commission, 2017).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

29.3.2 LEGISLATION

There are several provisions concerning metals, including REEs, created by European Union, which are related to recycling activities. Directive 2012/19/EU on waste electrical and electronic equipment (WEEE) focusing on waste collection schemes that allow consumers return their end of life electronic device free of charge (European Commission, n.d.). Directive 2006/66/EC on batteries and accumulators, elaborating on rules regarding placing batteries on the market as well as their collection, recycling, treatment and disposal after end of life (European Parliament, 2006). Directive 2000/53/EC on end-of-life vehicles to prevent generation of waste from vehicles and improve environmental performance of the vehicles' life cycle (European Parliament, 2000). Directive 2009/125/EC that establishes a framework of eco-design requirements for products related to energy. There is a big potential for improving the environmental impact of energy-related technologies. Appropriate design can help to save energy and subsequently be more economically attractive for businesses as well as end-users (European Parliament, 2009).

29.3.3 R&D AND SUPPORTING PROJECTS

Research and development in the area of REEs recycling is motivated by high price fluctuations in recent years and supply issues. Some of the research activities are focused on rare metals use reduction in products (Wall, 2014).

Apart from legislation, other projects supporting recycling of REEs have been created. Generally, they support the idea of creating a recycling economy, where products are designed to use fewer REEs and collection, dismantling and recycling activities are promoted. The European Pathway to Zero Waste was created in order to introduce programmes for eliminating waste to landfill in European regions (Remeur, 2013). Other action concerning REEs at EU level is the raw material initiative created by European Parliament in 2008 and European innovation partnership on raw materials created in 2012. Those initiatives aim to assure raw materials availability in the future of EU. They treat recycling as valuable source of materials, emphasize the importance of supply chain from extraction to end of life and stress the potential of better product design to enable recyclability of waste (European Commission, 2012; European Parliament, 2008; Remeur, 2013). In 2011 European Parliament issued a report on effective raw material strategy in Europe, drawing attention to importance of recycling valuable elements and implementing research and development activities in this area (European Parliament, 2011). Other research projects concerning REEs recycling funded by the EU can be found in the table below.

Table 1. EU research project on REEs recycling (Tsamis & Coyne, 2015)

Project name	Duration	Key objectives
RECLAIM	1/2013- 12/2016	Develop technological solutions that relieve bottlenecks in the recycling of gallium, indium, REEs Demonstrate their application potential by means of a pilot implementation in an industrial setting

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

RECYVAL NANO	12/2012- 11/2016	Develop an innovative recycling process for recovery and reuse of indium, yttrium and neodymium metals from Flat Panels Displays
REEcover	12/2013- 11/2016	Improve European supply of REEs (Y, Nd, Tb, Dy) Strengthen SME position in REE production and recovery value chain research routes for metallurgical recovery of REEs Demonstrate viability and potential of different types of deposited industrial wastes including magnetic waste material from the WEEE recycling industry.
Hydro- WEEE	10/2012- 9/2016	Develop innovative plant technology that uses liquid solvents to extract metals including REEs in high purity from electronic waste Accommodate the needs of (SMEs) in the process of adopting new technologies and processes.
Biolix	10/2012- 09/2015	Develop bacterially-catalyzed process for the selective recovery of purified metals out of low grade polymetallic materials. Develop first bio-hydrometallurgical unit by 2014.
REWARD	08/2009– 07/2012	Present a design for a new prototype facility for the generation of recyclable products from WEEE to substitute virgin primary materials and to decrease dependency on imports.
EREAN	09/2013 – 08/2017	The FP7 MC-ITN project “EREAN” - European Rare Earth (Magnet) Recycling Network. EREAN trains 15 young researchers (12 ESR + 3 ER) in the science and technology of rare earths, with emphasis on the recycling of these elements from Nd-Fe-B permanent magnets.

29.3.4 TECHNICAL ASPECTS IN PRIMARY PRODUCTION

Difficulties with primary production of REEs can be seen as incentives for acquisition of secondary materials. All of REEs reserves are found in low concentrations and their separation from each other is difficult due to similar chemical composition. Also, they are not equally present in mined minerals and the value of rare earth oxides strongly depend on their purity. Whole supply chain of REEs requires chemical treatment, is energy consuming, and has negative impact on the environment. Moreover, opening a new mine is a complicated and long process, which can take 10 to 15 years (Remeur, 2013). All those negative aspects of mining should be considered and can be supporting the implementation of circular economy principles.

Mining activities can hinder the circular economy of rare earths, especially from perspective of demand and supply. There are several large REE mining projects operating. Greenland Minerals and Energy A/S is acquiring rare earths, uranium and zinc from big resources in the south of Greenland (Greenland Minerals & Energy A/S, n.d.). In the US some old mines has been reopened, as well as closed down. The REE mine Mountain Pass in California, US has been reopened after a shut down in 1990s, which could radically influence the supply chain of

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

rare earths. The facility was fully functioning until 2015, but after owners reported bankruptcy it was shut down again and bought by MP Mine Operations, who is working on recommencing mining activities.

29.3.5 CURRENT RECYCLING TECHNOLOGIES AND ACTIVITIES

There is recycling technology present at different stages of development for some of REE-containing applications, for example lamp phosphors, ceramics and batteries. Several studies mention existing refining technologies mostly on laboratory scale for REEs from waste electronics and rising number of patents worldwide in this area. Leaders in the number of new patents are Japan-based companies, followed by US, China, Germany and France. Recent research activities are concentrated in recycling from products containing most valuable REEs and where their concentration is high, in particular permanent magnets, NiMH batteries, lamp phosphors. For Nd, Pr and Dy the most relevant waste streams are permanent magnets and batteries.

In the case of permanent magnets contained in hard disc drives (HDD), the approach is to either shred and subsequently extract various metals, including REEs, or remove magnets from the drives before shredding to obtain higher concentrations of rare metals that can be recovered in smelters. In some cases separated magnets can be reused after further processing, for example magnets from wind turbines. Example of physical separation method used in practice can be NbFeB magnet recovery from HDD and compressors of air conditioners developed by Hitachi (Tsamis & Coyne, 2015). Other methods are present such as using hydrogen to pulverize the NdFeB magnets from the magnet containing components, but still in laboratory scale. Many hydrometallurgical and pyrometallurgical methods are also available to recover the REEs from the magnet scrap or wastes with or without intensive physical pre-processing, however, they are mostly in the R&D stage, and upscaling to commercial operation is still highly needed (Binnemans et al., 2013; Yang et al., 2017).

Nd and Pr can be found in NiMH batteries, which were lost in the previous smelting of whole batteries. Recently there has been research done by Umicore and Solvay Rhodia on recovery of REEs from those batteries using metallurgical technologies. (Tsamis & Coyne, 2015). Solvay Rhodia has had an operation in France but closed down due to economic reasons (low prices in the market).

29.4 ENVIRONMENTAL ISSUES

29.4.1 PRODUCTION OF METALS

Primary mined REEs ores contain radioactive elements, namely thorium and uranium, fluorides, sulphides and heavy metals. The radioactive tailings from mining are usually stockpiled creating a risk for people working on the site as well as for the environment. Toxic substances can leach to the ground water or soil with rain water flow. Another danger is posed by storm water run-off in case of strong rainfalls that cannot be held by the ponds containing tailings. Next to the water pollution, air emissions can be caused by inappropriate mining, mainly dust

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

particles containing radioactive elements or heavy metals transported by the wind. The environmental footprint of rare earth oxides production reaches 38.5 CO₂-eq/kg for neodymium and 41.4 CO₂-eq/kg for praseodymium (Haque, Hughes, Lim, & Vernon, 2014). Figure 3 below shows the GHG footprint of REE oxides and their materials and energy contributions.

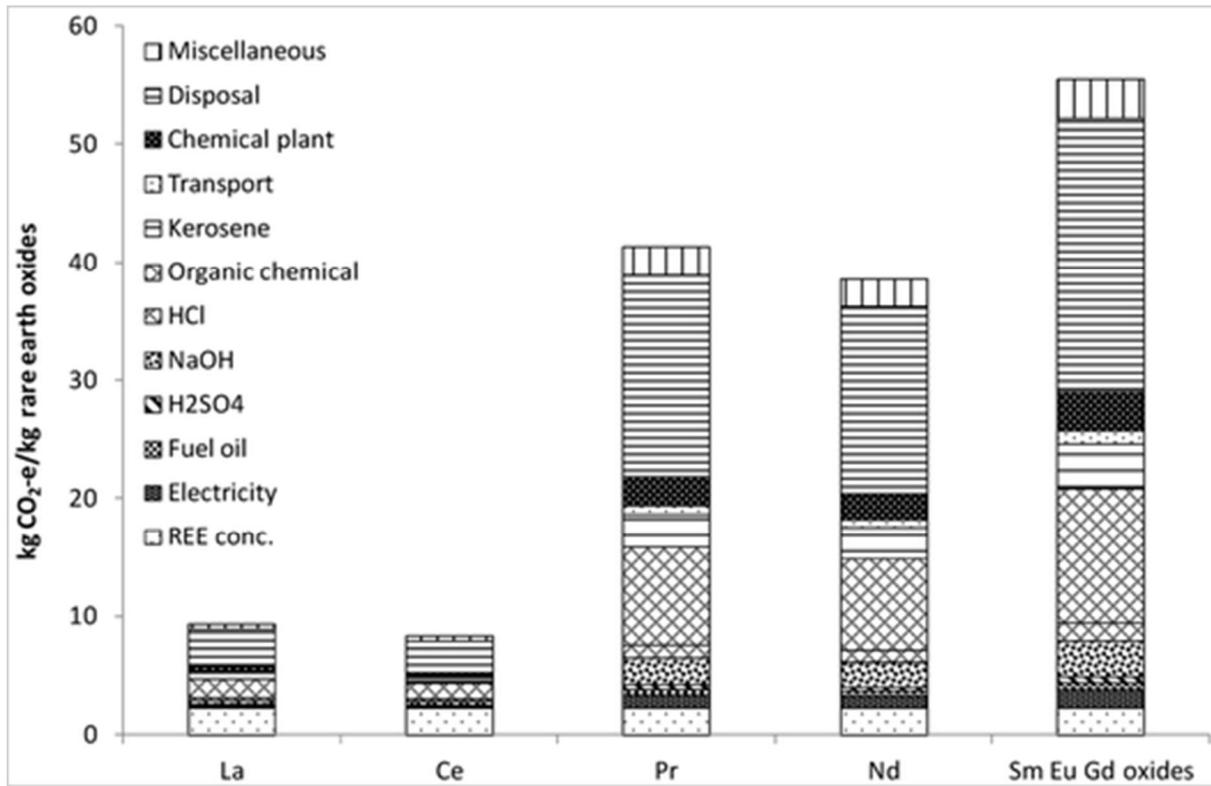


Figure 3. GHG footprint of selected REE products (Haque et al., 2014)

Recycling and use of secondary raw materials can help at least partially avoid those issues. Using recyclates can to some extent prevent opening new mines and save the land from degradation.

29.4.2 END OF LIFE RECYCLING

Although recycling of REEs can contribute substantially to circular economy, it also has negative impact. Some elements of recovery process can have significant environmental footprint. The technologies used for material separation and refining use high amounts of water, energy and chemical substances, subsequently generating large amounts of waste water that require special treatment. Impact level of hydrometallurgical recovery methods can even be compared to primary extraction of raw materials since it requires acids and chemicals that cannot be recycled (Schüler, Buchert, Liu, Dittrich, & Merz, 2011; Tsamis & Coyne, 2015). For example, recycling of REEs from NdFeB magnets using wet process is a common method for scrap processing. However, several

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

stages of the process require dissolution with strong acid and generate large amounts of waste from dissolving solution preparation. The environmental loads increase together with higher amount of processed scrap (Takeda & Okabe, 2014). Pyrometallurgical methods used for treatment of spent NdFeB magnets also have disadvantages for the environment. They require very high energy inputs. Although they don't generate waste water or effluents, electroslag refining as well as glass slag method generate substantial amounts of solid waste (Yang et al., 2017).

29.5 SUMMARY

Neodymium, Praseodymium and Dysprosium are rare earth minerals that play very important role in new technologies. They are used in permanent magnets and also other smaller applications. The supply of all REEs for Europe is completely reliant on import in the form of RE metals or alloys, metal oxides and compounds, which can hinder the supply and demand of those metals. There are several aspects hindering the implementation of circular economy principles for REEs. Recycling activities of rare earths are at an early stage of development and all three REEs are not being functionally recycled on industrial scale due to their dissipative use in major applications, issues with separation of individual metals from other components, low collection rates and export of WEEE outside of the EU. Also, low prices of primary RE metals cause lack of incentives to recycle them. However, there are also aspects supporting circular economy. There are several supporting initiatives concerning metals, including REEs, created by European Union, which are related to recycling activities of REEs. Another element is substitution or using less metal in current applications, which is still under research and development. Several other research projects have been launched in EU to promote closed loop activities and incentivise implementing currently available recycling technologies on industrial scale. Environmental dangers appearing during primary as well as secondary production are important issues in the circular economy.

29.6 REFERENCES

Binnemans, K., Jones, P. T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., & Buchert, M. (2013). Recycling of rare earths: A critical review. *Journal of Cleaner Production*, 51, 1–22. <https://doi.org/10.1016/j.jclepro.2012.12.037>

European Commission. (n.d.). Waste electronic equipment - Environment - European Commission. Retrieved April 9, 2018, from http://ec.europa.eu/environment/waste/weee/index_en.htm

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- European Commission. (2012). COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS MAKING RAW MATERIALS AVAILABLE FOR EUROPE'S FUTURE WELL- BEING PROPOSAL FOR A EUROPEAN INNOVATION PARTNERSHIP ON RAW MATERIALS. *COM*, 29(82). Retrieved from <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2012:0082:FIN:EN:PDF>
- European Commission. (2017). *Study on the review of the list of critical raw materials. Critical Raw Materials Factsheets*. Luxembourg: Publications Office of the European Union. <https://doi.org/10.2873/398823>
- European Parliament. (2000). Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles. *Official Journal L 269* , 21/10/2000 P. 0034 - 0043; Retrieved from <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0053:EN:HTML>
- European Parliament. (2006). DIRECTIVE 2006/66/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL. Retrieved April 9, 2018, from <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32006L0066&from=EN>
- European Parliament. (2008). The raw materials initiative — meeting our critical needs for growth and jobs in Europe. Brussels. Retrieved from <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2008:0699:FIN:EN:PDF>
- European Parliament. (2009). DIRECTIVE 2009/125/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 establishing a framework for the setting of ecodesign requirements for energy-related products (recast). *Official Journal of the European Union* . Retrieved from <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:285:0010:0035:EN:PDF>
- European Parliament. (2011). An effective raw materials strategy for Europe. Retrieved April 10, 2018, from <http://www.europarl.europa.eu/sides/getDoc.do?type=TA&language=EN&reference=P7-TA-2011-364>
- Greenland Minerals & Energy A/S. (n.d.). About Greenland Minerals and Energy. Retrieved April 22, 2018, from <http://www.gme.gl/en/about-greenland-minerals-and-energy>
- Haque, N., Hughes, A., Lim, S., & Vernon, C. (2014). Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact. *Resources*, 3(4), 614–635. <https://doi.org/10.3390/resources3040614>
- Remeur, C. (2013). Rare earth elements and recycling possibilities. Library of the European Parliament. Retrieved from [http://www.europarl.europa.eu/RegData/bibliotheque/briefing/2013/130514/LDM_BRI\(2013\)130514_R EV1_EN.pdf](http://www.europarl.europa.eu/RegData/bibliotheque/briefing/2013/130514/LDM_BRI(2013)130514_R EV1_EN.pdf)
- Schüler, D., Buchert, M., Liu, R., Dittrich, S., & Merz, C. (2011). *Study on Rare Earths and Their Recycling*. Darmstadt. Retrieved from <https://www.oeko.de/oekodoc/1112/2011-003-en.pdf>
- Takeda, O., & Okabe, T. H. (2014). Current Status on Resource and Recycling Technology for Rare Earths. *Metallurgical and Materials Transactions*, 1(2), 160–173. <https://doi.org/10.1007/s40553-014-0016-7>
- Tsamis, A., & Coyne, M. Recovery of Rare Earths from Electronic wastes: An opportunity for High-Tech SMEs

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

(2015). Retrieved from http://www.europarl.europa.eu/RegData/etudes/STUD/2015/518777/IPOL_STU%282015%29518777_EN.pdf

Ueberschaar, M. (2017). *Assessing recycling strategies for critical raw materials in waste electrical and electronic equipment*. Technische Universität Berlin, Berlin.

Wall, F. (2014). 13. Rare earth elements. In G. Gunn (Ed.), *Critical Metals Handbook* (pp. 312–339). John Wiley & Sons, Ltd.

Yang, Y., Walton, A., Sheridan, R., Güth, K., Gauß, R., Gutfleisch, O., ... Binnemans, K. (2017). REE Recovery from End-of-Life NdFeB Permanent Magnet Scrap: A Critical Review. *Journal of Sustainable Metallurgy*, 3(1), 122–149. <https://doi.org/10.1007/s40831-016-0090-4>

30 SAMARIUM

30.1 INTRODUCTION

Samarium (Sm) is a typical member of the rare earth elements, a group of seventeen metals. It is a moderately hard silvery metal that readily oxidizes in air. It has a hardness and density similar to those of zinc and a melting point at 1072 °C. The major commercial application of samarium is in samarium–cobalt magnets due to its advantageous magnetic properties and especially the alloy’s high Curie point (700 °C). Samarium has no significant biological role while it is considered as a non toxic element [1, 2]. Rare earth elements are divided into three subgroups according to their specific properties and applications; light rare earth elements (LREE), heavy rare earth elements (HREE) and scandium. Samarium (along with lanthanum, cerium, praseodymium and neodymium) is included in Light Rare Earth Elements (LREEs).

Samarium, and more generally the total of REE, have been classified as critical raw metals by the EU Commission taking into account their; chemical properties, geological availability, and supply demands. As can be seen in Figure 1, REE are produced under strong monopoly conditions (as China produces the 90% of the global REE amount), while they present a high supply risk (Figure 2) [3].

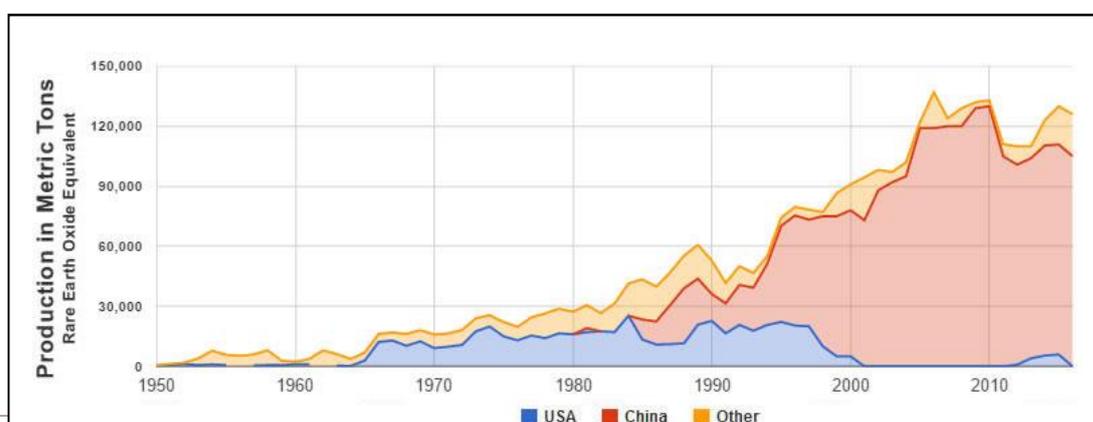
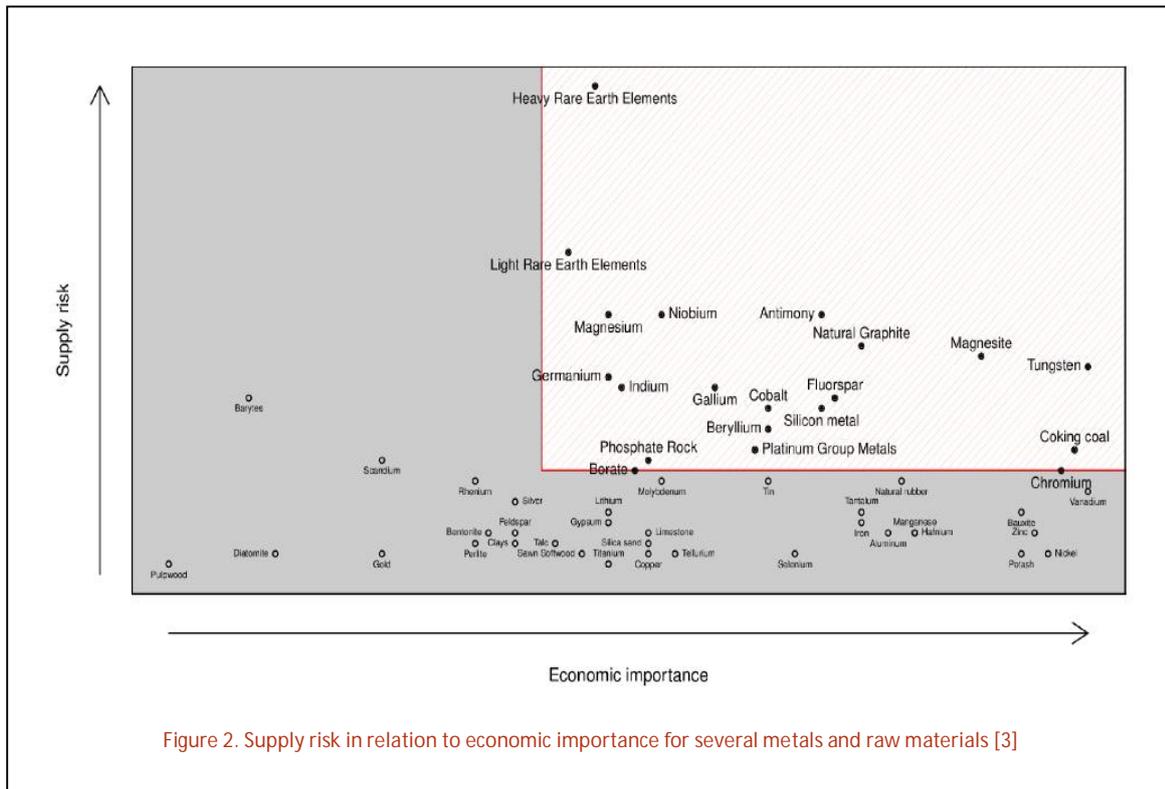


Figure 1. Global production of REE (metric tons of equivalent REE oxides) [3]



Samarium is primarily utilized in the production of samarium–cobalt (SmCo_5 or $\text{Sm}_2\text{Co}_{17}$) permanent magnets. Samarium-cobalt magnets replaced the more expensive platinum–cobalt magnets in the early 1970s. They are utilized in lightweight electronic equipment, where size or space is a limiting factor and where functionality at high temperature is a concern. Applications include electronic watches, aerospace equipment, microwave technology and servomotors. An alternative alloy, rich in Sm, appropriate for permanent magnets was discovered in 1984 and it is described by the $\text{Nd}_2\text{Fe}_{14}\text{B}$ formula. The Nd–Fe–B magnets are high strength magnets with a magnetic energy of up to 50 MGOe, which is a factor 2.5 times greater than that of SmCo_5 magnets, with high remanence and coercive force. Samarium (II) iodide, also known as Kagan's reagent, is widely used as a common reducing agent in chemical synthesis. It consists of a powerful reductor which can easily reduce water to hydrogen. Other applications of samarium include radioactive dating and an X-ray laser [1,2].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

30.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

30.2.1 PRODUCTION

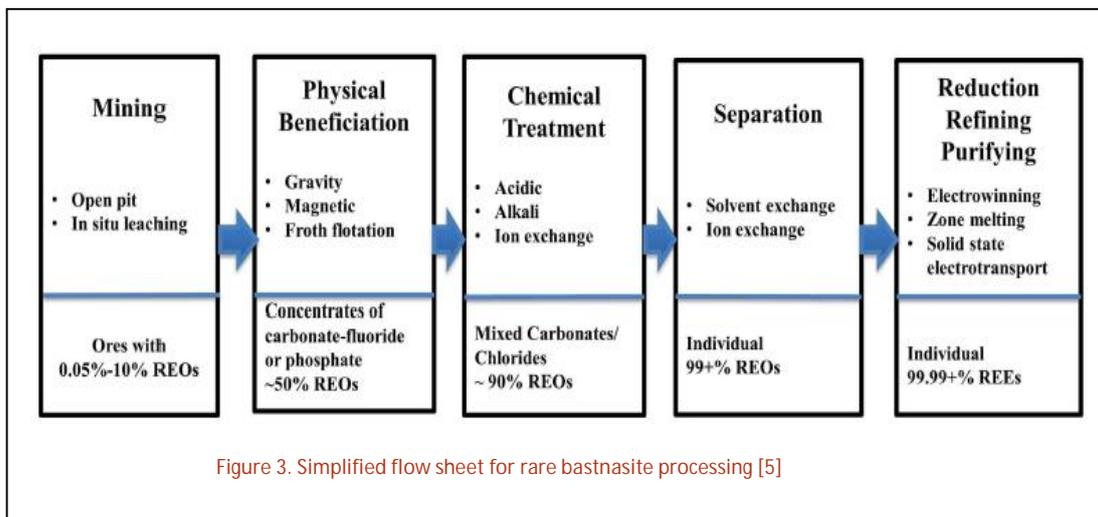
30.2.1.1 FROM MINERAL ORE TO SAMARIUM-COBALT MAGNETS

Samarium, like other rare earth elements, is contained in complex silicate minerals including monazite, bastnäsite, cerite, gadolinite and samarskite. Monazite [(Ce,La)PO₄] and bastnäsite [(REE)CO₃F] are the two main minerals sources from which Sm is extracted while in monazite, in some cases, samarium concentration is up to 2.8% w/w. World production of samarium oxide is about 700 tonnes per year and world-wide reserves are estimated to be around 2 million tonnes. China is the major Sm producer, however, significant resources of the metal occur also in: US, Brazil, India, Sri Lanka and Australia. It is expected that new mines in Australia, Canada and the United States will provide additional supply of the metal. The main current world Sm deposits occur in southern Jiangxi, western Fujian provinces where Sm with neodymium and europium contained in weathering profiles of granite complexes (consisting of biotite, biotite-muscovite and muscovite granites). Phalaborwa complex in South Africa consists of a second notable Sm rich deposit. Samarium is contained in fluorapatite [3Ca₃(PO₄)₂·CaF₂] phase [4].

As can be seen in Figure 3, the major steps in the processing of a REEs (including samarium) ore include: mining, beneficiation, chemical treatment, separation, reduction, refining and purifying [5]. The first step comprises the mining of the ores with a REEs concentration ranging between 0.05 and, in some cases, 10%. The majority of rare earth ores are produced via open pit mines. The second step concerns the beneficiation of the REE ore resulting in the production of a concentrate with a 50% REE oxide content. A combination of physical and flotation methods are used for the enrichment of REE ores. Usually prior to flotation typical ores are submitted to magnetic and electrostatic separation. Ilmenite, garnet, xenotime, and monazite, in decreasing order of magnetizability, behave as magnetic minerals. In electrostatic separation, ilmenite and rutile behave as conducting minerals and at other times behave as non-conducting phases. Step 3 of the REE processing route involves the chemical treatment of the concentrate aiming to the decomposition (dissolution) of the mineral phases. At this stage the concentration of rare earth oxides is increased to 90%. The chemical treatment process reagents can include inorganic acids [sulphuric acid (H₂SO₄), hydrochloric acid (HCl), and HNO₃], alkalis (NaOH and Na₂CO₃), and electrolytes ((NH₄)₂SO₄, NH₄Cl, and NaCl) [5]. H₂SO₄ and the alkalis are mainly used for phosphate and carbonate-fluoride ores like monazite and bastnasite. High temperature acid roasting is a common practice used in China, emitting fluoride (HF), sulphur dioxide (SO₂), sulphur oxide (SO₃), and silicon tetra fluoride (SiF₄). Step four of the process involves separation to get individual REOs, for which solvent extraction is commonly used. This process utilizes the small differences in basicity, and through this step, the REO content can be in excess of 99%. However, since the differences in basicity among REEs are small, separation for individual REOs is both time and cost intensive. Multiple stage solvent extraction is a very common procedure, and the following scheme is typically used: separation of REO in trivalent stage, fractionation of REOs into three or four groups, separation of Y, extraction of Ce (Ce⁴⁺) and Eu (Eu²⁺), and separation of desired individual REO (samarium). Common extractants

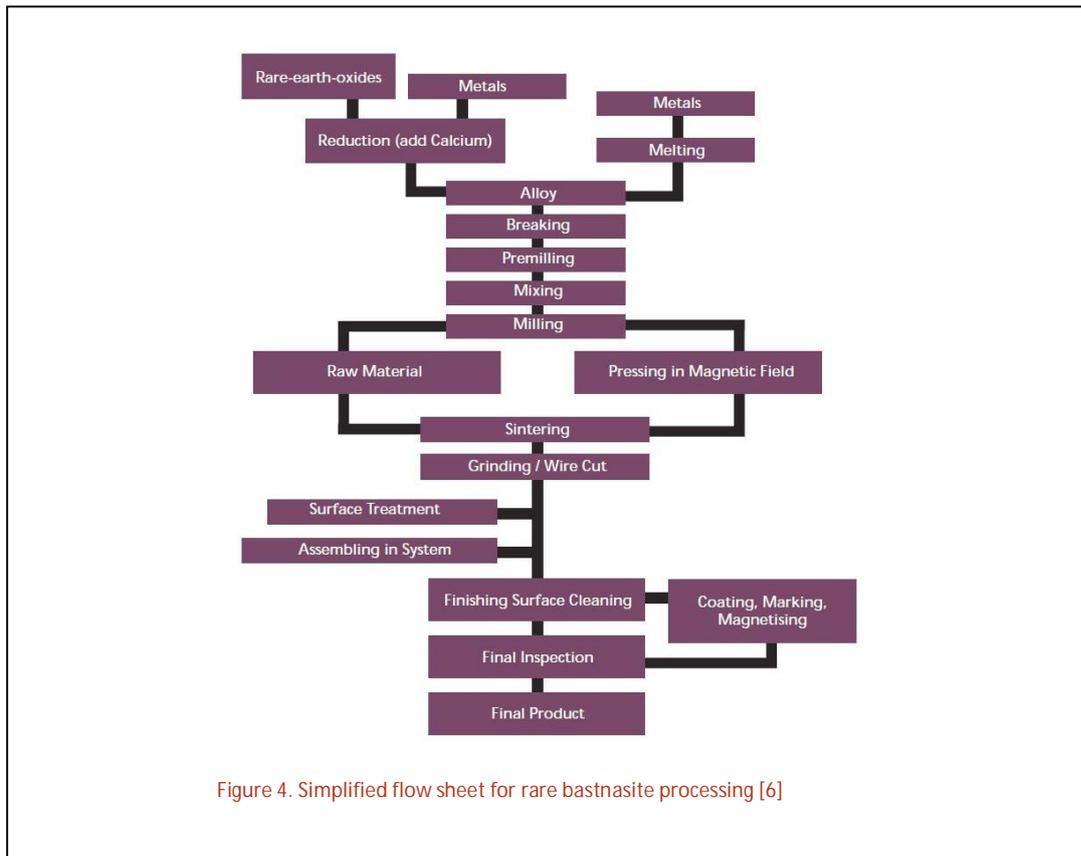
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

used in industry include di-2-ethylhexyl-phosphoric acid (D2EHPA or P204) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP or P507). Step five involves the reduction, refining, and purifying of the isolated samarium. On an industrial scale, this is generally achieved through metal other microreduction in molten salt or fused salt electrolysis (electrowinning). Finally, the refining and purifying stage can involve fused salt electrolysis, molten salt oxide reduction, metal other microreduction, zone melting, solid state transport (solid state electrolysis), etc., where the samarium purity can reach 99.99 + % [5].



After its production, metallic samarium is ready to be used as a component in Sm-Co alloy. The final process includes the appropriate shaping of the alloy in relation to the specifications of each Sm-Co product. The processes that followed are described in the flow sheet of Figure 4.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227



Concerning environmental aspects, the recovery of samarium generated significant quantities of metallurgical wastes. Although there are no available data concerning the production of samarium specifically, estimations can be based on the production of REE as a total. Rare earths metallurgy in China has raised serious environmental concerns, particularly with regards to heavy metal and radioactive emissions in groundwater, river ways, soil, plants, and the atmosphere around mine sites. The Chinese Society of Rare Earths, estimate that a ton of REE produces 8.5 kg of fluorine and 13 kg of flue dust, while refining with H_2SO_4 generates 9,600–12,000 m^3 of gas containing flue dust concentrate, HF, SO_2 , and H_2SO_4 . Other estimates indicate that producing one ton of REEs creates 60,000 m^3 of gases mixed with H_2SO_4 and HF, 200 m^3 of acid water, and 1.4 tons of radioactive waste [5].

30.2.1.2 SAMARIUM-COBALT ALLOYS

$SmCo_5$ (SmCo Series 1:5) and Sm_2Co_{17} (SmCo Series 2:17) are the most widely used Sm alloys used for the production of permanent magnets. Both alloys have similar strength properties with neodymium alloys and they are brittle, and prone to cracking and chipping [7].

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

SmCo_5 alloy has one atom of rare earth samarium per five atoms of cobalt. By weight this magnet alloy will typically contain 36% wt/wt samarium. SmCo_5 alloy has a very high coercivity indicating a resistance in demagnetizing.

$\text{Sm}_2\text{Co}_{17}$ alloys contain a number of a wide number of other elements such as iron and copper as well as zirconium and hafnium in minor quantities in order better heat treatment response be achieved. By weight, the alloy generally contains 25% w/w of samarium.

The reduction/melt method and reduction/diffusion method are used to manufacture samarium–cobalt alloys that will be used for magnets construction. Sm, Co and trace metals are melted in an induction furnace filled with argon gas. The mixture is cast into a mould and cooled with water to form an ingot. The ingot is pulverized and the particles are further milled. The resulting powder is pressed in a die of desired shape, in a magnetic field to orient the magnetic field of the particles. Sintering is applied at a temperature of 1100°C–1250°C, followed by solution treatment while tempering on the magnet at about 700°C–900°C.

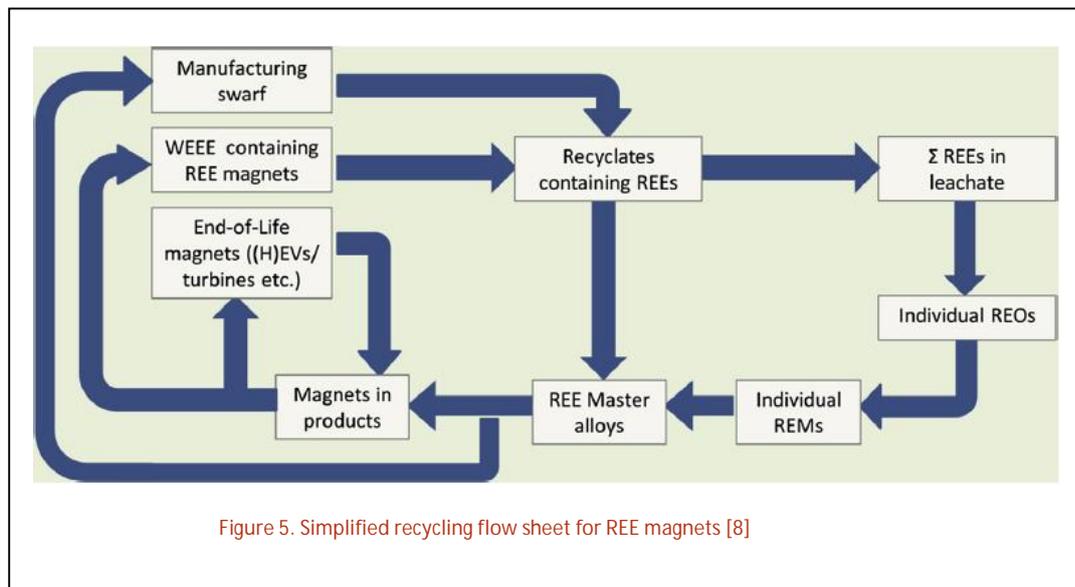
30.2.2 USAGE

Samarium-cobalt alloys are used for the construction of permanent magnets. The most widely applications comprise: high-performance permanent magnet motors, medical instruments, magnetic couplings, magnetic bearings, gyroscopes, accelerometers, voice coil motors, particle accelerators, sputtering deposition, Halbach arrays, magnetic separation devices, speakers, microphones, undulators, wigglers and particle beam focusing devices.

30.2.3 END OF LIFE

Over the 90% of the globally produced samarium is used for the construction of magnets, consequently their recycling is critical. In figure 5, a simplified overall recycling flow sheet for the REEmagnets is shown. Three different material flows are considered: (1) swarf originating from magnet manufacturing, (2) small magnets in End-of-Life consumer products, (3) large magnets in hybrid and electric vehicles, as well as in wind turbines. Direct recycling and re-use is only relevant for the large magnets. In all other cases, the REEs magnet alloys have to be further processed. For applications where there is a very narrow distribution in the composition of the REE magnets among the different manufacturers (as in the case of computer hard disk drives, HDDs), one can consider direct use of the alloy by powder processing or by remelting of the recycled magnets to REE master alloys for the production of new REE magnets. In other cases, it is necessary to separate the rare earths from the transition metals and other elements [8,9].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227



Both the recycling of samarium and cobalt from Sm-Co magnets was economically justified in the early 1990s, however a large industrial scale process for the recovery of samarium from Sm-Co magnets is not so far applied due to several processing obstacles such as [8]:

- The manufacturing process of REE magnets produces large amounts of scrap and other residues, because of the cutting, grinding and polishing operations.
- The hydrometallurgical processing of magnets scrap generate large amounts of liquid residues.
- Up to 30% of the starting REE alloy can be lost during the manufacturing process.
- The metallurgical technologies that have been so far examined are complex and high cost.

Recycling of samarium magnets is being performed at a limited extent by the magnet manufacturing companies, but only few details about the actual recycling processes have been disclosed. The most common recycling practice is the re-melting and the re-using of the Sm-Co alloy. Nevertheless, significant efforts have been performed for the recovery of recovery of metallic samarium or samarium oxide from Sm-Co magnets. Rhône-Poulenc (now Rhodia Solvay Group) developed an aqueous process for the recycling of valuable elements from SmCo_5 and $\text{Sm}_2(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr})_{17}$ swarf. The Sm/Co swarf can be dissolved in a number of acids such as sulfuric, nitric, hydrochloric and perchloric [8, 10]. The selection of the acid that is used depends on the further process. Nitric or hydrochloric acid are preferred for a solvent extraction process, whereas sulfuric acid can be used with selective precipitation. Samarium can be almost completely precipitated as an oxalate or as a sulfate double salt with an alkaline metal or ammonium. The oxalate can be precipitated by the addition of oxalic acid. Samarium oxide (Sm_2O_3) can be obtained by calcination of the oxalate or the sulfate double salt. The transition metals will not be precipitated by oxalic acid or by sodium sulfate under these conditions. Additionally to selective precipitation, samarium can also be removed from the acidic solution by solvent extraction with tributylphosphate (TBP) or with di-(2-ethylhexyl) phosphoric acid as extractants [11].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Gas-phase extraction has been also developed for the recycling of Sm. The method is based on the transformation of Sm into volatile chloride and its separation by other metals due to differences in volatility. The method has been tested in case of $\text{Sm}_2\text{Co}_{17}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet scrap [12].

30.2.4 RESIDUE TREATMENT

As previously described the majority of Sm is recycled by the re-melting of the Sm-Co magnets. However, there are not available detailed data concerning the wastes that generated by this process.

30.3 SUMMARY

World production of samarium oxide is about 700 tonnes per year, however its demand is expected to be increased in the near future due to the next few years after the decision of automotive industries to move towards the production of electric cars. Therefore Sm-Co alloys for permanent magnets in electrical motors of vehicles will be widely used. Concerning the EU level, Volvo Company has already announced that all the new cars to be produced from 2019 and onward will be completely or partially electric-driven (hybrid), while more automotive industries are going to follow this strategy [4, 5]. The analysis of the samarium value-chain from production from primary ores to the end-of-life of Sm-Co alloy products has not been extensively described, however similar studies have been performed in case of REE in general. The recycling of Sm-Co alloys from permanent magnets is so far problematic due to the complexity of the processing routes and the generation of significant amounts of liquid wastes. The loss of metallic samarium could be significantly reduced by replacing of SmCo_5 magnets by the second generation $\text{Sm}_2\text{Co}_{17}$ magnets. The last alloy has the best reversible temperature coefficient of all rare-earth alloys, typically being $-0.03\%/^{\circ}\text{C}$ while can be used at higher temperatures.

30.4 REFERENCES

- [1] Hammond, C. R. "The Elements". Handbook of Chemistry and Physics (81st ed.). CRC press.
- [2] R. Weast, 1984. Handbook of Chemistry and Physics. Boca Raton, Florida: Chemical Rubber Company Publishing.
- [3] European Commission, 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials.
- [4] C. K. Gupta, N. Krishnamurthy, 2005. Extractive Metallurgy of Rare Earths, CRC PRESS, Boca Raton, London, New York Washington, D.C.
- [5] Rare Earths" (PDF). United States Geological Surveys. January 2010.
- [6] <https://magnet.com.au/production-flow-diagram-for-samarium-cobalt-magnets.html>

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [7] Dayton Contributes to the History of Magnetic Materials". 1998.
- [8] K. Binnemans, P. T. Jones, B. Blanpain, T. V. Gerven, Y. Yang, A. Walton, M. Buchert, 2013. Recycling of rare earths: a critical review, *Journal of Cleaner Production*, 51, pp. 1-22.
- [9] J. Navarro, F. Zhao, 2014. Life-cycle assessment of the production of rare-earth elements for energy applications: a review, *Frontiers in Energy Research*, 2 (45), pp. 2-17.
- [10] Bounds, C.O., 1994. The recycle of sintered magnets. In: Liddell, K.C., Bautista, R.G., Orth, R.J. (Eds.), *Symposium on Metals and Materials Waste Reduction, Recovery and Remediation*, at the 1994 Materials Week Meeting Location: Rosemont, IL, October 03e06, 1994. The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, pp. 173-186.
- [11] R. Torkaman, M.A. Moosavian, M. Torab-Mostaedi, J. Safdari, 2013. Solvent extraction of samarium from aqueous nitrate solution by Cyanex301 and D2EHPA, *Hydrometallurgy*, 137, pp. 101-107
- [12] K. Murase, K. Machida, G. Adachi, 1995. Recovery of rare metals from scrap of rare earth intermetallic material by chemical-vapor transport. *J. Alloys Compd.* 217, pp. 218-225.

31 TERBIUM

31.1 INTRODUCTION

Terbium (Tb) with number 65, is a silvery-white, rare earth element - the ninth member of the lanthanide series. It is a fairly electropositive metal that reacts with water, evolving hydrogen. Terbium is a silvery-white rare earth metal that is malleable, ductile and soft enough to be cut with a knife. Tb reacts with several anions and metalloids such as; nitrogen, carbon, sulfur, phosphorus, boron, selenium, silicon and arsenic at elevated temperatures, forming various binary compounds such as TbH₂, TbH₃, TbB₂, Tb₂S₃, TbSe, TbTe and TbN. In those compounds, Tb mostly exhibits mainly the oxidation states +3 and sometimes +2. The terbium(III) cation is brilliantly fluorescent, in a bright lemon-yellow color that is the result of a strong green emission line in combination with other lines in the orange and red [1,2].

Terbium is contained along with other rare earth elements in monazite [(Ce,La,Th,Nd,Y)PO₄] with up to 0.03 wt% terbium, xenotime (YPO₄) and euxenite [(Y,Ca,Er,La,Ce,U,Th)(Nb,Ta,Ti)₂O₆] with 1 wt% terbium. At the moment, the richest commercial sources of terbium are the ion-adsorption clays of southern China. Small amounts of

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

terbium occur also in bastnäsite and monazite ores. The crust abundance of terbium is estimated at about 1.2 mg/kg, while no terbium-dominant mineral has been found so far.

Terbium as a heavy rare earth element, has been classified as critical raw metal by the EU Commission taking into account its; chemical properties, geological availability, supply demands and cutting edge applications. Terbium is produced under strong monopoly conditions (as China produces the 90% of the global REE amount), therefore it presents a high supply risk [3].

Terbium is mainly used for fluorescence purposes. Terbium oxide applied in the construction green phosphors in fluorescent lamps and color TV tubes. Sodium terbium borate is used in solid state devices. The brilliant fluorescence allows terbium to be used as a probe in biochemistry. Terbium "green" phosphors (which fluoresce a brilliant lemon-yellow) are combined with divalent europium blue phosphors and trivalent europium red phosphors to provide the trichromatic lighting technology which is by far the largest consumer of the world's terbium supply. Terbium is also used as a dopant in calcium fluoride, calcium tungstate, and strontium molybdate, materials that are used in solid-state devices, and as a crystal stabilizer of fuel cells which operate at Terbium is also used in alloys and in the production of electronic devices. As a component of Terfenol-D, terbium is used in actuators, in naval sonar systems, sensorselevated temperatures [1,4].

31.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

31.2.1 PRODUCTION

31.2.1.1 FROM MINERAL ORE TO METALLIC TERBIUM

Terbium is mainly extracted by ion-adsorption clays in China. These ores comprised by aluminosilicate minerals (e.g. kaolinite, illite, and smectite) containing 0.05-0.3% %wt. REEs are physically adsorbed at sites of permanent negative charge. The ion-adsorption clay deposits are the result of in-situ lateritic weathering of rare-earth rich host rocks (granitic or igneous), which lead over geological times to the formation of aluminosilicate clays. These very fine mineral particles have the capability of adsorbing lanthanide ionsreleased/dissolved during weathering. Sub-tropical climates present ideal conditions for this lateritic process to occur. The best example of this formation process exists in Southern China (latitudes 24- 26°N), where many of such deposits are known to exist. Ion-adsorption clay ores are mined by open-pit methods and no ore beneficiation is required. A simple leach using monovalent sulphate or chloride salt solutions at ambient temperature can produce a high-grade REO product [5].

Crushed terbium-containing ion adsorption minerals are treated with hot concentrated sulfuric acid to produce water-soluble sulfates of rare earths. The acidic filtrates are partially neutralized with caustic soda to pH 3–4. Thorium precipitates out of solution as hydroxide and is removed. After that the solution is treated with

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

ammonium oxalate to convert rare earths into their insoluble oxalates. The oxalates are decomposed to oxides by heating. REE oxides are dissolved in nitric acid that excludes one of the main components, cerium, whose oxide is insoluble in HNO_3 . Terbium is separated as a double salt with ammonium nitrate by crystallization. The most efficient separation routine for terbium salt from the rare-earth salt solution is ion exchange. In this process, rare-earth ions are sorbed onto suitable ion-exchange resin by exchange with hydrogen, ammonium or cupric ions present in the resin. The rare earth ions are then selectively washed out by suitable complexing agent. Metallic terbium is produced by reducing the anhydrous chloride or fluoride with calcium metal. Calcium and tantalum impurities can be removed by vacuum remelting, distillation, amalgam formation or zone melting [6].

The environmental impact generated by the processing of terbium-rich ores is mainly related with the radioactivity of these ores. Especially, it has been found that monazite presents the higher radionuclide concentrations. It is expected that the cost and space to dispose of the radioactive waste products originated by monazite ore will rise and remain a problem to be tackled as this can result in limiting of the use of this mineral [6].

31.2.1.2 TERBIUM OXIDE TO $\text{LaPO}_4:\text{Ce,Tb}$ PHOSPHORS

$\text{LaPO}_4:\text{Ce,Tb}$ is an efficient green component of trichromatic lamp phosphors. The material is synthesized using terbium using the following mixtures : $0.65\text{La}_2\text{O}_3 + 0.40\text{CeO}_2 + 0.10\text{Tb}_4\text{O}_7 + 2.10(\text{NH}_4)_2\text{HPO}_4$ or $0.65\text{La}_2\text{O}_3 + 0.40\text{CeO}_2 + 0.10\text{Tb}_4\text{O}_7 + 2.10(\text{NH}_4)_2\text{HPO}_4 + 0.04\text{Li}_2\text{CO}_3$. The compounds react under solid state in several steps up to 1400°C . At 200°C $(\text{NH}_4)_2\text{HPO}_4$ decomposes to form syrupy $\text{P}_2\text{O}_5 \cdot \text{xH}_2\text{O}$, at 600°C (in the presence of Li_2CO_3) and 800°C (in the absence of Li_2CO_3), P_2O_5 begins to react with rare earth oxides to form mixed rare earth orthophosphates. The reaction is completed between 1000°C and 1400°C [7].

Recently, some experimental efforts have been performed for the synthesis of $\text{LaPO}_4:\text{Ce,Tb}$ through spray pyrolysis technique. Lanthanum nitrate, terbium nitrate and cerium nitrate are dissolved in distilled water and nitric acid 0.6 M is added to prepare homogeneous liquid solution. The dissolved solution is poured into an aqueous solution of phosphoric acid 0.3 M. The temperature of the hot-wall reactor is increased from 600 to 1550°C . In order to prevent oxidation of Ce^{3+} to Ce^{4+} , a mixture of H_2 and N_2 is used as carrier gas. The overall gas flow rate is 2 L/min and the corresponding residence time of particles inside the reactor was around 4 s. The spray pyrolysis technique is more simple in comparison to the conventional while the properties of the produced $\text{LaPO}_4:\text{Ce,Tb}$ material are comparable. The main difference between commercial and spray pyrolysis synthesized $\text{LaPO}_4:\text{Ce,Tb}$ concerns their particles size (Figure 1) [8].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

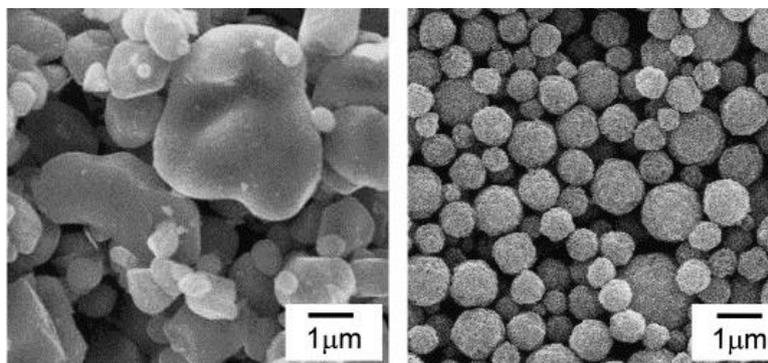


Figure 1. Commercial (left) and laboratory produced via spray pyrolysis (right) $\text{LaPO}_4:\text{Ce},\text{Tb}$ material [8].

31.2.2 USAGE

Terbium is used for pale yellow emission in $\text{Ce}^{3+}:\text{YAG}$ material in light-emitting diodes (LEDs) as a substitution material of cerium. YAG is a material which called yttrium aluminium garnet (YAG , $\text{Y}_3\text{Al}_5\text{O}_{12}$). Due to their small size and small energy consumption, LEDs are used in a wide range of status indicators and displays on a variety of equipment and installations including; stadium displays, dynamic decorative displays, and dynamic message signs on freeways. Thin, lightweight message displays are used at airports and railway stations, and as destination displays for trains. Buses LEDs are used as street lights and in other architectural lighting. Also, due to their mechanical robustness and long lifetime, LEDs are successfully applied in automotive lighting on cars, motorcycles, and bicycle lights. The light from LEDs can be modulated very quickly so they are used extensively in optical fiber and free space optics communications. This includes remote controls, such as for TVs, VCRs, and LED Computers, where infrared LEDs are often used. Opto-isolators use an LED combined with a photodiode or phototransistor to provide a signal path with electrical isolation between two circuits. In TVs and computer green phosphors, Tb is usually contained under $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ form.

31.2.3 END OF LIFE

The improvement in recycling rates for terbium is a strategic necessity. It can only be realized by developing efficient, environmental-friendly and fully integrated recycling routes. Currently, commercial recycling of terbium from the waste phosphor is still extremely low. Despite the vast literature dealing mostly with lab-scale [9]. Figure 2 shows the flow sheet of two different routes that have been developed for the recovery of REEs from a scrap containing red ($\text{Y}_{0.95}\text{Eu}_{0.05}$) $_2\text{O}_3$, green ($\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$) and the blue ($\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$) phosphors [10]. The first process (Figure 2a) includes the alkali fusion of the scrap with sodium hydroxide using a 1:1.5 waste phosphor/NaOH mass ratio. The sintering of the mixture is performed in a furnace at 800°C for 120 min. The fusion product is cleaned several times and the insoluble matter is filtered and dried. The product afterwards is leached with hydrochloric acid at 60°C. The selective precipitation of the REE is realized with oxalic acid. Finally after oxalate precipitation and calcination, rare earth oxides (REOs) are obtained. According to the second

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

process (Figure 2b) prior to the alkali fusion, the scrap is submitted to acid hydrolysis with hydrochloric acid for 4 h at 60°C and calcium is removed by adding Na_2SO_4 . A Y–Eu chloride concentrate is obtained. The leaching residue and sodium hydroxide are mixed as 1 :2 residue /NaOH mass ratio. The mixture is sintered at 800°C for 2 h. The insoluble matter is filtered and leached with hydrochloric acid. A Tb–Ce chloride concentrate is finally obtained. The second method has an optimum yield recovery for Y, Eu, Ce and Tb 94.6%, 99.05%, 71.45%, and 76.22% respectively.

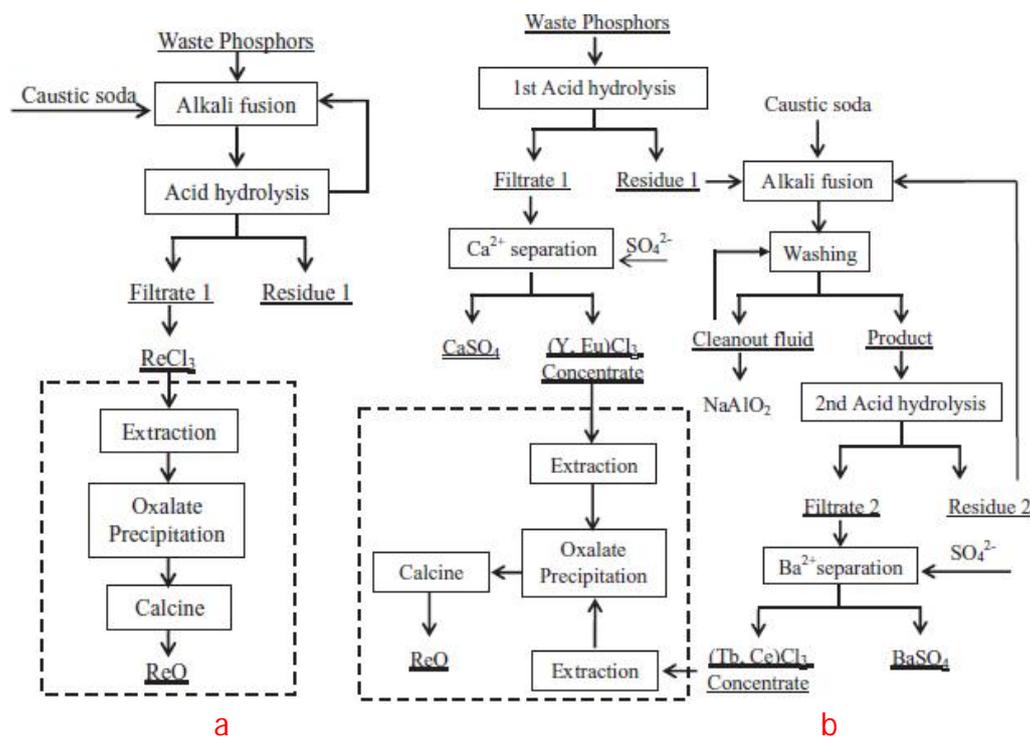


Figure 2. Flow sheet of two processes for REEs recovery from the waste phosphor [10].

31.2.4 RESIDUE TREATMENT

There are no available data concerning the environmental impact that is created by the recovery of Tb by secondary sources. However, the recycling processes which were previously described indicate that acid liquid wastes are produced as leaching with hydrochloric acid is involved in several steps.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

31.3 SUMMARY

Terbium is a soft, malleable, ductile, silver-gray metal member of the lanthanides group. It is reasonably stable in air, but it is slowly oxidised and it reacts with cold water. Terbium is rare and expensive, so it has few commercial uses. Some minor uses are in lasers, semiconductor devices, and phosphorous in colour television tubes. It is also used in solid-state devices, as stabilizer of fuel cells which operate at high temperature. The main ores of terbium are monazite, bastnasite and cerite. The main mining areas are in China, while less important mining areas exist USA, India, Sri Lanka, Brazil and Australia. The global terbium reserves are estimated at 300.000 tonnes and the world production is 10 tonnes annually. During the last years, significant research efforts have been realized concerning the recovery of Tb by secondary resources such as TV phosphors, however it is evident that acidic liquid wastes are generated via the recycling processes. Therefore, a detailed environmental impact analysis is necessary to be performed revealing the advantages Tb rich scraps treatment.

31.4 REFERENCES

- [1] P. Patnaik, 2003. Handbook of Inorganic Chemical Compounds. McGraw-Hill
- [2] C.R. Hammond, 2005. The Elements : In Lide, D. R. CRC Handbook of Chemistry and Physics (86th ed.). Boca Raton (FL): CRC Press
- [3] European Commission, 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials.
- [4] C. Rodriguez, et al., 2009. New elastomer–Terfenol-D magnetostrictive composites. Sensors and Actuators A: Physical. 149.
- [5] V. G. Papangelakis, G. Moldoveanu, 2014. Recovery of rare earth elements from clay minerals, ERES2014: 1st European Rare Earth Resources Conference, Milos, Greece.
- [6] C. K. Gupta, N. Krishnamurthy, 2005. Extractive Metallurgy of Rare Earths, CRC Press.
- [7] M-Z Su, J. Zhou, K-S. Shao, 1994. Reaction mechanism for the solid state synthesis of LaPO₄:Ce,Tb phosphor, Journal of Alloys and Compounds, 207/208, pp. 406—408.
- [8] I.W. Lenggoro et al., 2001. Synthesis of LaPO₄:Ce,Tb phosphor particles by spray pyrolysis, Materials Letters, 50, pp. 92-96.
- [9] F. Yang, F. Kubota, Y. Baba, N. Kamiya, M. Goto, 2013. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system, Journal of Hazardous Materials, 254–255, pp. 79–88.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

[10] Hu Liua et al., 2014. Rare earth elements recycling from waste phosphor by dualhydrochloric acid dissolution, Journal of Hazardous Materials 272, pp. 96–101.

32 YTTRIUM

32.1 INTRODUCTION

Yttrium (Y) with atomic number 39 is a silvery-metallic transition metal chemically similar to the lanthanides and classified as a rare-earth element (REE). It has similar physical properties to scandium. One of the few differences between yttrium the rest of lanthanides is that yttrium is almost exclusively trivalent, whereas about half the lanthanides can have valences different than +3. Yttrium is always found in combination with lanthanides in rare-earth minerals, and is never found in nature as a free element. The pure element is relatively stable in air atmosphere due to passivation of a protective oxide (Y_2O_3) film that forms on its surface. Its melting point is high (1526 °C) [1].

Yttrium, as a rare earth element, has been classified as critical raw metals by the EU Commission taking into account its chemical properties, geological availability, supply demands and cutting edge applications. Yttrium is produced under strong monopoly conditions (as China produces the 90% of the global REE amount), therefore it presents a high supply risk [2].

The average concentration of Y in Earth's crust is about 31 ppm, rendering it the 28th most abundant element, 400 times more common than silver [3]. Despite this relatively high concentration, Y is characterized as "rare" due to the limited exploitable deposits that exist worldwide and its complex and high cost metallurgical processing. Yttrium is related and occurs with the heavy rare-earth elements (HREE) group because of its ion size, though it has a lower atomic mass. Yttrium is mainly extracted by phosphate and fluoride ores. The major (almost exclusive) yttrium producer country is China (7000 metric tons), while minor amounts are produced in India, Brazil and Malaysia (100 metric tons) (US Geological Survey data for 2013).

Yttrium is mainly extracted by fluoride and phosphate minerals. Bastnäsite ($[(Ce, La, etc.)CO_3]F$) contains an average of 0.1%wt yttrium. The main source for bastnäsite until 1990s was the Mountain Pass rare earth mine in California, making the United States the largest producer of REEs during the period 1960-1990. Monazite ($[(Ce, La, etc.)PO_4]$) contains Y concentrations up to 2 %wt which and their deposits originate by the transportation and gravitational separation of eroded granite [4]. The largest Y-rich monazite deposits were found in India and Brazil in the early 20th century, making those two countries the largest producers of yttrium in the first half of that century. However, these deposits are currently already exhausted. Huge Y-rich bastnaesite and monazite ores,

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

with an average Y concentration of 0.3 % wt, exist in Bayan Obo deposit in China, making China the largest HREEs exporter. Finally, the weathered crust elution-deposited REE ore (also called ion adsorption REE deposit) in Jianxi Province, China consists the Y-richest ore worldwide containing up to 60% yttrium as yttrium phosphate (YPO_4).

Yttrium presents a wide number of cutting-edge applications. Yttria (Y_2O_3) doped with europium cation (Eu^{3+}) phosphors is used for the construction of television cathodes. The red colour itself is emitted from the europium while the yttrium collects energy from the electron gun and passes it to the phosphor [5]. Yttrium compounds can generally serve as host lattices for doping with different lanthanide cations. Yttrium is used in the production of a large variety of synthetic garnets. $Y_3Fe_5O_{12}$ garnet ('also called as "YIG") is a very effective microwave filter, while yttrium aluminium garnet (YAG) are useful for phosphors and are an important component of white LEDs. Yttrium compounds are used as a catalyst for ethylene polymerization while yttrium barium copper oxide ($YBa_2Cu_3O_7$) is an excellent superconductor [5].

32.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

32.2.1 PRODUCTION

32.2.1.1 FROM BASTNAESITE AND MONAZITE TO YTTRIUM OXIDE

Bayan Obo REE-Fe-Nb ore deposit in Inner Mongolia consist a major source of yttrium globally. It is a giant polymetallic rare earth element (REE)-Fe-Nb ore deposit of hydrothermal origin. The estimated total REEs reserves of Bayan Obo deposit (6 %wt) are 48 million tons being the world's largest known REE ore deposit. About 15 rare earth minerals species are found in the deposit while the principal ones are bastnaesite and monazite with the ratio of 7:3 or 6:4. Figure 1 presents the beneficiation process of the Bayan Obo REE ore. The route is based on low intensity magnetic separation (LIMS) – high intensity magnetic separation (HIMS) – flotation methods for the removal of the iron content (magnetite-hematite phases). High purity magnetite is received in the LIMS concentrate, while the tailings of LIMS are processed through HIMS to recover hematite with REEs. At the REE flotation circuit, the feed grade in REO is 9.78 –12% wt. The flotation is performed at low alkaline condition (pH9) and the flotation reagents contained naphthyl hydroxamic acid. Flotation is performed at three consecutive stages with a combined REEs recovery of 72–75%. According to 2012 data, the Bayan Obo rare earth flotation concentrator had an annual productivity of 250,000 t of REE concentrates (containing 50% REO) [6].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

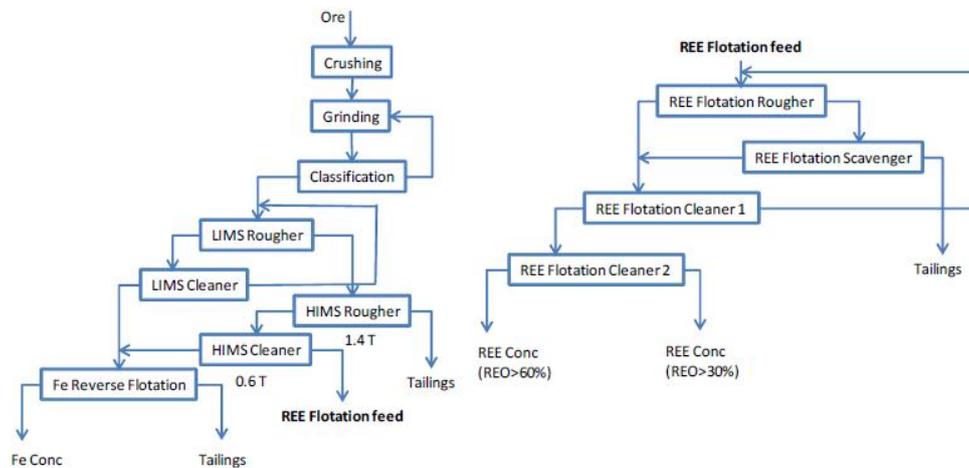


Figure 1. Beneficiation process of the xenotime ore from Bayan Obo deposit, China [6].

REE rich concentrate is submitted to hydrometallurgical processing for the production of a mixture of REEs oxides – among them yttrium oxide. Since 1980s $(\text{NH}_4)_2\text{SO}_4$ is used as leaching solvent and a high grade (REO 92%) of RE concentrate is achieved. The process is run in a cement bath with the volume of about 10–20 m³ while the added $(\text{NH}_4)_2\text{SO}_4$ solution has a concentration of 1-4% wt/vt and the pregnant solvent is obtained at the bottom of the bath. Subsequently, oxalic acid is used as a precipitant to get mid product of oxalic acid–rare earths and further processed by calcination to get final rare earths product (>REO 92%) (Figure 2). Ammonium bicarbonate also has been used as an alternative precipitant.

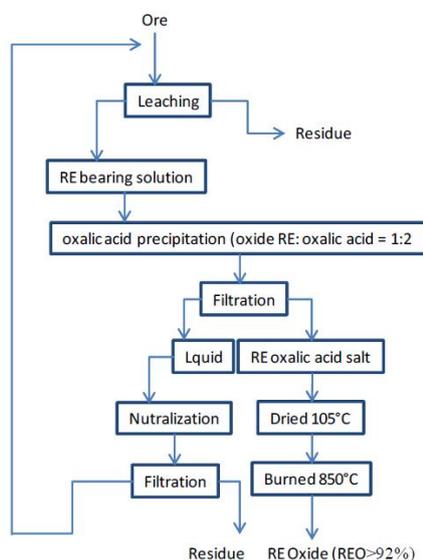


Figure 2. Metallurgical processing of xenotime concentrate [6].

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

The environmental life cycle perspective on REE oxides production from Bayan Obo deposit, China has been recently examined and quantified. Plots in Figure 3 present the primary energy consumption and greenhouse gas (GHG) emissions for producing light, medium, heavy REOs, as well as neodymium oxide. Yttrium, as has already be mentioned, comprises among heavy REOs, therefore its cycle carbon footprint is about 35 kg CO₂ eq/kg-REO, while its primary energy consumption about 579 MJ/kg-REO [7].

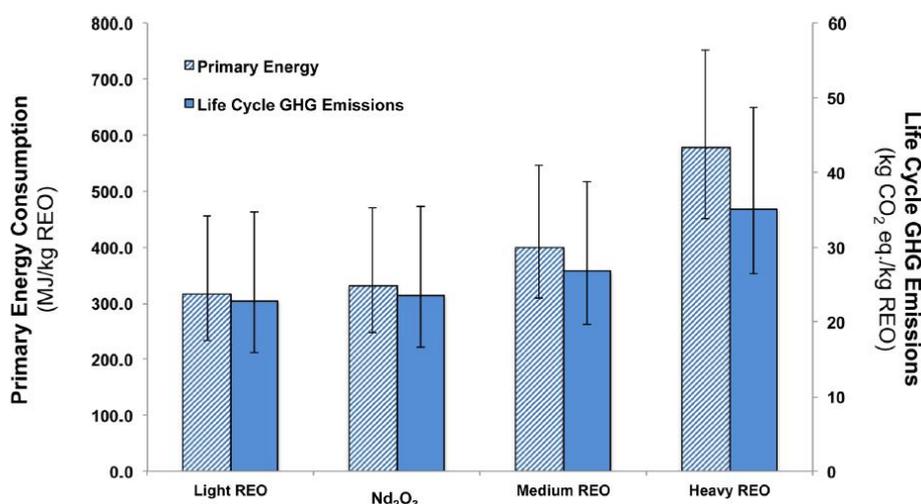


Figure 3. Life cycle greenhouse gas emissions and energy consumption for the production of various REE oxides (light, medium, heavy and Nd) [7].

A similar environmental impact analysis has been performed in case of Y rich eudialyte ore from Norra Kärr (Sweden) [8]. The study reveals that the main impact at the mining process is the release of radioactive ThO₂ and U₃O₈ rich dust contained in the raw ore. ThO₂ and U₃O₈ concentrations in the dust amount are about 0.0026 %wt and 0.0018 %wt, respectively. Environmental impact at beneficiation step is mainly due to flotation chemicals such as oxalic acid, Na₃PO₄ and H₂SO₄. The energy consumption at the metallurgical step is calculated on the basis of Dy and Nd production, therefore no exact data concerning yttrium can be received. A number of indicators such as; electric energy consumption (expressed in equivalent CO₂), human toxicity and ozone depletion are significantly lower in case of Norra Kärr in comparison to Bayan Obo [8].

Finally, it deserved to be mentioned that the leaching process for the extraction of Y in a mixture with other REEs presents a significant environmental impact. Two major technical weaknesses of the in-situ leaching process have been reported: (a) the leaching reagent solution frequently spreads around the wells resulting an environmental pollution and (b) there is a lack of an available technique for the recovery/recycling of the leachate in order its amount be minimized [6].

32.2.1.2 YTTRIM OXIDE FOR THE PRODUCTION OF EUROPIUM DOPED YTTRIA

Nanocrystalline Eu: Y₂O₃ nanoparticles with 1% Eu doping have been successfully synthesized by a novel hydrolysis assisted coprecipitation method. The materials was characterized and proved that it has advanced

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

photoluminescence in comparison to conventionally produced Eu doped yttria. The size of the nanoparticles was found to be varying between 7 and 14 nm. Yttrium nitrate hexa hydrate and europium nitrate hexa hydrate were used as precursor materials. A standard amount of water solution of yttrium nitrate and europium nitrate hydrolysed for 72 h reacts with an added amount of ammonia was added and the precipitate is obtained, washed with water and dried at room temperature. The as-prepared samples were annealed at 500 and 800 °C for 1 h in air [9].

32.2.2 USAGE

The main application of europium doped yttrium is its use for the construction of TV cathodes. Until a few years ago, colour television display tubes employed the red luminescing component using a cathode constructed by a silver activated sulphide of zinc and cadmium. Since a few years ago, many alternative compounds have been discovered for cathodes construction presenting advanced results. Rare earth oxides activated with trivalent europium show a red luminescence upon excitation by electrons. Yttrium oxide doped with europium is the most suitable material for displaying colour television. It presents a higher lumen equivalent than the sulphides upon excitation by electrons. Since the emission is moreover concentrated in a narrow wavelength range, a more natural reproduction of deep-red colours can thus be obtained and the brightness of the entire colour television picture can be increased.

32.2.3 END OF LIFE

Recently, the quantities of obsolete computers and TVs with cathode ray tube (CRT) increase and this is becoming a real major environmental problem. The waste of TVs and computers contain valuable materials as well as large quantities of hazardous elements. An ordinary CRT unit contains about 63.2% of screen glass, 24% of cone glass, 12% of ferrous materials, 0.4% of getter plus electron gun, 0.4% of ceramic seal and 0.04% of fluorescent powder. The last material contains many metals such as yttrium, europium and cadmium sulphide [10]. The recovery of Y from waste electronic equipment (lamps, CRTs, LCDs, PCBs and Li ion batteries) via metallurgical processes has been studied extensively, however the commercialization of these techniques is poor so far. An innovative laboratory scale process to recover Y and Eu from waste phosphors of TV screens has been performed. The treatment comprises the following steps: (a) roasting of the waste with ammonia chloride, (b) dissolution of yttrium chloride and europium chloride with water, (c) purification with sodium sulphide, (d) precipitation with oxalic acid and (e) calcination at high temperature (Figure 4). It was found out that when 1 g sample reacts with 8 g of ammonia chloride, the recovery rate of Y and Eu could reach 92 % and 90% respectively after 30 min reaction at 90 °C [11,12].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

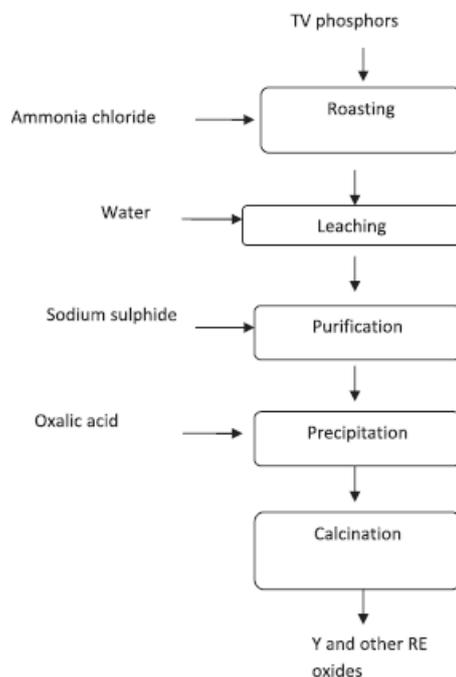


Figure 4. Metallurgical process for the recovery of yttrium oxide from TV phosphors wastes [11, 12].

Recently, a two stage HydroWEEE demo (2012–2016) project was designed for the recovery of yttrium from electronic wastes (among them TV phosphors) through an innovative hydrometallurgical process. Semi-industrial scale baths were used for the leaching of solid wastes (Figure 5). The average value of purity of the REE oxalates in general was about 70%, while the total recovery for Y was 90% [11]. The project consists a significant effort for the commercialization and the scaling up of the yttrium recovery from secondary resources.



Figure 5. Pilot scale reactor for the leaching of electronic wastes containing yttrium [11]

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

32.2.4 RESIDUE TREATMENT

The recovery of yttrium by electronic wastes scrap (lamps, CRTs, LCDs, PCBs and Li ion batteries) involves in all cases a hydrometallurgical treatment. Therefore, significant quantities of acidic liquid wastes are produced. The environmental impact of the recycling processes has been quantified so far.

32.3 SUMMARY

Yttrium is considered as a heavy rare earth element, however it has similar physicochemical properties to those of scandium. It is extracted, among other REEs, mainly from monazite and bastnäsite. China is the major Y producer country (7000 metric tons), while insignificant amounts are produced in India, Brazil and Malaysia (100 metric tons). Yttrium (mainly yttrium oxide) is used as a component in various cutting-edge applications, among them, the most important is the construction of TV cathodes. Yttrium oxide is recovered from primary resources via hydrometallurgy using various leaching agents such as H₂SO₄ and oxalic acid. The environmental impact of yttrium is well defined as there is available in the bibliography a detailed environmental life cycle analysis on heavy REE oxides production. The recovery of Y by electronic wastes is extensively examined at laboratory scale, while some efforts have been performed at semi-industrial scale (HydroWEEE demo project). Market demand data concerning Y between 2008 and 2016 [13] show a significant increase rate which is expected to be continued due to the cutting-edge applications of the metal. EU policies on CRM should be focused on the development for recycling processes for Y production taking into account the vast amounts of electronic wastes that are annually generated in EU countries.

32.4 REFERENCES

- [1] R. Weast, 1984. CRC, Handbook of Chemistry and Physics. Boca Raton, Florida: Chemical Rubber Company Publishing
- [2] European Commission, 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials.
- [3] J. Emsley, 2001. "Yttrium". Nature's Building Blocks: An A-Z Guide to the Elements. Oxford, England, UK: Oxford University Press. pp. 495–498.
- [4] A.V. Naumov, 2008. Review of the World Market of Rare-Earth Metals. Russian Journal of Non-Ferrous Metals, 49 (1), pp. 14–22.
- [5] CRC contributors (2007–2008). "Yttrium". In Lide, David R. CRC Handbook of Chemistry and Physics. 4. New York: CRC Press.
- [6] L. Zhi Li, X. Yang, 2014. China's rare earth ore deposits and beneficiation techniques, ERES2014: 1st European Rare Earth Resources Conference, Milos, Greece.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [7] G.G. Zaimes, B.J. Hubler, S. Wang, V. Khanna, 2015. Environmental life cycle perspective on rare earth oxide production, *ACS Sustainable Chemistry & Engineering*, 3 (2), pp. 237–244.
- [8] A. Schreiber, J. Marx, P. Zapp, J-F. Hake, D. Voßenkaul, B. Friedrich, 2016. Environmental impacts of rare earth mining and separation based on eudialyte: A new European way, *Resources*, 5 (32), pp. 1-22.
- [9] R. Srinivasana, N. R. Yogamalar, J. Elanchezhiyan, R. J. Joseyphus, A. C. Bose, 2010. Structural and optical properties of europium doped yttrium oxide nanoparticles for phosphor applications, *Journal of Alloys and Compounds*, 496, pp. 472–477.
- [10] V. Innocenzi, I. De Michelis, F. Ferella, F. Beolchini, B. Kopacek, F. Vegliò, 2013. Recovery of yttrium from fluorescent powder of cathode ray tube, CRT: Zn removal by sulphide precipitation, *Waste Management* 33, pp. 2364–2371.
- [11] V. Innocenzi, I. De Michelis, B. Kopacek, F. Vegliò, 2014. Yttrium recovery from primary and secondary sources: A review of main hydrometallurgical processes, in *Waste Management* 34(7).
- [12] X. Pan, L. Peng, W. Chen, J. Wang, Z. Chen, 2013. Recovery of Y and Eu from waste phosphors of CRT TVs and the preparation of yttrium europium oxide. *Applied Mechanics and Materials*. 295–298, pp. 1840–1845.
- [13] <http://www.argusmedia.jp/~media/files/pdfs/regional-specific/jp/downloads/argus-metal-pages-forum082016-rareearths.pdf?la=en>

33 SCANDIUM

33.1 INTRODUCTION

Scandium, together with yttrium and the lanthanides, is classified as a Rare Earth Element (REE). Its predominant oxidation state is $+3$. It is a soft metal with a silvery appearance while it is easily oxidized at the presence of air to a slightly yellowish or pinkish cast. Scandium is susceptible to weathering and dissolves slowly in most dilute acids however it does not efficiently react with nitric (HNO_3) and hydrofluoric (HF) acids [1].

Scandium is present in most of the deposits of rare-earth and uranium compounds, but it commercially exploitable in a limited number of deposits worldwide. It does not consist of an extreme rare metal as its concentration in Earth's crust (18-25 ppm) is comparable with the respective concentration of cobalt however, its low availability and its complex extractive processing are the main factors for its limited produced amount [2].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

Scandium has been classified by EU Commission as a candidate critical raw material as it presents a number of specialized applications. Despite its classification as a REE, scandium has been treated completely separately as its production and applications are not strongly linked to the other REEs [3]. Its production is limited in only 3 localities worldwide; the uranium and iron mines in Zhovti Vody in Ukraine, the rare-earth mines in Bayan Obo, China and the apatite mines in the Kola peninsula, Russia, therefore its supply can be easily affected by future economic and political instabilities [4].

Metallic scandium is mainly used as an additive in the aluminum alloys. A small addition (0.2-0.6 wt.%) of Sc in aluminum dramatically improves the mechanical and physical characteristics. It has been possible to achieve an ideal combination of strength, density, and thermal stability because due to the formation of the Al₃Sc phase and the unique precipitation-hardening characteristics that are introduced. Al-Sc alloys were firstly developed in Soviet Union while currently are gaining a wide popularity in aeronautical, automotive, and transportation industries. In addition to Al-Sc alloys, Al-Mg-Sc alloys have been also developed presenting extremely advanced mechanical properties [5].

Other major Sc applications comprise the construction of metal-halide lamps containing scandium iodide, the synthesis of a very hard mixed carbide by mixing about 20 percent scandium carbide with titanium carbide and its using as a host phosphorous materials in TV and computer monitors ion activators [6].

33.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

33.2.1 PRODUCTION

33.2.1.1 FROM BASTNASITE TO SCANDIUM OXIDE

The scandium minerals containing appreciable quantities of scandium such as thortveitite, euxenite, and gadolinite are rare. Pyroxenite, ilmenite, zircon and bauxite consists of the main Sc raw sources. In these ores, Sc⁺³ substitutes elements with a similar ionic radius such as Fe²⁺, Mg²⁺, Ca²⁺, Mn²⁺, Al³⁺ and Zr⁴⁺. Ores with the scandium content between 0.002 and 0.005 wt.% are considered as exploitable resources. Australia, USA, China, Kazakhstan, Madagascar, Norway, Russia and Ukraine are the countries with main scandium resources. In US, scandium resources are mainly found in uranium, tantalum, aluminium and zirconium ores; in Australia in nickel laterite ores; in China in iron, tin and tungsten ores; in Kazakhstan in uranium ores; in Madagascar and Norway in pegmatite rocks; and in Russia and Ukraine in iron ores. The global annual Sc production is 2 tonnes. Only about 400 kg are extracted by primary sources while the rest amount is originate stockpiles of Russia generated during the Cold War. Several pyrometallurgical and hydrometallurgical methods have been developed for the recovery of Sc by primary ores and metallurgical wastes. Below, the most significant processing routes are described.

The scandium contained in relatively notable concentrations ranging between 20 and 50 ppm in REEs ores such as monazite and bastnasite in Baotou, China. The main mineral in the ore is bastnasite containing scandium,

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

yttrium, lanthanides, iron and thorium and about 50% of the REE mass is cerium [7]. Scandium is industrially extracted into solutions by roasting the ore in concentrated sulphuric acid at 250–300 °C and then leaching with water. Scandium is subsequently separated by impurities (Th, Fe, Ca, F and P) in the leach liquor with acidic organic-phosphorus extractants [8]. The flowsheet in Figure 1 presents the processing of ionic-adsorption rare earth deposit (IARED) in China containing a trace amount of ionic-state scandium (9–11 ppm). The metal is leached by $(\text{NH}_4)_2\text{SO}_4$ solution and precipitates as oxalate salts. The REE concentrates are calcined to obtain rare earth oxides. The scandium oxide is dissolved with HCl and the other rare earth oxides are co-dissolved [7].

Scandium is separated by REEs using two different solvent extraction circuits (Figure 1); an organic solution consisting of naphthenic acid and iso-octanol in sulphated kerosene. In the first circuit, the scandium was enriched from 0.02–0.04% to 15–20% Sc_2O_3 in REO (rare earth oxides), while in the second circuit, the obtained scandium concentrate was further purified to 99.99–99.999% grade.

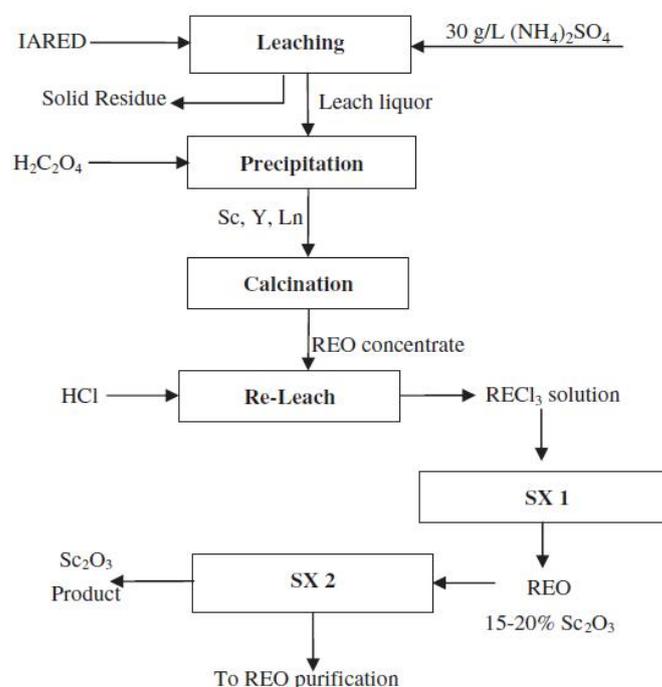


Figure 1. Flowsheet to recover scandium from ionic-adsorption rare earth deposit in China [7].

At this point, it should be mentioned that scandium is also commercially extracted by a number of alternative raw sources. The recovery of Sc from uranium ores deserves to be mentioned. Trace amounts of scandium are found in most uraninite ores and in some cases (Ukraine iron-uranium ore) these ores are processed aiming Sc recovery. The general processing concept comprises the leaching of the uranium ore with sulphuric acid, and the generation of a leach liquor containing up to 1 mg/L Sc_2O_3 . Uranium can be completely extracted with dodecyl phosphoric acid (0.1M), while scandium, thorium and titanium are recovered by treating an organic bleed stream with hydrofluoric acid which precipitates both scandium and thorium (Fig. 2). The scandium–thorium fluoride

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

precipitate containing 10 wt.% Sc_2O_3 and 20 wt.% ThO_2 . The precipitate is then dissolved with a NaOH solution at 75–90 °C, filtrated and Sc is separated using oxalic acid.

Finally, the Sc recovery from metallurgical wastes has been attempted at laboratory scale. The recovery of Sc from red mud residue is achieved by leaching with sulfuric acid followed by separation with ion exchange processing [7]. Scandium has also been extracted by titanium residues and ilmenite slags [9].

33.2.1.2 SCANDIUM OXIDE TO ALUMINUM-SCANDIUM ALLOY

As already has been described, by adding a small amount of Sc to aluminum alloys, appreciable improvements are attained concerning the mechanical strength, thermal resistance at high temperatures, as well as, enhancement in super plasticity due to fine grained recrystallized structures. An innovative method for the production of an Al-Sc alloy by metallothermic reduction has been developed [10].

Aluminum (Al) and calcium chloride (CaCl_2) are used as the collector metal and flux for the reduction, respectively. A mixture of Sc_2O_3 , Al, and CaCl_2 in a tantalum crucible is placed inside a stainless steel reaction container, and the feed mixture reacts with calcium (Ca) vapor at 1273 K for 6 h (Figure 2). After reduction process, the reaction product (CaO), CaCl_2 flux, and excess Ca reductant are removed from the obtained alloy sample by leaching with an aqueous solution. The formation of Al_3Sc in the Al matrix phase of the alloy is confirmed by X-ray diffraction (XRD) and electron microprobe analysis. The results indicates that Sc_2O_3 is successfully reduced to metallic Sc and alloyed in situ to form liquid Al-Sc alloy during the reduction.

The method has been so far examined at laboratory scale, however the results are encouraging concerning its scaling up.

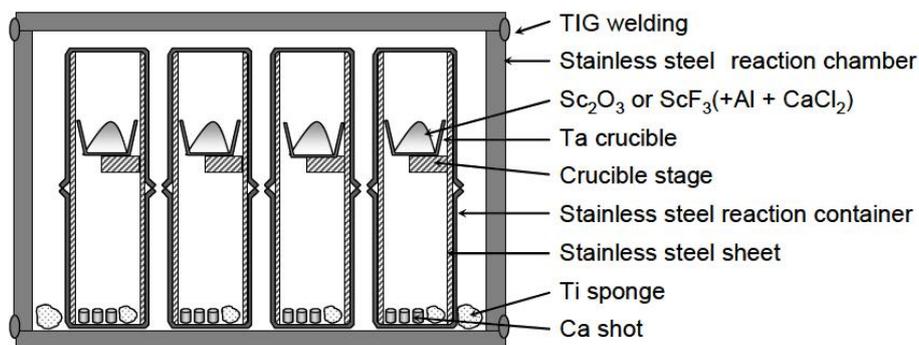


Figure 2. Experimental set up for the metallothermic reduction of scandium oxide [10].

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

33.2.2 USAGE

In addition to its use in specific aeronautic applications (parts of fighter MIG 29), aluminum-scandium alloys are increasingly used in various advanced products. Recently softball and baseball bats were successfully constructed by Al-Sc alloys. This success was followed by the manufacture of mountain and road bicycle frames and components. The bicycle frames showed a 12% reduction in weight, a 50% increase in yield strength, and a 24% improvement in fatigue life over the best-selling aluminum bicycle [5]. The use of Sc in aerospace sector is possible to be extended in the near future for applications such as; bulk heads, heat shields, forgings and extrusions for seat tracks, wheels, running gear, and fuel and exhaust systems. Aluminum-scandium-magnesium alloys are promising for automotive and air transportation applications because of their capability of weight reduction on critical moving parts. Al-Sc alloys could also be used in the cylinders of diesel engines for power boats due to their exceptional corrosion resistance shown saltwater environment. Furthermore, Al-Sc alloys could be used for the construction of heat exchanger tubes in desalination plants. The potential of scandium alloys is highly promising, however the low availability of the metal and the complex process for its production detains its wide use in cutting edge applications.

33.2.3 END OF LIFE

The metallurgical practice of simple aluminum parts recycling comprises the smelting at $750\text{ °C} \pm 100\text{ °C}$ to produce molten aluminium. Dross is removed and the dissolved hydrogen, which is formed as molten aluminium readily disassociates hydrogen from water vapour and hydrocarbon contaminants, is degassed using chlorine and nitrogen gas [11]. However the process is more complex in case of Al-M (where M is Mg, Li, Sc) alloys where metals separation should be performed. There are no available detailed bibliographic data concerning the recycling of Al-Sc alloys possibly due to the limited use of these specific alloys. The patent US7550028B2 describes a pyrometallurgical process for the recycling of aluminum-lithium alloys that can also be applied in case of aluminum-scandium alloys [12]. The method is based on the submersion of the scrap particles into a liquid metal bath. Different liquid metal layers are formatted with an intermediate concentration in lithium (alternatively scandium). The lithium layer is gradually enriched and received. Unfortunately, no further precise data are provided in the description of the patent.

33.2.4 RESIDUE TREATMENT

The recovery/recycling of scandium from aircraft industry scrap (Aluminium-scandium alloy parts) has not been so far extensively described in the bibliography. A limited number of available data (mainly patents) describe a pyrometallurgical route that has been developed in case of Al-Sc alloys. Therefore, the expected environmental impact of the recycling process concerns the high electrical energy consumption and the generation of metallurgical drosses.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

33.3 SUMMARY

The absence of reliable and long term Sc primary resources in combination with the high price of the metal has limited its commercial applications. The global scandium production does not exceed the 2 tonnes per year under scandium oxide form, while only three exploitable scandium-mining areas exist worldwide (the uranium and iron mines in Zhovti Vody in Ukraine, the rare earth mines in Bayan Obo, China and the apatite mines in the Kola Peninsula, Russia). According to 2009 data, the prices of scandium oxide (Sc_2O_3) in 99.0% and 99.9% purity are US\$ 900/kg and US\$ 1400/kg, respectively [13].

There is a lack of a detailed analysis of Scandium value-chain from primary ores production to the end-of-life aluminium-scandium products revealing that scandium is recycled at industrial scale. The recycling of aerospace components, constructed during the cold, in Russia consists of an exception.

The scandium demand and its globally produced amount are expected to increase at the close future as new applications involving the use of Sc have been recently developed in the sectors of aerospace and high tech industry. Currently, EU Commission finances an ambitious engineering project (SCALE) that examines the recovery of Sc from secondary resources such as bauxite residues resulting from alumina production and acid wastes (50-100 ppm) from TiO_2 pigment in which Sc concentration is ranged between 50 and 150 ppm [14].

33.4 REFERENCES

- [1] R. Weast, 1984. CRC, Handbook of Chemistry and Physics. Boca Raton, Florida: Chemical Rubber Company Publishing.
- [2] Lide, David R. (2004). CRC Handbook of Chemistry and Physics. Boca Raton: CRC Press.
- [3] Report on critical raw materials for EU, Report of the Ad hoc Working Group on defining critical raw materials, 2014.
- [4] Mineral Commodity Summaries 2015: Scandium, United States Geological Survey.
- [5] A. Zaki, 2003. The Properties and Application of Scandium-Reinforced Aluminum, The Journal of The Minerals, Metals & Materials Society, 55 (2), pp. 35-39.
- [6] C.R. Hammond, CRC Handbook of Chemistry and Physics 85th ed., Section 4: The Elements.
- [7] W. Wang, Y. Pranolo, C. Y. Cheng, 2011. Metallurgical processes for scandium recovery from various resources: A review, Hydrometallurgy 108, pp. 100–108.
- [8] D.Q. Li, Y. Zuo, S.L. Meng, 2004. Separation of thorium(IV) and extracting rare earths from sulfuric and phosphoric acid solutions by solvent extraction method. Journal of Alloys and Compounds. 374, pp. 431–433.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [9] R.J. Feuling, 1991. Recovery of scandium, yttrium and lanthanides from titanium ore. United States Patent No. US5049363.
- [10] M. Harata, T. Nakamura, H. Yakushiji, T. H. Okabe, 2008. Production of scandium and Al-Sc alloy by metallothermic reduction, *Mineral Processing and Extractive Metallurgy*, 117 (2), pp. 95-99.
- [11] <http://www.keytometals.com/Article83.htm>
- [12] <https://patents.google.com/patent/US7550028>
- [13] Hedrick, J.B., 2010a. Scandium. *Mineral Commodity Summaries 2010*. U.S. Geological Survey.
- [14] <http://scale-project.eu/>

34 SILICON METAL

34.1 INTRODUCTION

Silicon is a tetravalent metalloid semiconductor and the second most abundant element in the Earth's crust (about 28% by mass) after oxygen. Over the 90% of Earth's crust is composed of silicate minerals while rarely occurs as a pure element [1]. At standard temperature and pressure, silicon is a shiny with a bluish-grey metallic lustre; as typical for semiconductors, its resistivity decreases as temperature rises. Pure silicon is an insulator at room temperature. Its doping with phosphorus, arsenic, or antimony introduces one extra electron per dopant and these may then be excited into the conduction band either thermally or photolytically, creating an n-type semiconductor. Silicon crystallises in a giant covalent structure at standard conditions, specifically in a diamond cubic lattice rendering a high melting point (1414 °C) [1,2]. Most of produced silicon amount is commercially used under silicon oxide form (silica-SiO₂) for the synthesis of ceramics, glasses and constructive materials. Silica is also used for the production of Portland cement for walkways, foundations, and roads. However, elemental silicon also has a large impact on the modern world economy. Highly purified silicon used in semiconductor electronics which are the main components of photovoltaic (PV) cells, integrated circuits, computers, cell phones, therefore the modern technology depend on it [2]. The photovoltaic industry is booming, growing at double-digit growth rates per year, and is anticipated to maintain this demand increasing for the next years. The dominant material used in PV cells is silicon and particularly multi-crystalline silicon [3].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

The global elemental Si production is 7.2 million tons (2016 data). China is the major producer (4.6 million tons) followed by Russia (747.000 tons), United States (396.000 tons), Norway (380.000 tons) and France (121.000 tons) [4].

Elemental silicon was comprised in the list of critical materials by European Commission for first time in 2013. Silicon is characterized as a high supply risk due to high proportion of production from China, with the remainder spread out across other countries. The economic importance is calculated as high due to use in metallurgy and chemicals sectors. There is no recycled input and the options for substitution are limited. It is expected that Si will present a moderate average demand growth to 2020 [5].

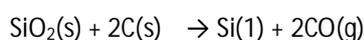
34.2 ENVIRONMENTAL ISSUES AND CIRCULAR ECONOMY ASPECTS

34.2.1 PRODUCTION

34.2.1.1 FROM MINERAL ORE TO ELEMENTAL SILICON

Silica exists in nine different crystalline forms or polymorphs. The most common of them are quartz, tridymite and cristobalite. It also occurs in a number of cryptocrystalline forms such as chalcedony, opal and onyx. Quartz is the second most common mineral in the earth's crust. It is found in all three of the earth's rock types - igneous, metamorphic and sedimentary. It is particularly prevalent in sedimentary rocks since it is extremely resistant to physical and chemical breakdown by the weathering process, however in only few cases quartz deposits have a commercial significance [6]. The crucial factor that determines the exploitability of a quartz deposit is its purity degree. The most usual impurities comprise clay minerals and iron-chromium oxides. Silica under fine quartz crystalline form (also called "sand") mining is performed in open pits and the materials grain size in ranged between 0.06 and 2.00 mm. Deposits with at least 95% SiO₂ are considered as pure. Silica contained in quartzite rock or in quartz veins is preferred as mineral source for the production of elemental silicon. The most significant high purity silica deposits exist in Australia, Brazil and United States [6].

The metallurgical processing of silica can be seen in the flowsheet of Figure 1. The main step comprises the carbothermal reductive smelting of silicon dioxide in submerged arc furnaces at high temperatures (>1900 °C). The raw materials preferred are lumpy quartz and carbon. Reducing agents generally consist of metallurgical-grade coal, woodchips, charcoal and coke. The reduction is described by the following general reaction:



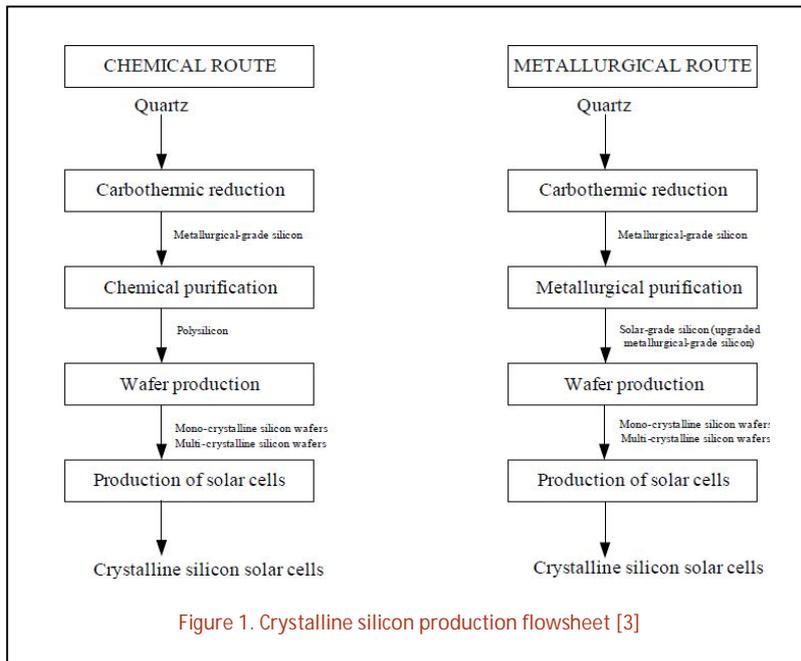
The mixture of quartz and reducing agents is charged from the top and heated by an intense electric arc sustained between the tips of three submerged electrodes and the electrical ground of the furnace. Liquid silicon metal is then tapped from the bottom of the furnace in 97–99%. Silicon with this purity is called "metallurgical-grade" silicon and it can be used for aluminum and steel alloying. Approximately 12 kWh/kg of electrical energy is consumed for its production and its total cost is 4\$/kg [7]. The impurities present in metallurgical-grade silicon

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

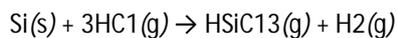
include Fe, Al, Ti, Mn, C, Ca, Mg, B and P. The minimum required purity of silicon for photovoltaic applications is 99.9999 wt% corresponding to solar-grade silicon. The cost of solar-grade silicon is ranged between 15 and 50 \$/Kg. The production of solar-grade silicon based on the further processing (refining) of the metallurgical grade silicon through two alternative processes; metallurgical and chemical (Figure 1).

The refining process consists of several techniques, each of them focusing on the elimination of specific type of impurities. Among the most important techniques can be mentioned; slagging, alloying, evacuation, gas blowing, oxidation, volatilization, electron beam melting, plasma purification, acid leaching and solvent refining. The above techniques are usually used combinatorially aiming to the receiving of high purity silicon [7-10]. Slagging is usually done by treating molten silicon with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$, CaO-SiO_2 , $\text{CaOSiO}_2\text{-CaF}_2$ or $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slags at high temperatures (about 1500 °C). Impurities such as Al, S, P, Ga, Ca, B and Ge oxidize and dissolve in the slag. It is crucial that the type of slag used in removing impurities has a higher solubility for impurities than molten silicon in order Si losses be minimized. Evacuation involves heating molten silicon under vacuum aiming to the volatilization of impurities with high vapor pressure, such as P. Oxidation and volatilization techniques are used to convert impurities in molten silicon to other species, which can be received as a slag. Oxidation is performed by bubbling oxygen through molten silicon leading to the formation of oxides. Boron is removed by this technique as boron oxides are stable in the vapor phase. The volatilization method involves the reaction of impurities such as B, P, Al, and Mg with species such as oxygen, hydrogen or chlorine and subsequently removing them in the vapor phase. Through the alloying process, metallurgical-grade silicon is melted in the presence of a low melting solvent metal alloy such as Si-Al. Impurities such as B, Ni, Fe, Al, Cu and P which have low solubility in solid silicon can be removed in the Si-Al phase during solidification. The refining efficiency depends on these segregation behavior of impurities in solid silicon and the liquid phase. Impurities such as B, Ni, Fe, Al, Cu and P which have low solubility in solid silicon can be removed in the Si-Al phase during solidification. Directional solidification is the most important process in the purification route and it is performed as a final stage after the removal of impurities with high segregation coefficients by other techniques as previously described. Ni, Ti, Cr, Fe, Co, Ni, Cu and Zn are characterized as low segregation coefficients. Directional solidification is taking place in heat exchanger furnaces. The directional solidification method is based in the redistribution of the impurities (which initially are uniformly distributed) during the solidification of the melt. Impurities which lower the freezing point of the solvent are accumulated at the end of the charge, while impurities which raise the melting point travel opposite zones and are accumulated at the beginning of the charge.

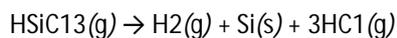
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227



In the chemical approach, the production of solar-grade silicon is achieved through reduction and pyrolysis of volatile silicon compounds produced from metallurgical-grade silicon such as SiHCl_3 , SiH_4 and SiCl_4 [7-10]. The most commonly applied chemical process, which contributes about 90% of high purity silicon production, is the Siemens batch-wise process (Figure 2) [3,7]. In this process, metallurgical-grade silicon is hydrochlorinated without using a catalyst to form trichlorosilane at 300 °C and 1 bar according to the equation:

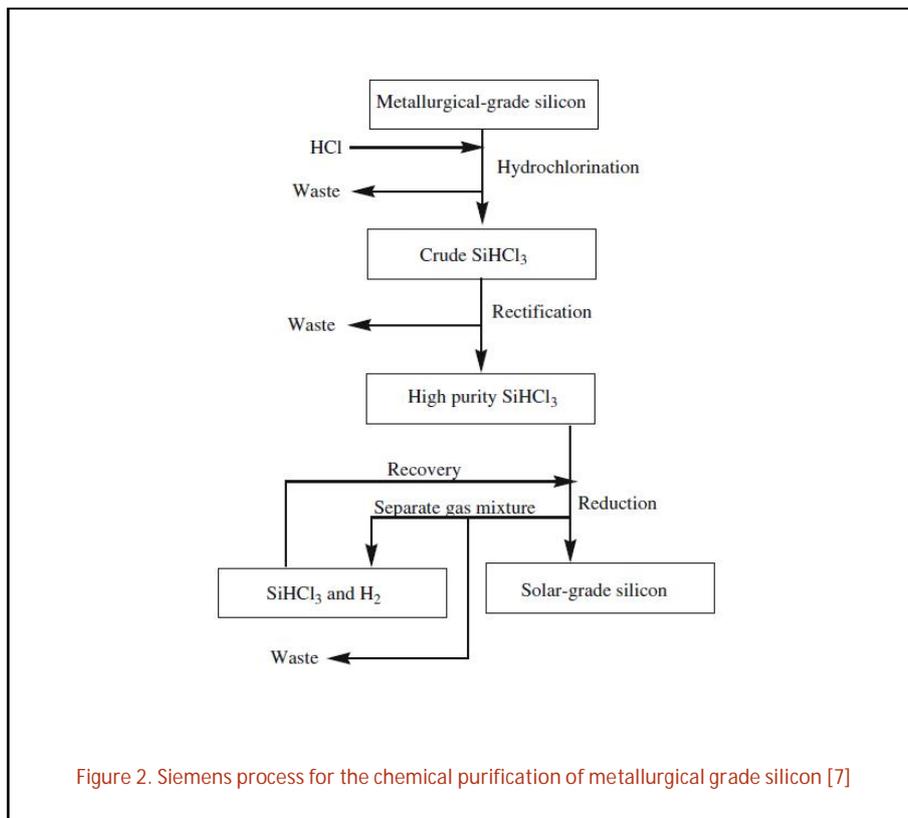


The trichlorosilane is subjected to purification by fractional distillation. High-purity SiHCl_3 is then vaporized, diluted with high-purity hydrogen at 1100°C and introduced into the deposition reactors, where pure polycrystalline silicon is formed according to:



The high energy consumption consists of an important disadvantage of the method, as it requires 200 kWh/Kg of high purity silicon.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

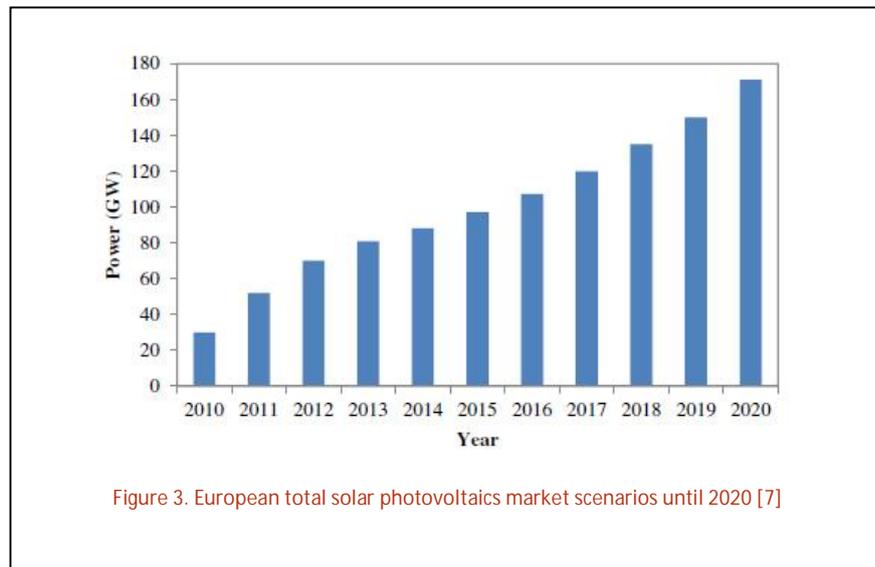


The environmental impact of the production of elemental silicon is mainly caused by; (a) the high electrical energy consumption during the carbothermal reduction of silica and therefore the high CO₂ amounts which are released and (a) the wastes that generated by the chemical purification processes. More specifically, significant quantity of chlorosilanes are produced when hydrochloric acid is involved in the purification process. These compounds are corrosive and toxic and therefore pose safety and environmental problems.

34.2.1.2 HIGH PURITY SILICON IN PV CELLS

The photovoltaic (PV) industry consists of an important sector in the renewable energy segment, and the electricity generation from photovoltaics (solar cells) is deemed to be one of the key technologies of the 21st century. Photovoltaic solar electricity presents an number of advantage such no moving parts, zero emissions, and no noise. Figure 3 shows the continuously increased power produced by PV cells in Europe which can be directly correlated with the increasing of the annual high purity silicon production [3].

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227



Until 1997, the silicon used in the production of solar cells was received by waste materials from the electronic industry, however this became unsustainable due to the high increase of high purity silicon demand the next years [3]. After its production, high-purity silicon is submitted to further processing in order good crystallographic quality sheets with a thickness of about 100 microns be constructed. Production of crystalline wafers can be achieved either by ribbon growth, or a two-step process starting with ingot casting or crystallization followed by wafer manufacturing. Multi-ingots are cut to blocks with a cross-sectional area equal to the wafer size. About 25% and 15% of the material is lost from cutting of the mono-crystalline and multi-crystalline ingots respectively. Finally, silicon PV cells are submitted to emitter diffusion in order p-type (boron-doped) and n-type (phosphorus-doped) wafers be synthesized. The process is carried out in a furnace at a temperature of approximately 900°C for phosphorus diffusion. Typical processing time is limited to about 30 minutes, and a penetration depth of about 0.5 microns is achieved [3].

34.2.2 USAGE

PV systems are connected to inverters that convert the DC produced by the PV modules to AC. The electricity can subsequently power household appliances or can be sold directly to the grid [11]. As a building receives this energy, it is distributed to appliances and lighting, or other devices where needed. Since PV systems are restricted to function only under the sun light, a backup system is frequently required to ensure continuous supply of electricity irrespective of the weather conditions. These systems are widely used in houses or commercial buildings to offset electricity cost. Additional applications that involve the usage of PV cells include; signal

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

systems (such as light houses, highway and aircraft warning signals), water pumping, charging vehicle batteries and consumer products (toys, watches, calculators, radios, televisions etc.).

34.2.3 END OF LIFE

The recycling of PV modules is not viable at the present due to their long lifespan. However, a large volume of PVs scrap is expected to be generated by 2030 while after this year over 130,000 tpa will be produced in EU countries rendering recycling sustainable [13,14]. Silicon-based PV modules, except silicon, contain also a number of valuable metals such as Ag, Cu, and Al. The recycling technology of silicon PVs has been already developed, however it has not been applied at industrial level due to the low scrap quantities at present. The simplified flowsheet in Figure 4, presents the general recycling route. According to the method Si, which is the main and most costly component of crystalline-Si cells, is received simultaneously with Ag, Al and Cu.

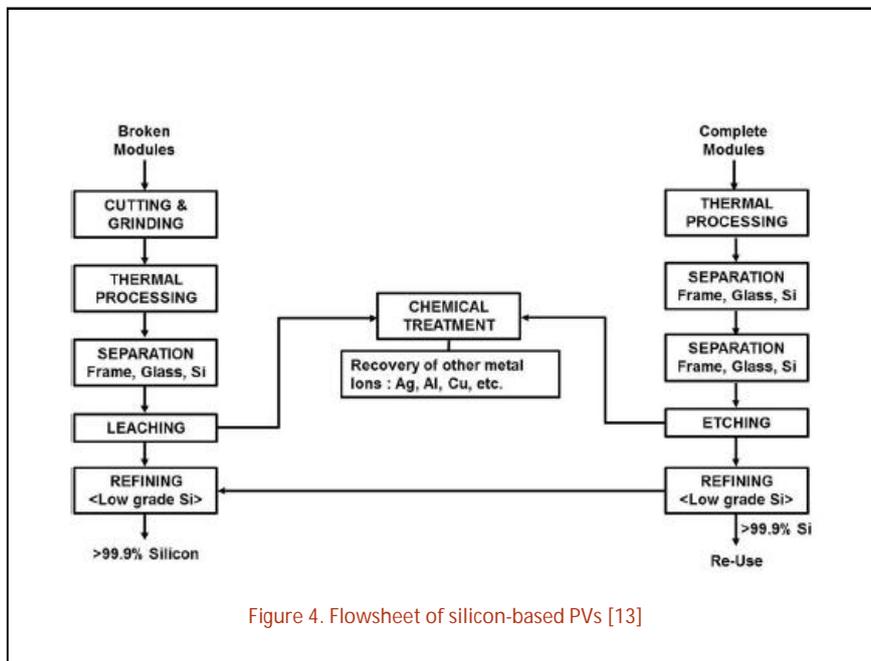


Figure 4. Flowsheet of silicon-based PVs [13]

The processing route comprises the chemical leaching of the silicon parts (with HCl or H₂SO₄ or HNO₃ and NaOH) after their separation from the frames and the glass. Via leaching, about the 100% of Ag is recovered while an alloy 99% rich in Si is received. Subsequently, Si is purified by melting at 1520°C with CaO–CaF₂–SiO₂ to produce >99.998% Si [14,15].

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

A second parameter which it deserves to be studied according the PVs recycling concerns the Si amount which is being lost during cutting and fabrication of thin Si sheets. It has been estimated that the amount that lost at mechanical treatment processes can reach the 40% w/w of the initial Si amount.

34.2.4 RESIDUE TREATMENT

The environmental impact that created by the recycling of silicon-based PV modules has not so far studied in detail due to the laboratory only scale application of the recycling processes. However, a life cycle analysis that was performed by Deutsche Solar AG (Müller's research group)[16] to determine environmental effects of the recycling process, showed that the recycling process reduces the environmental burden of processing new silicon as well as the burden associated with disposing of the PV modules through more conventional means. However, on the other hand it should be mentioned that through the recycling process, there is an environmental burden which created mainly by the thermal delamination and etchant wastes. Groups like Klugmann-Radziemska are already working to create thermal processes and etching sequences that are more environmentally friendly than the existing methods.

34.3 SUMMARY

The elemental silicon demand is expected to be increased the next years due to its usage to cutting edge technologies in electronics and mainly in silicon-based PVs. PV has experienced a constant growth in the last decades at an average rate of more than 40% since 2000. At 2013 it provided 0.1% of total global electricity generation and it is expected to provide 5% in 2030 and 11% in 2050 [10]. The end of life of the first generation silicon PVs which is expected around 2030, is going to render their recycling sustainable. After 2030, it has been estimated that over 130.000 tons of Silicon PV scrap will be generated in the European Union. The production of secondary high purity silica by the PVs scrap is expected to be crucial for the EU taking into account that the vast majority of elemental Si is produced in non-European countries. Currently, efficient recycling technologies have been developed and tested at laboratory scale. The methods comprise the isolation and purification of Si sheets. High purity silicon and other valuable metals (such as Ag, Cu and Al) are recovered using a combination of simple hydrothermal (acid leaching) and pyrometallurgical (melting at the presence of $\text{CaO}-\text{CaF}_2-\text{SiO}_2$) techniques. Life cycle analyses have shown the PVs recycling has a significant environmental benefit in comparison to primary silicon production.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

34.4 REFERENCES

- [1] Nave, R. Abundances of the Elements in the Earth's Crust, Georgia State University
- [2] Crystalline silicon-Properties and uses, 2011, Editor Sukumar Basu, InTech Publisher
- [3] B.S. Xakalashé, M. Tangstad, 2011. Silicon processing: from quartz to crystalline silicon solar cells, Southern African Pyrometallurgy 2011, Edited by R.T. Jones & P. den Hoed, Southern African Institute of Mining and Metallurgy, Johannesburg, 6-9 March 2011.
- [4] <https://minerals.usgs.gov/minerals/pubs/commodity/silicon/mcs-2017-simet.pdf>
- [5] European Commission, 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials
- [6] <http://www.eurosil.eu/what-silica>
- [7] F. Chigondo, 2017. From Metallurgical-Grade to Solar-Grade Silicon: An Overview, Silicon, pp. 1-10.
- [8] D. Luo, N. Liu, Y. Lu, G. Zhang, T. Li, 2011. Removal of boron from metallurgical-grade silicon by electromagnetic induction slag melting. Transactions of Nonferrous Metals Society of China, 21, pp. 1178–1184.
- [9] T. Yoshikawa, K. Arimura, K. Morita, 2005. Boron removal in the solidification refining of Si with Si-Al melt. Metallurgical and Materials Transactions B,36, pp. 842–847.
- [10] R. Kvande, 2008. Incorporation of impurities during directional solidification of multicrystalline silicon for solar cells. Thesis. Norwegian University of Science and Technology, Trondheim.
- [11] http://www.labri.fr/perso/billaud/Helios2/resources/en10/Chapter_10_EN.pdf
- [12] PV Cycle. 2011. Annual Report 2011. http://www.pvcycle.org/wp-content/uploads/PV-CYCLE_Annual-Report_2011_FINAL.pdf.
- [13] Y. K. Yi, H. S. Kim, T. Tran, S. K. Hong, M. J. Kim, 2014. Recovering valuable metals from recycled photovoltaic modules, Journal of the Air and Waste Management Association, 64 (7), pp. 797–807.
- [14] http://www.bine.info/fileadmin/content/Publikationen/Englische_Infos/projekt_0210_engl_internetx.pdf

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

[15] C. Latunussa, F. Ardente, G.A. Blengini, L. Mancini, 2016. Life Cycle Assessment of an innovative recycling process for crystalline silicon photovoltaic panels, *Solar Energy Materials and Solar Cells*, 156, pp. 101–111.

[16] A. Müller, K. Wambach, E. Alsema, E. 2005. Life cycle analysis of solar module recycling process, 20th European Photovoltaic Solar Energy Conference, Barcelona, Spain

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

35 TANTALUM

Tantalum is a chemical element with the atomic number of 73. It is a part of refractory group metals which are widely used for alloys. The common occurrence is in minerals like tantalite, columbite and coltan (a mixture of columbite and tantalite).

Important tantalum resources have been identified to be contained in tantalum minerals in: Brazil 38%, Rwanda 25%, Australia 8%, Canada 8% and other sources cca 2%.

Tantalum metal resources have been identified to be in: China 19%, Indonesia 10%, Kazakhstan 9%, Austria 9% and other countries cca 53%.

Tantalum waste and scrap: Indonesia 19%, Austria 19%, China 14% and other 50%.

The total imports were: China 37%, Kazakhstan 25%, Germany 14%, Thailand 12% and other 12%.

There are other (natural) identified resources for tantalum in the world: Australia, Brazil and Canada, which are considered to meet the need of the consumption in the world. US has about 1500 tons of tantalum resources which were/are considered uneconomical to exploit due to the current low prices, Figure 1.

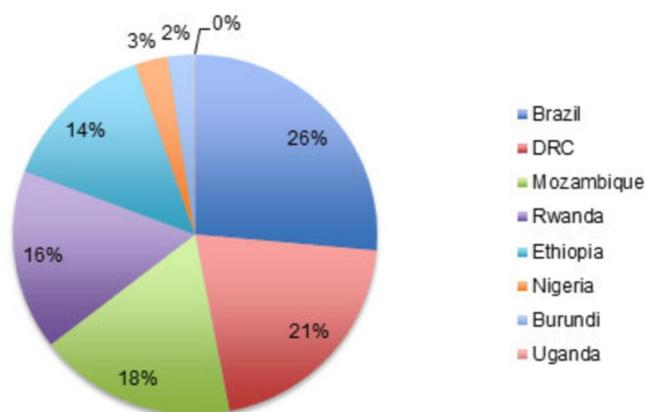


Fig. 1. Global tantalum production (USGS)

Tantalum can be extracted together with Niobium, thus can be counted as a possible secondary product from niobium mining.

Major uses of tantalum are in tantalum capacitors mostly for automotive capacitors, mobile phones and personal computers. Tantalum oxide (Ta_2O_5) is used in glass lenses, for making them more flexible and lighter, as well as to improve the sharpness. Tantalum carbide is used in cutting tools.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

The value of the consumed tantalum in 2016 has been estimated to be around 290 million US dollars.

Tantalum is recycled especially from electronic waste. There is no readily available numbers on the quantities produced this way.

Tantalum-niobium industry is a well-organized, rather exclusive circle, where the producers and users form a compact mass.

Tantalum is one of the four so-called conflict minerals, which means that the regions where the metals are extracted are conflict-affected, high-risk areas, with reports on human right abuses and instable political scene. A lot of SMEs (small medium-size companies) are part of or contribution to the extraction industry of tantalum-niobium. They are as well under the same umbrella, because, according to the latest T.I.C (Tantalum-Niobium International Study Center) bulletin (TIC 2018), large industries rely on the entire chain to meet their responsibilities.

Rather than a circular economy, in the case of tantalum there is a much broader societal outreach, teaching-training aspects, aimed at improving and training the communities directly connected to the exploitation areas. One of the reasons is that in some communities, tantalum mining companies have experienced, there are so-called “artisanal mining” of tantalum, which sips in and came to be partly the largest source of new tantalum, mostly organized in central Africa. The percent of the artisanal mining is as high as 56% compared to 34% of conventional mining.

A rather dramatic change has been observed on the dynamics of the supply and consumption of tantalum: the Chinese production is almost entirely consumed by the Chinese market, Australia has decreased dramatically the production (2% now), while a whole 63% is provided by African countries. The market is seen as a very volatile and unsteady and there is relatively little tantalum-focused mining left, and most of the potential projects are either on hold or shut down.

35.1 SUMMARY

The conclusion of the T.I.C is that Central Africa is a potential and relative accessible source of tantalum, but not necessarily a low-cost source, despite the significant progress achieved by the countries in the region.

One possible solution is that, since the Lithium is on high demand and potentially getting even more attention, tantalum which follows lithium (in some cases) could thus be another resource. However, even Lithium is in locations which experience political unrest and security issues.

35.2 REFERENCES

TIC – TIC Bulletin no. 172, January 2018.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730227

USGS (2017) – Tantalum, <https://minerals.usgs.gov/minerals/pubs/commodity/niobium/mcs-2017-tanta.pdf>, retrieved January 2018

36 TUNGSTEN

36.1 INTRODUCTION

Tungsten is used as the raw material for cemented carbides, also called hardmetals, and special steels, such as high-speed steels and heat-resistant alloys. Cemented carbides are the most important application area of tungsten today, corresponding to approximately two thirds of the annual use of tungsten. (Ishida, Itakura, Moriguchi, & Ikegaya, 2012) However, the figures concerning the primary uses of tungsten vary locally, as shown by Fig. 1.

Cemented carbides are composite materials, containing hard particles of tungsten monocarbide, WC, embedded in Co-based alloy matrix, which is strong and tough. In special steels, the tungsten contents vary from approximately 6 up to 14 wt.% (Roberts, 1998), yet the tungsten alloying amounts in steels in general may also be much lower, e.g., down to impurity level. In superduplex stainless steels, tungsten alloying may be used to improve resistance to pitting corrosion, with typical alloying amounts of, e.g., 0.7 wt.%. Tungsten has the highest melting point of all metals, thus tungsten finds use in many high-temperature applications, such as arc-welding electrodes, heating elements in high-temperature furnaces and filaments in old-style incandescent light bulbs (which have been phased out in many countries).

Fig. 2 shows the global mass flows of tungsten in 2010. The grade of different flows has direct implications in the recyclability of tungsten, as will be highlighted in the next section. In hardmetals and other carbide products, typical tungsten contents range from 65 to 95 wt.%, being considered as high grade tungsten flow. In tungsten mill products, such as wires, the composition may be even richer with respect to tungsten, >99%. Steels, in which tungsten is included as alloying element, are considered as low-grade flows, with tungsten contents <21 wt.%. Similarly, in chemicals and specialist applications, tungsten exists in low-grade form. (Leal-Ayala, Allwood, Petavratzi, Brown, & Gunn, 2015)

According to various recycling rate metrics (which do not reflect the use of a variety of metals in complex products), the EoL-RR functional recycling rate of tungsten falls between 10-25%, global average recycled content is within the category of 25-50% and the global average old scrap ratio is above 50%. (Reuter, 2013) For comparison, Leal-Ayala et al. (Leal-Ayala et al., 2015) have acknowledged that approximately 25% of total tungsten supply was end-of-life scrap in 2010. Roughly half of the tungsten scrap was recovered by chemical recycling, with another half being subjected to zinc process.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

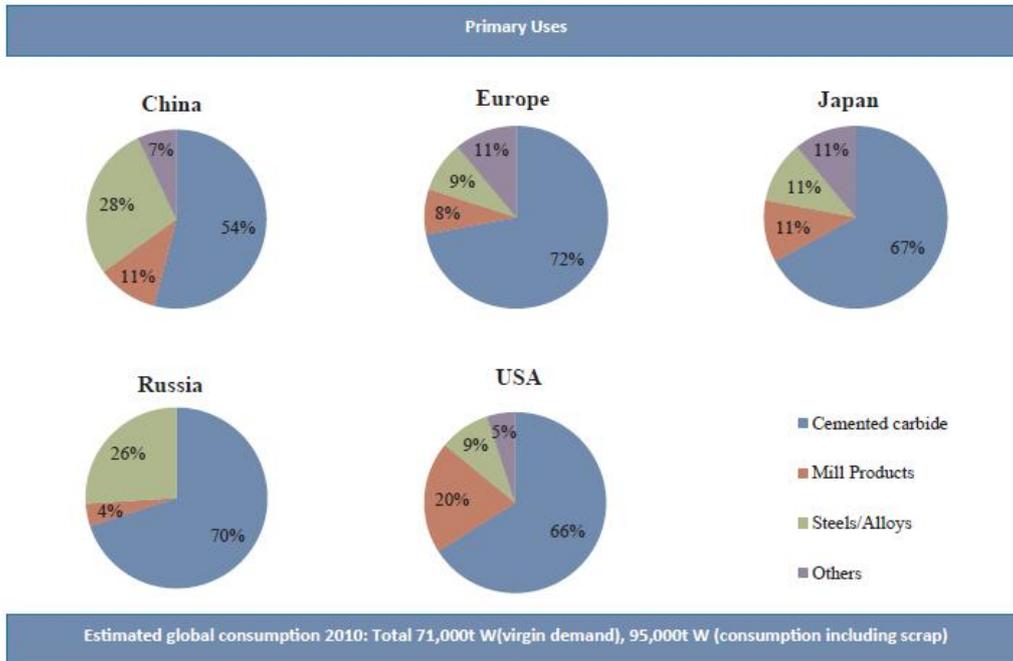


Figure 1. Primary uses of tungsten. (Shemi, Magumise, Ndlovu, & Sacks, 2018)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

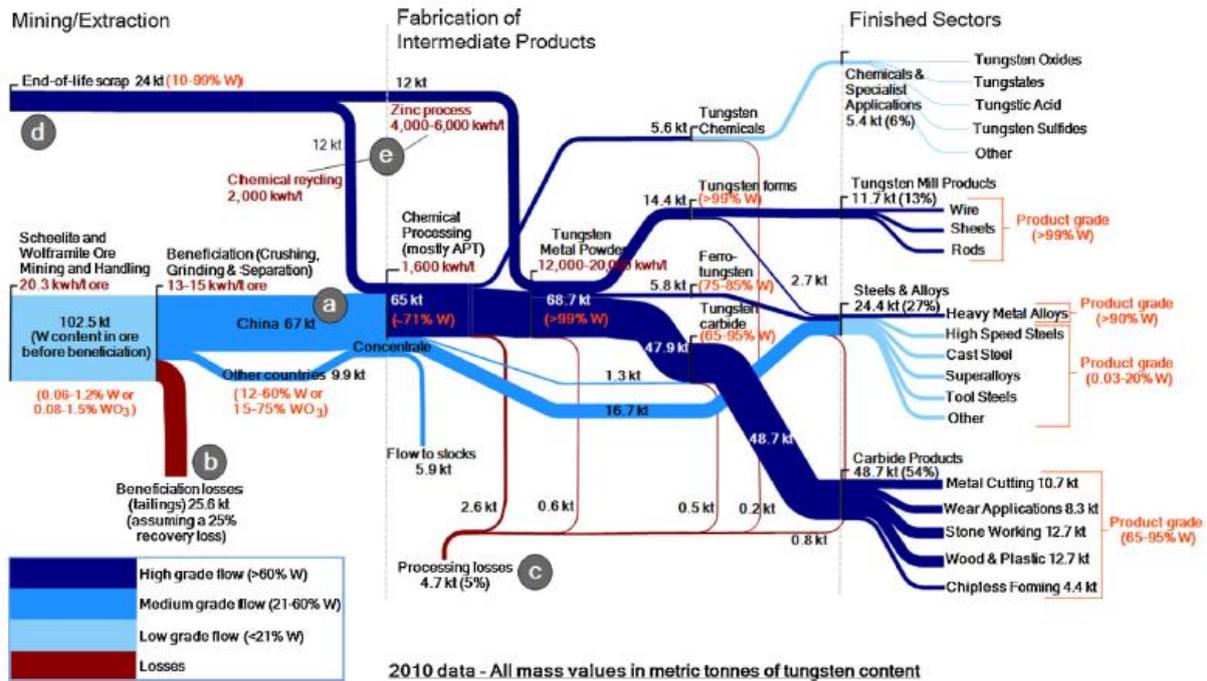


Figure 2. Global mass flows of tungsten in 2010. The definition of grades is given in the box on the down left-hand side corner of the figure. (Leal-Ayala et al., 2015)

36.2 GAPS LIMITING CIRCULAR ECONOMY

Tungsten recycling is not significantly constrained by technological availability but rather by its use in such applications where recycling is not possible due to dispersion or dilution in the material/structure. For example, tungsten contained in ferrous (steels) and non-ferrous alloys, categorized as low-grade tungsten flows as shown above, is not commonly recycled. In Fig. 2, this covers 27% of the tungsten flows. Equally, tungsten used for chemical and specialist applications, Fig. 2, is not recycled because of the high dispersion of tungsten in the material. This end sector accounts for 6% of the tungsten flows. (Leal-Ayala et al., 2015)

Besides the use as low-grade material, another key factor that limits the circular economy of tungsten is the lack of appropriate post-consumer collection systems for open-loop recycling. Vertical integration of industrial actors is one solution to seize the problem. However, also more awareness is needed among end-product consumers about the collection systems and strategies. The third gap that limits the recyclability of tungsten is the poor economic viability. Based on the energy consumption related to processing of tungsten (Fig. 2), it is evident that tungsten recycling is less energy intensive than primary production. Nevertheless, despite the energy savings, tungsten recycling is not necessarily cheaper than buying ore concentrate, due to the high cost of tungsten scrap. The experience has shown that high prices act as incentive to pursue alternative material efficiency strategies,

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

such as re-designing the same products with less tungsten. (Leal-Ayala et al., 2015) However, as pointed out above, when the tungsten content goes to low enough level, then the further recovery becomes more challenging.

At present, tungsten loss flows are most pronounced in mining and extraction. These beneficiation losses correspond to 10-40% of the original ore content and are related to the friable nature of tungsten minerals, introducing excess of fine particles that are lost during the operations. The main reasons for the loss of the fines are the poor capturing capability of the separation methods and high density of tungsten that leads to misclassification of fines by cyclones or hydraulic classifiers. Some methods have been proposed to overcome either the fine particle generation issue of extract tungsten from the mixture of tungsten ore fine particles and tailings, but the problem is that the technical viability of the proposed approach has to be accompanied by economic profitability. (Leal-Ayala et al., 2015)

36.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

The most important aspect that supports circular economy of tungsten is its availability as high-grade material. Indeed, high-grade tungsten flows are well suited to recycling. The recycling methods involve both direct physical re-use methods and semi-direct or indirect processing methods. In direct processes, the composition of scrap must be the same as that of the final product, typically of high purity. Examples of this are zinc process and cold-stream process, Fig. 3. The direct processes are well suited for hardmetal scrap and are, indeed, the preferred recycling route for hardmetal waste streams. However, these recycling processes are typically energy intensive, need special equipment and probably even further process steps to fully separate WC from the binder. The semi-direct methods involve selective dissolution of one component, leaving the other phase(s) intact. These methods are low in energy consumption and lead to recovery of both the tungsten carbides and the binder metal in the hardmetal scrap, but are not suited for the treatment of grinding sludges or other contaminated powders and are characterized by high reagent consumption and slow process kinetics. Finally, indirect recycling methods involve chemical modification of the scrap into intermediate products which are then processed to obtain pure metals. Indirect recycling methods are applicable to lower-grade tungsten sources, such as grinding sludges, floor sweepings, contaminated powder qualities etc. The process produces high-quality tungsten powders with low energy input, but involves several steps and is characterized by high reagent and time consumption. (Shemi et al., 2018)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

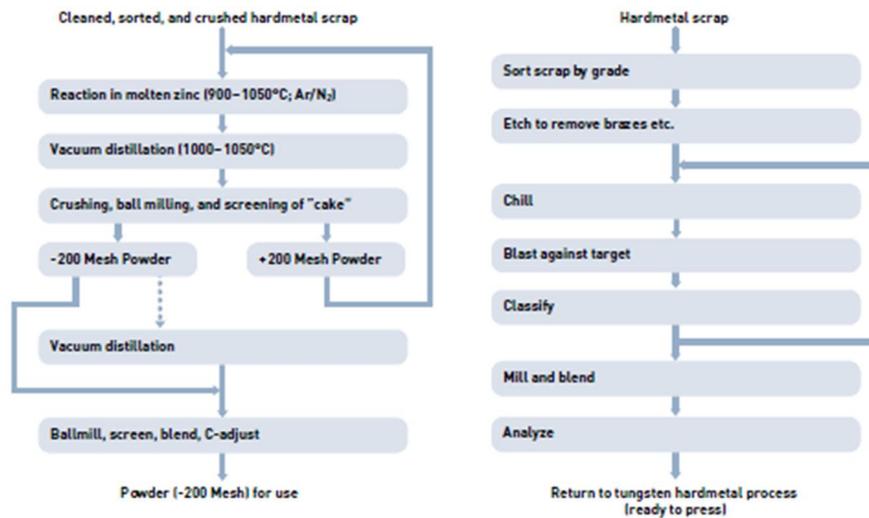


Figure 3. Flowsheets for the zinc process and the cold-stream process, from (Reuter, 2013).

Some identified drivers for tungsten recycling are the limitation of tungsten resources, environmental and energy conservation regulations, capital resource savings and savings on tungsten raw materials and import costs for countries that don't have exploitable tungsten reserves. (Shemi et al., 2018) China accounts for 62% of the amount of deposits and 85% of the ore production volume (Ishida et al., 2012), yet some reserves have been encountered also in Australia, Canada and UK (Leal-Ayala et al., 2015). This concentration of resources implies that most countries do not have tungsten resources, which should serve as incentive to recycle it. Indeed, it has been acknowledged that the balance between the primary (tungsten raw material producer, tungsten carbide manufacturers, product manufacturer) and recycling industry is leads to improved predictability and stability in tungsten raw material costs and supply. Thus, nurturing, maintaining and balancing the relationship between primary production and recycling industries is very important for supporting tungsten circular economy. (Shemi et al., 2018)

36.4 ENVIRONMENTAL ISSUES

There is emerging evidence that tungsten has toxic health effects. The potential involvement of tungsten in the development of cancers has been arisen, based on the findings of high tungsten levels in urine of leukemic patients in Fallon, Nevada. Nevertheless, also non-leukemic controls showed high body contents of tungsten (Witten, Sheppard, & Witten, 2012) In turn, Strigul et al. (Strigul et al., 2009) have demonstrated that, in aquatic systems, polytungstates are significantly more toxic than monotungstates. Overall, more work in this area needs to be done before any solid conclusions about the toxicity may be drawn.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

36.5 SUMMARY

Tungsten has the highest melting point of all metals. It is widely used in hardmetals to provide the hardness and in steels and other alloys to improve, e.g., thermal resistance. In hardmetal applications, tungsten included in monocarbides can be relatively easily recycled with established technologies. In turn, in steels and in other applications where tungsten is diluted in the material, its recycling is problematic and tungsten cannot really be recovered. It is also emphasized that tungsten mining actions are characterized by relatively poor material efficiency rates, due to excessive generation of fine particles that are lost during the operations.

36.6 REFERENCES

- Ishida, T., Itakura, T., Moriguchi, H., & Ikegaya, A. (2012). Development of technologies for recycling cemented carbide scrap and reducing tungsten use in cemented carbide tools. *SEI Technical Review*, (75), 38–46.
- Leal-Ayala, D. R., Allwood, J. M., Petavratzi, E., Brown, T. J., & Gunn, G. (2015). Mapping the global flow of tungsten to identify key material efficiency and supply security opportunities. *Resources, Conservation and Recycling*, 103, 19–28. <https://doi.org/10.1016/j.resconrec.2015.07.003>
- Reuter, M. (2013). *Metal Recycling Acknowledgments*.
- Roberts, G. A. (1998). Tool steels.
- Shemi, A., Magumise, A., Ndlovu, S., & Sacks, N. (2018). Recycling of tungsten carbide scrap metal: A review of recycling methods and future prospects. *Minerals Engineering*, 122(September 2017), 195–205. <https://doi.org/10.1016/j.mineng.2018.03.036>
- Strigul, N., Galdun, C., Vaccari, L., Ryan, T., Braida, W., & Christodoulatos, C. (2009). Influence of speciation on tungsten toxicity. *Desalination*, 248(1–3), 869–879. <https://doi.org/10.1016/j.desal.2009.01.016>
- Witten, M. L., Sheppard, P. R., & Witten, B. L. (2012). Tungsten toxicity. *Chemico-Biological Interactions*, 196(3), 87–88. <https://doi.org/10.1016/j.cbi.2011.12.002>

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

37 VANADIUM

37.1 INTRODUCTION

Vanadium is a hard, silvery grey, ductile and malleable transition metal. Its melting point is 1910°C and its boiling point is 3407°C. Vanadium has oxidation states of +2, +3, +4, and +5. When heated in air at different temperatures, it oxidizes to a brownish black trioxide, a blue black tetraoxide, or a reddish orange pentoxide. It reacts with chlorine at fairly low temperatures (180 °C) forming vanadium tetrachloride and with carbon and nitrogen at high temperatures forming VC and VN, respectively. The pure metal in massive form is relatively inert toward oxygen, nitrogen, and hydrogen at room temperature.[1]

Vanadium occurs in many minerals (phosphate rock, titaniferous magnetite, bauxite as well as in deposits of fossil fuels such as oil and coal), among which titaniferous magnetite ore is the most important resources of vanadium and the ore concentrate usually contains 1.0% to 1.5% V₂O₅. [2] By far, 85% of vanadium production is from the titaniferous magnetite (26% from the primary titaniferous magnetite mines and 59% from vanadium slag generated from the processing of titaniferous magnetite ore in steel production) and 15% from the other resources (such as catalyst and residuals from the power plant fired with heavy oils). [2][3][4][5] Around 60% of vanadium is used to produce high-strength low-alloyed steels with vanadium contents in the range of 0.01-0.15%. [6], [7] Around 30% of vanadium is used to produce special steels (such as high-speed tool steels) with vanadium ranging from 0.1-5%. [8] Further, vanadium is also used to produce super alloys, chemicals, cast iron, certain types of stainless steels, etc.

Global vanadium supply from the mine in 2015 amounted to 79400 tons and was dominated by China (53%), South Africa (24%), Russia (19%) and Brazil (3%). [9]

Vanadium has been classified as a Critical Raw Material for the EU since 2017. [3]

37.2 GAPS LIMITING CIRCULAR ECONOMY

37.2.1 PRODUCTION

37.2.1.1 VANADIUM OXIDE PRODUCTION

Vanadium oxide can be produced either from titaniferous magnetite concentrate or the vanadium slag from the hot metal production by applying the roast-leach process.

- (1) Production from vanadium oxide directly from titaniferous magnetite concentrate

The production of vanadium oxide from titaniferous magnetite concentrate typically consists of four stages, namely, roasting, leaching, precipitation and calcination. In this process vanadium in the concentrate is converted

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

into soluble sodium vanadate (NaVO_3), which can be leached out. The use of $\text{NaCl}/\text{Na}_2\text{SO}_4$ during the roasting can cause the formation of corrosive gases such as Cl_2 , HCl and/or SO_2/SO_3 , therefore Na_2CO_3 is normally used. The yield of vanadium from the roast-leach process is around 82% [10], [11] and the loss of the vanadium is due to the incomplete transformation of vanadium to sodium vanadate. The big drawback of the process is the generation of large amount of solid waste, which is about same quantity as the feed into the treatment. This direct roast-leach process is exemplified by Glencore Xstrata in South Africa and Australia.[12]

(2) Production from vanadium oxide from vanadium slag

The production of vanadium from vanadium slag consists of three steps, namely, production of V-rich hot metal, production of vanadium slag, production of vanadium oxide.

- Production of V-rich hot metal

In this step titaniferous magnetite (in the form pellets or sinter) is charged into the BF (blast furnace), where the iron and vanadium in the titaniferous magnetite is reduced. The main issue regarding reduction and smelting of titaniferous magnetite in the BF lies in the formation of carbonitride (TiN and TiC), and particles of these in the slag increases its viscosity and thus adversely affects the BF process.[13] To overcome this issue the BF is typically operated with high slag ratio at the expense of low energy efficiency.[4] However, when the contents of titanium oxides in the titaniferous magnetite exceeds certain limit, it may not be possible at all to smelt the titaniferous magnetite in the BF.[14] Another alternative is reduction and smelting of titaniferous magnetite in the submerged-arc furnace (SAF) process, which is characterized by the pre-reduction of the titaniferous magnetite in the rotary kiln followed by the smelting of the DRI in the SAF.[15] The product from these processes is the V-rich hot metal, which contains 0.3-0.5% vanadium.

- Production of vanadium slag

Vanadium slag is produced by oxygen blowing in combination with solid oxidants and coolants (such as mill scale, iron pellets and iron scrap) into the V-rich melt (containing 0.3-0.5% vanadium), during which the vanadium in the melt is oxidized and ended up in the slag. The residual vanadium in the hot metal is normally lower than 0.06%,[4] which is eventually get lost in the slag and in the steel without functional use.

- Production of vanadium oxide

The extraction of vanadium oxides from the vanadium slag is also carried out by applying the roast-leach process as described earlier. The cumulative yield of vanadium from the titaniferous magnetite concentrate has been reported to be 71% in the FeV slag and 58% in the final vanadium oxide, [11] which is lower than the production of vanadium oxide directly from titaniferous magnetite concentrate.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

37.2.1.2 FERROVANADIUM PRODUCTION

Ferrovandium is normally produced from vanadium oxide by aluminothermic reduction. The start material can be either V_2O_5 or V_2O_3 . The produced ferrovandium by the aluminothermic reduction contains around 75-85% vanadium and the yield of vanadium is around 95%. The aluminum consumption is 40% lower if the FeV is processed from V_2O_3 compared to V_2O_5 . Ferrovandium can also be produced directly from vanadium slag by two- and three-state processes. The production of ferrovandium directly from vanadium slag is much more cost-effectively, as a large cost component for the production of FeV80 is the roast-leach process for the production of the V_2O_3/V_2O_5 feedstock. However, the ferrovandium produced directly from vanadium slag contains only 40-50% vanadium.

37.2.1.3 V-CONTAINING STEEL PRODUCTION

V-containing steels are usually produced by adding ferrovandium into the ladle, during which the iron melt is alloyed with vanadium. During the alloying some vanadium is lost due to the high affinity of vanadium to oxygen. Therefore, the ferrovandium is usually added in the semi-killed steels, fully killed steels and even vacuum-degassed steels.

37.2.2 RECYCLING

37.2.2.1 VANADIUM RECYCLING FROM STEEL SCRAP

Vanadium use in low-vanadium-alloyed steels is almost entirely dissipative and this means that the recycling rate of vanadium from old steel scrap is almost zero. This is on one hand due to the low vanadium content in the steel scrap (e.g. 0.01-0.15% vanadium in the HSLA steels[6], [7]); on the other hand this is due to the fact that recovery of vanadium from steel scrap is chemically impeded under the oxidizing conditions in steelmaking furnaces. The vanadium in the end is lost in the dust and slag while only the iron content in the steel scrap is recycled. [16] Vanadium in the special steel scrap and vanadium alloy scrap are possible to be recycled, if these scrap is processed under reducing condition (such as in the Electric arc furnace with addition of strong reducing agent) or recycled by melting under vacuum condition.[16]

37.2.2.2 VANADIUM RECYCLING FROM SPENT CATALYST

Vanadium in the spent catalysts is normally recycled; this is due to the hazardous and toxic nature of the vanadium and other elements in the spent catalysts as well as due to the fact that, beside vanadium, the spent catalysts also contain other valuable elements, such as molybdenum.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

37.3 ASPECTS SUPPORTING CIRCULAR ECONOMY

The main challenge for ensure a circular economy of vanadium lies in the difficulty in recycling vanadium from the HSLA steels. This is on one hand due to that in quite many cases HSLA steels are not carefully sorted from the others in the steel scrap. On the other hand this is due to the oxidation and thereafter the loss of vanadium in the slag during the re-melting of the steel scrap. A circular economy of vanadium will reply on the improvement in the recycling logistics of the V-containing HSLA steel scrap as well as the scrap re-melting strategy.

37.4 ENVIRONMENTAL ISSUES

Vanadium occurs naturally in soil, water, and air. Natural sources of atmospheric vanadium include continental dust, marine aerosol, and volcanic emissions. Releases of vanadium to the environment are mainly associated with industrial sources, especially oil refineries and power plants using vanadium rich fuel oil and coal. [1] The toxicity of vanadium is dependent on its oxidation state. The pentoxide form is more toxic than the elemental form. Vanadium can cause a variety of toxic effects such as hematological and biochemical changes. Inhalation of vanadium may cause rhinitis, pharyngitis, chronic productive cough, tracheobronchitis, and bronchopneumonia. Moreover, the most often observed side effects include loss of appetite and significant reduction of body weight, often leading to anorexia, weakness, and nose bleeding, vomiting, diarrhoea, dehydration, pulmonary hemorrhage, or death.[17]

37.5 SUMMARY

Vanadium production is mainly produced from the titaniferous magnetite and being substantially used to produce HSLA steels. Vanadium can be directly extracted from titaniferous magnetite by the roast-leach process or extracted from titaniferous magnetite by producing the V-rich slag first and then by the roast-leach process. The overall vanadium yield from the direct roast-leach process is around 82% and the yield from the indirect roast-leach process is around 58%. The other vanadium is lost in the solid wastes and in the slag, respectively. The recycling of vanadium from HSLA steels is very rare due to the low contents of vanadium and the oxidation of vanadium during the scrap re-melting. The recycling of vanadium from spent catalyst is common due to the toxic property of vanadium as well as the existence of other valuable elements in the spent catalyst.

37.6 REFERENCES

- [1] U.S. Department of Health and Human Services, "Toxicological Profile for Vanadium," 2012.
- [2] "Making Vanadium." [Online]. Available: <http://vanitec.org/vanadium/making-vanadium>.
- [3] E. Commision, *Study on the review of the list of critical raw materials*, no. June. 2017.
- [4] M. Lindvall, "A study on vanadium extraction from Fe-V-P melts derived from primary and secondary sources," KTH-Royal Institute of Technology, 2017.
- [5] H. Y. Li, H. X. Fang, K. Wang, W. Zhou, Z. Yang, X. M. Yan, W. S. Ge, Q. W. Li, and B. Xie, "Asynchronous extraction of vanadium and chromium from vanadium slag by stepwise sodium roasting-water leaching," *Hydrometallurgy*, vol. 156, pp. 124–135, 2015.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

- [6] "Vanadium." [Online]. Available: <http://amg-v.com/vanadiumpage.html>.
- [7] T. Hsla, "High-Strength Low-Alloy Steels," vol. 45, no. 4, pp. 4–5, 2001.
- [8] "Vanadium Processing." [Online]. Available: <https://www.britannica.com/technology/vanadium-processing>.
- [9] U. National Minerals Information Center, "Vanadium," *U.S. Geol. Surv. Miner. Commod. Summ.*, no. 703, pp. 182–183, 2016.
- [10] S. Nkosi, P. Dire, N. Nyambeni, and X. C. Goso, "A comparative study of vanadium recovery from titaniferous magnetite using salt , sulphate , and soda ash roast-leach processes," in *3re Young Professionals Conference*, 2017, no. March, pp. 9–10.
- [11] X. C. Goso, H. Lagendijk, M. Erwee, and G. Khosa, "Indicative Vanadium Department in the Processing of Titaniferous Magnetite by the Roast – Leach and Electric Furnace Smelting Processes," no. August, pp. 1–3, 2016.
- [12] F. Cardarelli, *Materials handbook: a concise desktop reference*. Springer Science & Business Media, 2008.
- [13] L. A. Smirnov, M. A. Tret'yakov, and V. I. Gladyshev, "Processing Vanadium-bearing Titanomagnetites at the Nizhniy Tagil Metallurgical Combine," *Metallurgist*, vol. 45, no. 6, pp. 232–234, 2001.
- [14] V. E. Roshchin, A. V. Asanov, and A. V. Roshchin, "Possibilities of two-stage processing of titaniferous magnetite ore concentrates," *Russ. Metall.*, vol. 2011, no. 6, pp. 499–508, 2011.
- [15] W. S. Steinberg, W. Geysler, and J. Nell, "The history and development of the pyrometallurgical processes at Evraz Highveld steel & vanadium," *J. South. African Inst. Min. Metall.*, vol. 111, no. 10, pp. 705–710, 2011.
- [16] T. G. Goonan, "Vanadium Recycling in the United States in 2004," 2011.
- [17] S. K. Ghosh, R. Saha, and B. Saha, "Toxicity of inorganic vanadium compounds," *Res. Chem. Intermed.*, vol. 41, no. 7, pp. 4873–4897, Jul. 2015.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227