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Technological gaps hindering uptake of CRMs substitution in industrial application

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Technological gaps hindering uptake of CRMs substitution in industrial application

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Solutions for CRitical Raw materials - a European Expert Network

TECHNOLOGICAL GAPS/BARRIERS ON SUBSTITUTION

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TECHNOLOGICAL GAPS/BARRIERS ON SUBSTITUTES

INTRODUCTION

Nowadays the use of large amounts of scarce materials to satisfy the industrial and technological needs, have made the global community focus their efforts in analizing the alternatives to cover the current needs, minimizing the use of critical raw materials, recovering them when possible and recycling.

Substitution in the context of criticality of raw material refers to the ability to achieve the same function by other means using alternative materials. These alternative sets can provide an equivalent function and although often the best option is discussed according to the application or sector, different ways of evaluating it arise, but the importance of substitution in criticality seems unquestionable. For example, as already has been discussed thoughout this project, also during the evaluation of seminal criticality of the NRC (2008), the availability of substitutes is considered as a "key concept" to determine the importance of a raw material for a particular application. However, the European Commission mentions the lack of viable substitutes as a defining characteristic of criticality.

In addition, independent scientific experts' evaluation is required in such a decisive issue for the global economy and the environment.

This Deliverable aims to provide some scientific evidence to the substitution possibilities of each of the materials analysed, identifying the efforts already developed in that direction, barriers encountered, economic impact on the final product / service and status of the alternative products.

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ANTIMONY

Antimony is a soft, lustrous, silver-grey metalloid. According to EU Critical Raw Materials Report [28], primary extraction of antimony ores and concentrates does not take place in Europe, nor does the production of unwrought antimony metal. However, the EU does produce antimony trioxide (ATO). The EU is therefore entirely reliant on imports of unwrought antinomy metal to meet current demand from the European antimony trioxide industry. Apparent consumption of unwrought antimony metal in Europe (2010–2014) was on average about 18,200 tonnes per year, the majority of which was used in the production of antimony trioxide primarily for the manufacture of flame-retardants.

The main applications for antimony are as a flame retardant and in the manufacture of lead-acid batteries. It also has minor uses in the production of plastics, glass and pigments.

Substitution is suggested as the first step to reduce the amount of scarce material used in production, followed by increasing material efficiency and recycling [0]. In some applications, antimony can be substituted without much effort, for example in pigments and glass. In other cases, there is a risk of increased price or lower performance coming with substituting element. In case of lead alloys there are potential possibilities for substitution of antimony, yet each of the new metals may cause unwanted effects in the alloy. It can be observed that the incentive for antimony substitution in main applications is low from technical and economical perspective [28]. Antimony in glass colorants is considered 100% substitutable by other colorants. Figure 1 below depicts consumption of different flame-retardants in Europe in 2007. Different shades of blue colour were used for halogen-free retardants.

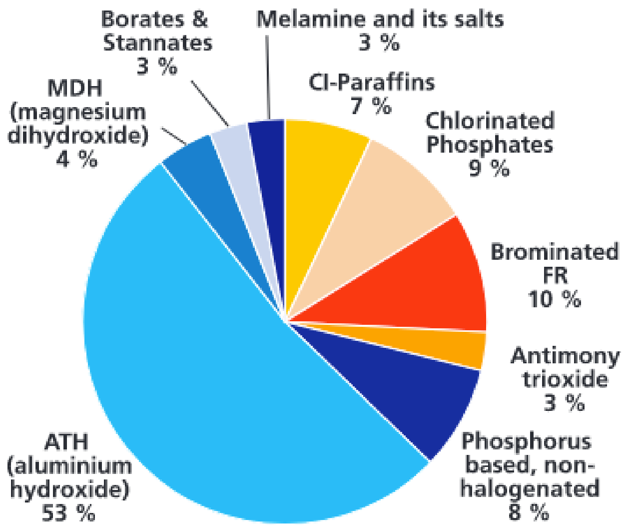

Figure 1. Consumption of flame retardants in Europe in 2007 [15].

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Table 1. General information concerning Sb products and applications.

CRM	Product	Application	Substitute
Antimony (Sb)	Lead-acid battery	Lead alloy	Replaced by antimony-free calcium–calcium lead acid batteries
	Other		Combinations of bismuth, indium, copper, zinc, silver and tin
	Electrical and electronic equipment (cable coatings, dopant in semiconductors for infrared detectors and diodes)	Flame retardant in plastics	Aluminum trihydroxide, Zinc compounds Bismuth trioxide Red phosphorus Magnesium hydroxide Ammonium polyphosphate ABS/PC blends with triphenyl phosphate Organic phosphorus compounds Melamine polyphosphate
	Textiles	Flame retardant	Zinc compounds Bismuth trioxide phosphorus constituents zirconium constituents ammonium polyphosphate aluminium trihydroxide
		Catalyst in the synthesis of polyester fibres	Titanium-based catalysts (potential substitute) phosphinic acid derivate co-monomer
	Glass and ceramics	Pigment	Sodium sulphate

Sources: WP 5.1; [0].

1. DESCRIPTION AND INDICATOR

Production and consumption in EU

Antimony ores and concentrates are neither mined nor processed in Europe, therefore EU is 100% reliant on their import. EU does produce antimony trioxide (ATO) from unwrought metal, but the raw material has to be mostly imported and partially comes from secondary resources (scrap lead-acid batteries). The yearly consumption of unwrought antimony reaches over 18 000 tonnes, which is used mostly in ATO production. ATO is produced mainly in Belgium, France, Spain and Italy [28].

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Future demand increasing

The demand for antimony is likely to increase in coming years. Sb compound are effective as flame retardant and their use in this application is likely to continue. The demand for antimony can be also driven by the more strict fire regulations [28]. Moreover, the growth of antimony use is expected to appear in glass panes for solar cells. However, in the long term the use of antimony is expected to decline globally, since it is often used together with halogenated hydrocarbons or lead. Those substances bring health and environmental hazards, therefore their safe use is presently analysed in detail [0].

2. SUBSTITUTE MATERIALS

According to USGS Minerals Yearbook [27], selected organic compounds and hydrated aluminium oxide are substitutes as flame retardants. Chromium, tin, titanium, zinc, and zirconium compounds substitute for antimony chemicals in enamels, paint, and pigments. Combinations of calcium, copper, selenium, sulfur, and tin are substitutes for alloys in lead-acid batteries.

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Table 2. General description, economic value and main applications of antimony substitute materials.

Substitute Material	**Description of the Material**			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Aluminum hydroxide	Inorganic salt used as an antacid, basic compound that acts by neutralizing hydrochloric acid [1]; high purity, fine-precipitated with low soluble electrolytes content that is suitable for demanding requirements such as electrical and electronic applications [6]	Manufactured and/or imported in the European Economic Area in 1 000 000 - 10 000 000 tonnes per year [1];	The most popular of flame retardants (53% use share in 2007)	- Flame retardant; - Pharmaceutical; - production of aluminum chemicals (aluminum sulfide, sodium aluminate, aluminum fluoride, and aluminum chloride hexahydrate) - Manufacture of petroleum catalysts, plastic and rubber goods, paper, glass and vitreous enamel, adhesives, varnishes, and toothpastes
Red phosphorus	One of two major forms of phosphorus; highly reactive non-metal [2] used mainly in glass fibre reinforced PA 6,6 at 5 to 8 % addition level, highly efficient with obtaining highest flame retarding properties	Phosphorus based flame retardants accounted for 8% of Europe's use in 2007	One of the ecologically and physically most harmless alternative for fire retardants [3]	- Flame retardant (especially in thermoplastics and thermosets) - Production of matches - Pyrotechnics [4]
Zinc compounds (stannate, borate)	Crystalline zinc stannate nanoparticles are chemically stable, non-toxic, and resource-abundant [5]		Efficient performance for applications in dye-sensitized solar cells [5] Increasingly used in green Sb-free applications, particularly in the electronics industry [7] Used to a lower extent than aluminium and magnesium hydroxides [15]	- Highly efficient flame retardant additive - Smoke suppressant used in both halogen contained and halogen-free polymers [6] - Solid lubricant additive in friction materials [7]

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Bismuth trioxide	Highly insoluble thermally stable Bismuth source suitable for glass, optic and ceramic applications [9]	North America and Europe are expected to be the major consumers of bismuth oxide [11] Supplied mostly by China Supplier in Germany: INTATRADE GmbH[12]	It's the most industrially vital compound of bismuth [9] Asia Pacific is expected to be the leading manufacturer of bismuth oxide [11]	- Used in advanced electronics and in light weight structural components in aerospace and electrochemical applications (fuel cells) [9] - Electronic ceramics - Colorant in glass - Superconductor [10] - occasionally used in dental materials to make them more opaque to X-rays than the surrounding tooth structure [8]
Magnesium hydroxide	Has excellent thermal stability of up to 340°C, which enables its use where; Environmentally friendly since no toxic or corrosive gases are generated during its decomposition process [6]	Global production of magnesium hydroxide increased from 613 K MT in 2012 to 788 K MT in 2017 and expect to keep growing. The major manufacturers mainly concentrate in Europe, North America, Japan and China [18]	Magnesium hydroxide is more attractive to plastics producers due to increasing legislation and concern about the use and recyclability of halogenated flame retardants [17] The global Magnesium Hydroxide market is valued at 1120 million US$ in 2017 and will reach 1260 million US$ by the end of 2025 [18]	- non-halogen flame retardants and smoke suppressants in cables and wires, rubbers, plastics, fibers and coating materials and thermoplastic olefin roofing materials [6] - suitable for wastewater treatment, bleaching pulp, flue gas treatment, production of paper, ceramics [16]
Ammonium polyphosphate	Colorless, non-hydroscopic and non-flammable [6]	Commercially produced by Clariant with production facilities in Germany and Switzerland[13] Phosphorus based flame retardants accounted for 8% of Europe's use in 2007		- Halogen-free flame retardant - Widely used in intumescent coatings, adhesives and sealants, polyurethane foams, thermoplastics, epoxy, polyester, wood, paper, etc.[6] - Fertilisers [14]
Triphenyl phosphate	Triphenyl phosphate is used in a solid form with 9.5% phosphorus content; based on aromatic phosphate esters; ABS/PC blends contain 14% triphenyl phosphate additive [15]	There are two known European production sites: Chemtura (formerly Great Lakes), UK and one additional European supplier. Information on production volume and market size is confidential [20]		- Flame retardant in polymers - Plasticizer in lacquers, varnishes, and hydraulic fluids

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		Phosphorus based flame retardants accounted for 8% of Europe's use in 2007		
Organic phosphorus compounds	Organic phosphorus compounds: halogen-free organic phosphorus compounds, chlorinated organic phosphorus compounds, brominated organic phosphorus compounds [19] Most used flame retardant in thermoplastics (such as PC/ABS and PPO/HIPS) and polyurethane foams [22]	Phosphorus based flame retardants accounted for 8% of Europe's use in 2007		- plasticizers - gasoline additives, and flotation agents - insecticides - in synthesizing organic compounds [21]
Melamine Polyphosphate	It is especially suited for glass fibre reinforced polyamide, where 25% of flame retardant is used; Has good thermal stability [15] Halogen-free [23]	Melamine based flame retardants accounted for 3% of Europe's use in 2007		- Specially used for glass-fibre reinforced nylon - Thermoplastics, thermosetting plastics, rubber, and fibre [23]

Sources:

[0] (Henckens et al., 2016).
[1] (European Chemical Agency, 2018)
[2] (Wkipedia, 2018)
[3] (Braun & Schartel, 2004)
[4] (The Essential Chemical Industry, 2017)
[5] (Miyauchi, Liu, Zhao, Anandan, & Hara, 2010)
[6] (3N International Inc., 2008)
[7] (William Blythe, n.d.)
[8] (Wikipedia, 2018a)
[9] (AMERICAN ELEMENTS, 2018)
[10] (Stanford Advanced Materials, 2018)
[11] (Future Market Insights, 2014)
[12] (Chemical Book, 2017)
[13] (Clariant, 2018)
[14] (International Plant Nutrition Institute, n.d.)
[15] (Döring et al., 2010)
[16] (Nedmag B.V., 2018)
[17] (Walter, Wajer, & Marietta, n.d.)
[18] (Wave3 News, 2018)
[19] (Bombardier Inc., 2005)
[20] (Brooke, Crookes, Quarterman, & Burns, 2009)
[21] (Kornblum, 2010)
[22] (SpecialChem, n.d.)
[23] (Century Multech, n.d.)

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

As described in the table below, main technological barriers hindering the use of substitutes for antimony is lower performance and higher cost of the new material. Another important issue come from non-technological point of view, which is the negative environmental, health and safety properties connected with substitutes. Solutions for those barriers are often difficult to find. It is suggested to search for a different substitute that does not compromise the performance and is not harmful for the environment.

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Table 3. Technological and non-technological barriers to the rollout of substitutes to antimony.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Aluminium hydroxide	Technological	Flame retardant in EEE	Lower performance than Sb	7	Use substitute that does not compromise performance	8
			Moderate thermal stability (starts to decompose at 200°C)	3	Use different retardant for high thermal stability requirements	8
	Non-Technological	Flame retardant in EEE	costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
Red phosphorus	Technological	Flame retardant	Degradation	7	precautions against degradation have to be taken	
			compounds are limited to red or black colours	3	Use different flame retardant	8
	Non-Technological	Flame retardant in EEE	Costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
			Negative environmental, health and safety properties	6	Use another substitute with lower environmental impact	7
ABS/PC blends with triphenyl phosphate	Technological	Flame retardant in EEE	Low efficiency	7	Use more efficient brominated phosphate instead of triphenyl phosphate[1]	7
	Non-Technological	Flame retardant in EEE	Negative environmental, health and safety properties	6	Use another substitute with lower environmental impact	7

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			costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
PPE/PS blends with organic phosphorus compounds	Technological		Flame retardants based on phosphorus have to be included in large amounts[2]	4	Use different, more efficient substitute	7
	Non-Technological	Flame retardant in EEE	costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
Zinc compound (oxide, borate, sulphide, stannate, phosphate)	Technological	Flame retardant in EEE	Substitution without compromising performance possible in 50%	7	Use substitute that does not compromise performance	8
		Textiles	Substitution compromises 100% performance	9	Use substitute that does not compromise performance	8
	Non-Technological	Flame retardant in EEE	Negative environmental, health and safety properties	6	Use another substitute with lower environmental impact	7
			costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
		Textiles	costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
PC containing organic phosphorus compounds	Non-Technological	Flame retardant in EEE	costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
polyketone with magnesium hydroxide	Non-Technological	Flame retardant in EEE	costs of the substitute or the replacement are >200 % of the costs of the original antimony	8	Use another substitute with comparable price range	8

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Ceramics	Non-Technological	Flame retardant in EEE	costs of the substitute or the replacement are >200 % of the costs of the original antimony	8	Use another substitute with comparable price range	8
Phosphorus constituents	Technological	Textiles	Substitution without compromising performance possible in 67%	6	Use substitute that does not compromise performance	8
Zirconium constituents	Non-Technological	Textiles	Negative environmental, health and safety properties	6	Use another substitute with lower environmental impact	7
			Costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
Sodium sulphate	Technological	Glass (fining agent)	Substitution without compromising performance possible in 33%	7	Use substitute that does not compromise performance	8
	Non-Technological	Glass (fining agent)	Costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
Combinations of bismuth, indium, copper, zinc, silver and tin	Non-Technological	Lead alloys	Geological scarcity of some substitutes	8	Use substitutes that are not scarce (copper, zinc)	7
			Costs of the substitute or the replacement are 120%-200% compared to the costs of the original antimony	7	Use another substitute with comparable price range	8
Triphenyl phosphate	Non-Technological	Flame retardant in EEE	Considered to be "very toxic" to aquatic life, with potentially long-lasting effects (the European Chemicals agency)[3]	7	Use another substitute with lower environmental impact	7

Sources:
[0] (Henckens et al., 2016)
[24] (Green, 1991)
[25] (Fink, 2014)
[26] (Wikipedia, 2018b)

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4. SUMMARY

In general, antimony can be substituted with different materials. In some applications, it does not require much effort, for example in pigments and glass. In other cases, there is a risk of increased price or lower performance of substituting element. In case of lead alloys there are potential possibilities for substitution of antimony, yet each of the new metals may cause unwanted effects in the alloy. The incentive for antimony substitution in main applications is considered low from technical and economical perspective.

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BERYLIUM

Beryllium (Be) is a chemical element, the lightest member of the alkaline-earth metals of Group II, used in metallurgy as a hardening agent and in many outer space and nuclear applications.

EU uses over 56000 Kg / year of beryllium in all forms:

- In over 500 SME and 40 larger enterprises.
- Employing over 10000 employees.
- Of which, 3000 use beryllium in the workplace.

1. DESCRIPTION AND INDICATOR

Three main type of applications are identified according to the content of Be in the final material, end product [1].

Three forms of beryllium are of strategic importance to the EU:

- Copper beryllium containing 0.1 – 15.0% beryllium.
- Metallic beryllium and alloys containing > 50% beryllium
- Beryllium Oxide ceramic.

a) 80% of the beryllium used in the EU goes into copper beryllium alloys (with a content range of 0.1 – 15.0%).

Copper beryllium alloys are used for the manufacture of high performance electrically conductive terminals such as:

- Extreme reliability automobile connectors for air-bag crash sensor and deployment systems, anti-lock brake systems and many other life safety applications;

- Life saving medical applications such as the connections in medical operating theatre and monitoring equipment;

- Critical connections and relays in electrical, electronic and telecommunications equipment where failure would disrupt the communications of emergency services like firefighters and police;

- No-fail aircraft electrical and electronic connectors which enable fly-by-wire commercial airliners to achieve previously impossible fuel efficiencies, and critical aircraft components such as altimeter diaphragms;

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- Extremely long service life fire sprinkler water control valve springs that must react to fires after decades of inactivity to save lives and control fire damage;
- Household appliance temperature and other function controls that provide reliability and safety to consumers while minimizing energy and water use; and
- Relays used for telephone exchanges and controlling industrial, domestic and automobile electrical equipment.

Copper beryllium alloys are used for the manufacture of mechanical components such as:

- Non magnetic equipment components used in oil & gas exploration, production and directional drilling equipment to improve extraction efficiencies and reduce land despoliation at drill sites by reducing the number and footprint of drill sites,
- Mineral mining equipment bearings that operate longer underground coal,
- Mine detection and minesweeping systems that keep the global forces safe,
- Undersea fiber optic cable signal amplification "repeater" housings that carry more simultaneous transmissions than ever conceived of in the original cable systems,
- Low friction high strength aircraft landing gear bearings, control rod ends and wing aileron / flap bearing bushings that allow significant weight loss to reportedly lower global fuel consumption by 24 billion litres per year, and reduces associated carbon dioxide emissions by over 11 million metric tons per year,
- High thermal efficiency, reduced icing, aircraft components such as pitot tubes to provide enhanced aircraft safety for passengers,
- Electrode holders and components of welding robots for automated automobile and appliance welding allowing better working environments for factory workers,
- Property modifier for aluminum and magnesium castings with enhanced properties that reduce weight to achieve fuel and pollution reduction in automobiles and trucks,
- Plastic and metal casting moulds with enhanced thermal efficiency that improve productivity and provide plastic products with enhanced tolerances

Beryllium in the form of master alloys containing 1 – 14% beryllium with aluminium, copper and nickel are added to metals and alloys to provide:

- Physical properties such as strength, ductility, fatigue strength for producing car body panels, seat frames, car steering components and wheels;
- Fluidity or the ability to cast precise, complex shapes in many industrial applications e.g robotics, welding;
- Magnesium loss prevention: Reduces "burn off" of magnesium by >50% when aluminium smelters add magnesium to make high performance alloys for use in beverage can alloys and aircraft skins.

b) 20% of the beryllium used is in the form of pure metal, as a metal matrix containing over 50% beryllium

- X-Ray transparent windows used to control and focus X-Ray beams in all medical, scientific and analytical devices incorporating X-Ray sources, providing finer resolution,

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- Gyroscope gimbals and yokes for use in guidance, navigational and targeting systems used on aircraft, armored vehicle and marine missile systems providing levels of precision,
- Satellite mounted directional control devices for astronomical and other telescopes and instruments to provide accurate GPS locations signals and a wealth of scientific, agricultural and climatic data,
- Satellite structural components that reduce weight, provide unmatchable rigidity at deep space low temperatures and enable longer, more capable space missions,
- Mirrors for terrestrial and space mounted astronomical telescopes,
- World leading science and technology programs like JET, CERN and ITER depend upon beryllium metal for critical components that cannot be substituted by any other material,
- Beryllium is critical for the success of the multi-national ITER (International Thermonuclear Experimental Reactor) fusion energy project located in Cadarache, France that offers the opportunity to provide sustainable energy sourced from non-radioactive nuclear fusion,
- Medical isotope production nuclear reactors in Belgium, Holland and the USA produce critical isotopes for treatment of many types of cancer as a result of the unique neutron beam reflective capabilities of beryllium,

c) Beryllium Oxide Ceramics are used to produce components with extremely high thermal conductivity while providing electrical insulation, a unique combination of properties exploited for use in the manufacture of such equipment as:

- Substrates for mounting high powered civil aviation radar systems and power amplifiers that need cooling to prevent self destruction, and for mobile telephone infrastructure equipment,
- Medical excimer laser beam focusing and control components, allowing surgeons unprecedented fine control of the high energy laser beam during surgery. Throughout the medical arena, beryllium is indispensable for use in mammography, medical imaging equipment and surgical devices. Lasers constructed with beryllia ceramic are providing the gift of restored or improved sight to millions around the world. Beryllium-containing ceramics are integral components in high-end cancer therapy machines, medical lasers for DNA analysis and equipment for skin resurfacing, non-invasive surgery, kidney stone removal, detection of blindness and HIV testing.

Beryllium annual consumption is expected to grow from about 300 in 2014 to 425 MT/year by 2020 and to >450 MT/year by 2030, driven by such applications as the International Thermonuclear Experimental Reactor (ITER) fusion energy project located in Cadarache, France that offers the opportunity to provide sustainable energy.

Table 4. General information concerning Be products and applications.

CRM	Product	Application	Substitute
Beryllium	Metallic beryllium and alloys containing > 50% beryllium	X-Ray transparent windows	None

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	Copper beryllium containing 0.25 – 2.0% beryllium	Critical connections and relays in electrical, electronic and telecommunications	High-strength grades of aluminum, pyrolytic graphite, silicon carbide, steel, or titanium
	Al, Cu and Ni master alloys containing 2-15% beryllium		Copper alloys containing nickel and silicon, tin, titanium
	Beryllium Oxide ceramic	Radar	Aluminum nitride or boron nitride
		Medical excimer Laser	None

Sources: WP 5.1; [3]

2. SUBSTITUTE MATERIALS

Substitution to alternative materials is generally not an option, since the functionality would be lost or performance substantially impaired. Be used in copper alloys could be replaced by Be-free copper alloys that are nanostructured (with nanometric grains). The US Department of Defence (DoD) [4] is conducting for a couple of year development work to substitute Be in copper alloys. This mainly driven by the toxicity of Be. The nanostructuration allows to gain in mechanical properties usually brought by the Be addition. No detail are disclosed about the solution developed by DoD except that the substitute material is a mixture of powders used as coating.

The substitution of Be alloys seems more complex since almost pure Be is needed to provide unique properties. As an example for ITER, Be contained in the first wall is used because it retain H_2 and do not contaminate the plasma, such unique properties are difficult to find in other materials [2].

Substitution barrier for Be is mainly the acceptance to loose performance with the substitute solution versus the Be-based solution. The good thing is the substitution driving force due to the toxicity and stricter related regulations: Because of the toxic nature of beryllium, various international, national, and State guidelines and regulations have been established regarding beryllium in air, water, and other media. Industry is required to carefully control the quantity of beryllium dust, fumes, and mists in the workplace.

Because the cost of beryllium is high compared with other materials, it is used in applications in which its properties are crucial (e.g. neutron absorption). In some applications, certain metal matrix or organic composites, high-strength grades of aluminum, pyrolytic graphite, silicon carbide, steel, or titanium may be substituted for beryllium metal or beryllium composites. Copper alloys containing nickel and silicon, tin, titanium, or other alloying elements or phosphor bronze alloys (copper-tin-phosphorus) may be substituted for beryllium-copper alloys, but these substitutions can result in substantially reduced performance. Aluminum nitride or boron nitride may be substituted for beryllium oxide.

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Table 5. General description, economic value and main applications of Be substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Copper alloys containing nickel and silicon, tin, titanium	Suppress Be use for safety raisons			- Electrical connections
Aluminum nitride or boron nitride	Suppress Be use for safety reasons		Abundant materials but difficult to synthesize	- Radar

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

According to a loss of properties some option can be envision to replace Be in alloys. Because of the toxic nature of beryllium, various international, national, and State guidelines and regulations have been established regarding beryllium in air, water, and other media. Industry is required to carefully control the quantity of beryllium dust, fumes, and mists in the workplace. This toxic aspect is makes a real driving force to minimize the use of beryllium and thus to replace it.

If beryllium containing materials were not available to EU manufacturers, end users would replace the end use products with imported articles, thereby eliminating EU leadership in a wide range of high technology industries, with a concomitant loss of employment and skills.

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Table 6. Technological and non-technological barriers to the rollout of substitutes to Be.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
High-strength grades of aluminum, pyrolytic graphite, silicon carbide, steel, or titanium Copper alloys containing nickel and silicon, tin, titanium	Technological	Electrical connections	Loss of performance of the substitute	5	Ad hoc dimensioning to recover the missing performances	7
Aluminum nitride or boron nitride	Technological	Radar	Completely different materials for the substitute	5	High tech sector can make the effort to integrate the novel substitute material	5

4. SUMMARY

Beryllium is used in numerous application and in various sectors. Because the cost of beryllium is high compared with that of other materials, it is used in applications in which its properties are crucial. Some possibilities do exist to substitute Beryllium in alloys but this is accompanied by a decrease in term of properties [1] [2].

5. REFERENCES

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BORATES

Borates are the name for a large number of boron-containing oxyanions, which are a ubiquitous family of flame-retardants found as boric acid and as a variety of salts, especially sodium borate (borax) and zinc borates.

Table 7. General information concerning B products and applications.

CRM	Product	Application	Substitute
Borates	Clay additives	Ceramic and glasses	None
	Thermal shock resistant glasses, fluxing additive		Phosphates
	Fire retardants	Polymer additives	None
	Anti-fungal additive	Wood treatment	None
	Detergent & personal care	Cleaning additive	Sodium based compound

Sources: WP 5.1; [3]

1. DESCRIPTION AND INDICATOR

Production and consumption in EU and future demand increasing

Numerous sectors in the EU are using borates [1] [2]:

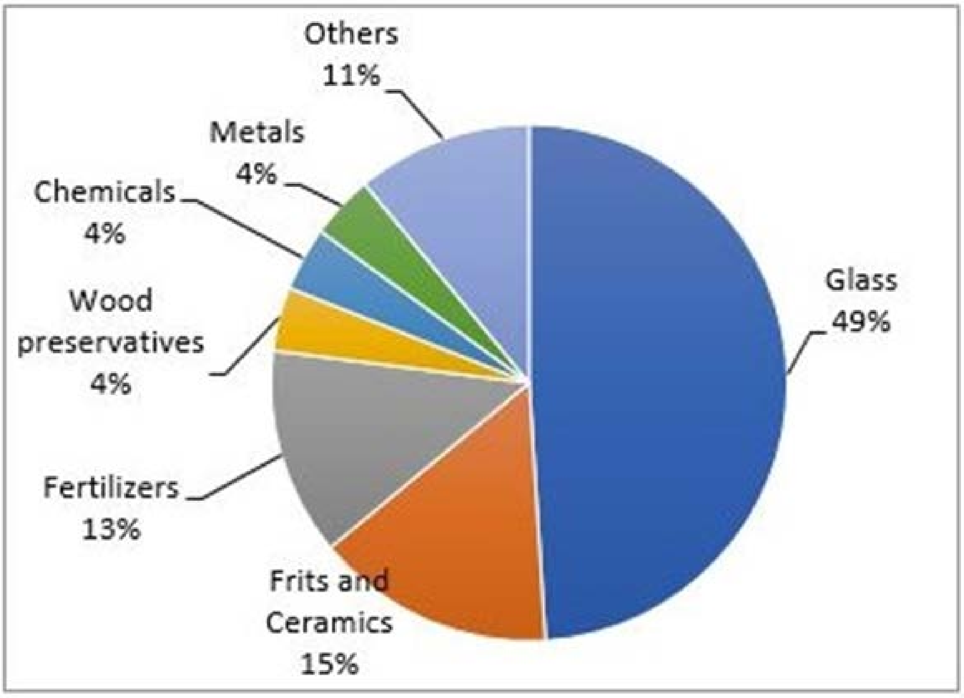

Figure 2. EU end uses of borates, average figures for 2010-2014 [1]

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- Agriculture: Boron is an essential micronutrient for plants, vital to their growth and development. Without sufficient boron, plant fertilisation, seeding and fruiting are not possible. On every continent of the world, crop yields and food quality are diminished due to insufficient boron concentrations in the soil. These deficiencies can be corrected with borate fertilisers. In areas of acute deficiency, borates can increase crop yields by 30 to 40 percent.
- Ceramics: Borates have been an essential ingredient in ceramic and enamel glazes for centuries, integral to affixing glazes or enamels, and enhancing their durability and lustre. Borates are gaining acceptance as ingredient in ceramic tile bodies, allowing manufacturers to use a wider range of clays, heightening productivity and decreasing energy usage.
- Detergents and Personal Care Products: Borates enhance stain removal and bleaching, stabilise enzymes, provide alkaline buffering, soften water and boost surfactant performance in detergents and cleaners. Their biostatic properties control bacteria and fungi in personal care products. New trials demonstrate that adding borates to laundry soap bars significantly improves their cleaning action and reduce levels of dirt redeposition.
- Fibreglass: Borates are an important ingredient in both insulation fibreglass – which represents the largest single use of borates worldwide – and textile fibreglass, used in everything from circuit boards to surfboards. In both products, borates act as a powerful flux and lower glass batch melting temperatures. They also control the relationship between temperature, viscosity and surface tension to create optimal glass fiberisation.
- Glass: Borosilicate glass is the foundation for all heat resistant glass applications and the myriad products they make possible – from cathode ray tubes to Pyrex® cookware. Borates increase the mechanical strength of glass, as well as their resistance to thermal shock, chemicals and water.
- Polymer Additives: Zinc borates are used primarily as a fire retardant synergist in plastics and rubber applications. They can also function as smoke and afterglow suppressants, anti-tracking agents, and can be used in polymers requiring high processing temperatures. Zinc borates can be found in polymers ranging from electrical parts and automobile interiors to wall coverings and carpeting.
- Wood Treatments: Borate treated wood is on the rise as a safe and long-lasting method to protect homes and other structures from wood-destroying organisms. Borate-based preservatives can be used to treat solid wood, engineered wood composites and other building materials like studs, plywood, joists and rafters. Borates prevent fungal decay and are deadly to termites, carpenter ants and cockroaches – but are safe for people, pets and the environment.

Glass and ceramic industry constitute the larger use of boron in volume. Although borates were used in more than 300 applications, more than three-quarters of world consumption was used in ceramics, detergents, fertilizers, and glass.

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In Europe and developing countries, more stringent building standards with respect to heat conservation were being enacted. Consequently, increased consumption of borates for fiberglass insulation was expected.
About 80% of borates placed on the EU market (285 kTons) are used in intermediate uses such as in the manufacture of glass & frits and/or for the synthesis of new substances, in mixtures below the specific concentration limits, and in biocidal applications. The remaining one-fifth is used in agriculture (13-14%), in articles (4-5%) and in other uses (2-3%) such as coatings, industrial fluids and/or metallurgical applications. Furthermore, for safety reasons, the use of borates is essential in nuclear power plants as neutron absorber.
In addition, boron is in essential micronutrient for normal, productive plant growth and is one of seven essential micronutrients for plants according to the EU Fertiliser Regulation (2003/2003/EC).

2. SUBSTITUTE MATERIALS

The substitution of other materials for boron is possible in detergents, enamels, insulation, and soaps. Sodium percarbonate can replace borates in detergents and requires lower temperatures to undergo hydrolysis, which is an environmental consideration. Some enamels can use other glass-producing substances, such as phosphates. Insulation substitutes include cellulose, foams, and mineral wools. In soaps, sodium and potassium salts of fatty acids can act as cleaning and emulsifying agents.

Substitution of borates in fiberglass seems to be unlikely due to the properties and considering the evolution of building standards in western countries.

Table 8. General description, economic value and main applications of borates substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Phosphate	Suppress the use of borate		Competition of usage	- Thermal shock resistant glasses, fluxing additive
Sodium based salts	Suppress the use of borate			- Detergent & personal care

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

There is no strong barrier to substitute borates in some application since some regulations (REACH) are pushing to substitute borate based compounds in detergents. Glass forming additive borates based compound could be substituted.

Table 9. Technological and non-technological barriers to the rollout of substitutes to Borates.

Substitute Material	Type of Barrier	Product/ Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Phosphate	Technological	Thermal shock resistant glasses, fluxing additive	Competition of usage of the substitute	3	Optimize the composition	5
Sodium based salts	Technological	Detergent & personal care	Loss of performance of the substitute	2	Adapt the additive content & composition	8

4. SUMMARY

Borates intervene in few key industrial applications such as glass industry. Europe has world leader in this sector. Substitution options could be considered in a short term since no major modification of the industrial tool is needed to implement this change. Since policy measures on energy efficiency of buildings are expected to drive building standards in Europe and the majority of developing countries, they are likely to increase the demand for borates used in fiberglass building insulation. Therefore the substitution solutions woulf be adopted.

5. REFERENCES

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COBALT

Cobalt is a shiny, silvery, brittle metal that is used to produce strong alloys, resistant to corrosion and heat. It has high melting (1493 ° C) and boiling (3100 ° C) points. This element has excellent catalytic properties that make it suitable for a wide range of applications, since ancient times it was used for the manufacture of ceramics and crystals. Its use has not been limited there, since it is a very versatile metal and from the last century it began to be used for a great variety of applications for example, metallurgy (in superalloys), electronics, magnets, rechargeable batteries, pigments and pigments, catalysts, alloys, medical applications, etc [1]. However, its main applications are summarized in the following table.

In addition, cobalt is included in the list of raw materials critical for the EU [2] [3] [4].

Table 10. General information concerning Co products and applications [1]-[5].

CRM	Product	Application	Substitute
Cobalt	Superalloys: Co-Ni / Co-Fe	Jet aircraft engines, turbine blades for gas turbines, space vehicles or chemical equipment.	Fiber-reinforced metal matrix composites (MMC), ceramic-ceramic and carbon-carbon composites, titanium aluminides, nickel-based single-crystal alloys or iron-based super-alloys.
	Hard metals	Reinforcing materials: cemented carbides in automotive, aerospace, energy, mining and general engineering. Binder for tungsten carbide (WC) and sometimes for titanium-carbo-nitrides or tantalum-carbides.	Possibility of nickel, chromium and iron
	Batteries	Li-Ion batteries ($LiCoO_2$)	Principally and $LiNiO_2$ and $LiMn_2O_4$
		Rechargeable batteries and cylindrical alkaline batteries	Alternatives used chemically: Gold and silver
	Catalysis	Catalyst to removal petrochemical compounds	Nickel
		Catalyst for the production of recyclable plastics	
		Catalyst in hydrogen fuel cells	
		Chemical reaction (hydroformylation and hydrodesulphurisation catalysts)	Rhodium
	Pigments	Ink and nail polish	Cerium, iron, lead, manganese and vanadium

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1. DESCRIPTION AND INDICATOR

Production and consumption in EU

According to the Study of the Data for a Raw Material System Analysis [7], the world's cobalt resources are estimated at around 25,000 Mt and 7,200 Mt of cobalt reserves worldwide, but there could be more than 120 million additional tons of nodules and crusts of manganese in the ocean floor. In the case of the EU, resources and reserves are not quantified.

The world's annual production of cobalt concentrate, before the refining stage, is around 130,000 kt, and the main producing country is the Democratic Republic of the Congo, which accounts for about two-thirds of world production. China, Zambia and Australia follow, with respectively 5%, 4% and 4%.

In the EU, 1.4 kt of cobalt concentrates are extracted per year in Finland. A total of around 15 kt of cobalt is refined in Finland, Belgium and France per year from imports of cobalt ore concentrates extracted in other countries outside the EU. Therefore, imports of primary materials to the EU amount to approximately 13 kt in cobalt content per year, and imports of refined materials are around 0.6 kt per year.

The European industry uses these cobalt substances produced and imports and manufactures several products that contain approximately 11 kt of cobalt and are mainly used in superalloys and hard metals. These products are sold mainly in the European market, around 8.4 kt of cobalt in products sold in the EU and 2.4 kt of cobalt in exported products. Some of these exported cobalt substances can be used to manufacture finished products that are imported into the EU in the use phase. The use of cobalt in batteries that entered the EU market in 2012 amounted to 10 100 tonnes, only 3% of the demand was met by European manufacturing processes. Imports of finished products represent around 11 kt of cobalt content, batteries and products containing batteries that account for almost 90% of the cobalt content in these imports. European final consumption of products containing cobalt is around 20 kt per year.

Future demand increasing

Due to the new market trends towards a more technological world, it is estimated in the next decade that a large part of the Co production will be used to satisfy the market of rechargeable batteries in electric vehicles (EV). This will likely increase the expected demand for Co in batteries for hybrid electric vehicles (HEV), also other elements used on a larger scale as La, Ce, Nd and Pr. It has been emphasized that cobalt recycling will be essential to obtain a sufficient supply for future demand [6]. Mention should be made of the fact that in the EU, between 2010 and 2017, sales of EV amounted to approximately 681,000 units, of which approximately 217,500 were sold in 2017. Of this volume, around 56% corresponded to the *Plug-in Hybrid Electric Vehicle* (PHEV) and the rest to the *Battery Electric Vehicle* (BEV). As of 2017, Europe had an estimated market share of 21% of global sales of electric vehicles, although it seems to have declined slightly due to the appearance of new competitors.

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Assuming that an average amount of cobalt of 4.5 kg per vehicle was used, the total amount of cobalt consumed in the European EV market to date can be estimated at around 3,000 tons. Finally, in the EU, the projections, suggest that the EV number will range between 1.7 and 3.1 million in the year 2020, increasing to 7-20 million in 2025 and 18-61 million in 2030. The most conservative scenario presents a compound annual growth rate of 22% in 2030, while in the high scenario, a growth rate of 34% is expected [8].

2. SUBSTITUTE MATERIALS

Cobalt is a material that is currently used, since it confers very good properties, improving the performances of the final products. However, although it is not always easy to replace, there are some possible alternatives for the different applications.

Superalloys developed for extreme conditions represents the most demading end use: high temperatures, severe mechanical stress and high surface stability. Alloys that have these requirements can be manufactured on a cobalt basis, but they can also be made from nickel and iron, the most common being the first one. These alloys used in applications such as aeronautics and aerospace (jet aircraft, engines, turbine blades, spacecraft and other chemical equipment) provide better thermal performance, weldability and resistance to corrosion and wear. A key sector for superalloys containing cobalt is the aerospace industry, where these properties are crucial for to achieve reliablility and efficiency [1].

The use as **hard metals** or **aggregates** of **reinforcing materials** is used in the form of cemented carbides. This range of composite materials consist of hard carbide particles bonded by a metal binder. At this point cobalt is key as a binder for tungsten carbide (WC) and sometimes for titanium nitride or tantalum carbide. The addition of cobalt to carbide increases wear resistance, hardness and toughness, essential properties for cutting tools, metal rollers and engine components. These are used in materials engineering and in many different sectors such as automotive, aerospace, energy, mining [1].

Technological advances are developing other elements as substitutes for these binders, including nickel and iron, but the truth is that not many metals meet these requirements and the search is limited. Another aspect to keep in mind is that although most of the substitute materials are cheaper and there is a notable loss of performance. Therefore, cobalt is practically irreplaceable for this application.

Cobalt is used as element to maintain the life of **rechargeable batteries** because the first versions of lithium ion batteries often overheated, failed and minimized their useful life. The membranes, between the cathode and the anode, were drilled soon but by including the cobalt in the cathode, this drawback is avoided. This new system gave it a longer battery life, along with fast charging capacity and low loss of standby power.

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Cobalt also extends the service life of cylindrical alkaline batteries and by adding cobalt to the internal surface of the battery, oxidation is reduced over the life of the battery and is more durable. For these cases, the possible substitution materials are gold and silver, however, for price reasons, they are not viable alternatives [1] [5].

In the case of battery applications (portable, mobile), although $LiCoO_2$ is the preferred material its replacement is potentially possible. Here are both $LiNiO_2$ and $LiMn_2O_4$ batteries. Additionally, the latest industry predictions indicate that many of the disadvantages of these alternative materials have been overcome and it is expected that the demand for Co rechargeable batteries may grow in the near future.

Cobalt is used as a **catalyst** for the removal of sulfur from petroleum products, in gases such as gasoline, diesel or kerosene. Another important use of cobalt catalysts is as a mixed catalyst of cobalt acetate / manganese bromide and sodium for the production of recyclable plastics. In addition, it is also used in the catalysis of gas-to-liquid processes [1]. Finally, a potential emerging use and, surely, an increase in demand for new market trends is like a catalyst in hydrogen fuel cells [5].

With respect to its application for hydrodesulphurisation, the most suitable substitutes would be the use of ruthenium, molybdenum, nickel and tungsten, depending on the nature of the power supply. The alternative ultrasonic process can also be dispensed with using cobalt, and rhodium can serve as a substitute for hydroformylation catalysts [4].

From antique times to our days, cobalt-containing minerals have been used as a source of powerful **colouring agents**, this has allowed their use in a wide variety of applications. Normally cobalt produces a characteristic light blue to black pigment, and is used to color glass, porcelain, ceramics, paints, inks and enamels. The pigments used for dyes comprise several formulations, and are prepared by mixing the ingredients as oxides. However, the cobalt oxide added to the final product depends on the color required. In addition, the final color depends on the application; for example, in an enamel.

On the other hand, cobalt (II) acetate is used in the production of drying agents for inks and pigments [5]. Finally, as substitutes we have: cerium, iron, lead, manganese and vanadium can be used as substitutes for cobalt for this application [4].

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Table 11. General description, economic value and main applications of cobalt substitute materials.

Substitute Material	**Description of the Material**			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Iron and Nickel	Used primarily in turbine engine components	Good , 7	Large scaling-up market	Superalloys (Co-Ni / Co-Fe)
	To reinforce metal structures and for the elaboration of tools in mining and construction, to manufacture tools for cutting and forming metals such as dies.	Low-Adequate, 4	Low-medium scaling-up market	Hard metal and manufacture tools
Manganese and nickel	Used in portable electronic devices, energy storage systems and electric vehicles.	Good, 6	Large scaling-up market	Batteries ($LiNiO_2$ and $LiMn_2O_4$)
Nickel	Used in petroleum refining, products for plastics and detergent manufacture, and polyester precursors.	Medium, 5	Medium scaling-up market	Catalyst
Others: Cerium, iron, lead, manganese and vanadium	Used in colouring glass and in paints	Medium, 5	Medium scaling-up market	Pigments

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

The technological and the non-technological barriers, as well as a short description of proposed solutions for the substitution of cobalt are presented in Table 3. The evaluation of the barriers and the possibility of their solution are quantified:

Table 12. Technological and non-technological barriers to the rollout of substitutes to cobalt.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Iron and Nickel	Technological	Superalloys: Co-Ni / Co-Fe	Fabrication process for alloy	8	Alloys standardization	9
	Non-Technological	Superalloys: Co-Ni / Co-Fe	Practical application in the market	6	Lab testing of a commercial product (vehicle and aerospace industry)	8
			Production and recovery policies in EU	6	Investigation of Co recovery, principally by specific secondary resources in EU.	6
	Technological	Hard metals	Easy to find substitutes more economic substitutes but the performances are worse	6	Development of new laboratory studies to search aggregates that improve performances.	6
	Non-Technological	Hard metals	Recovery is not very easy	6	New EU policies for the recovery	5

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Manganese and nickel	Technological	Batteries: $LiNiO_2$ /$LiMn_2O_4$	Stability under investigation	7	To boost studies of chemical stability, safety and toxicity.	9
	Non-Technological	Batteries: $LiNiO_2$ /$LiMn_2O_4$	-	8	Recovery investigation	6
Nickel	Technological	Catalyst: hydrodesulfurization and hydroformylation	Depending on the source to catalyze difficulty of finding the substitute	6	New studies to find compatible substitutes	6
	Non-Technological	Catalyst: hydrodesulfurization and hydroformylation	Difficult recovery due to the minimum quantities	4	Investigation of Ni recovery by specific secondary resources in EU	4
Others: Cerium, iron, lead, manganese and vanadium	Technological	Pigments	Due to the specific properties of the more complicated metal is the substitution in pigmentation	4	A greater effort to carry out innovative tests of similar pigmentation in laboratories	4
	Non technological	Pigments	There is not a significant non technological barrier	-	-	-

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4. SUMMARY

To summarize, due to its extraordinary properties, cobalt generally has limited replacement options because in the case of two of its main applications. On the one hand, in hard reinforcement metals as it appears as substitute materials, or combined in superalloys of iron-phosphorus, manganese, nickel-cobalt-aluminum or nickel-cobalt-manganese. Although it is true that the objective application must be taken into account as improper use would result in a loss in product performance. As substitutes we have, in the case of lithium-ion batteries, alloys with nickel and manganese. On the other hand, in the case of pigments, possible substitutes include cerium, iron, lead, manganese or vanadium. Finally, cobalt as a catalyst can be substituted to some extent by hydrodesulfurization and hydroformylation processes.

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HAFNIUM

Hafnium is a silvery metal with a high hardness and chemical behaviour very similar to zirconium. It is characterized by a high density, 13.3 g/cm3, and a high melting point, 2233°C, and it is a good absorber of neutrons [1]. In nature, hafnium is always found with zirconium and obtained as a by-product in zirconium extraction. Indeed, hafnium is included in two rare ores: hafnon, $(Hf,Zr)SiO_4$, and alvite, $(Hf,Th,Xr)SiO_4 \cdot H_2O$. Major producers of hafnium (i.e., refining of zirconium) are France (43%) and USA (41%), yet the largest reserves are located in Australia, South Africa, India and Mosambique. The annual production rate is approximately 72 000 t [2].

1. DESCRIPTION AND INDICATOR

Base metals and nuclear applications (indicated as “machinery parts”) constitute the most important end uses of hafnium, as shown by Figure 2, and described in more detail below. The third key application, corresponding to 13% of hafnium end use, is chemical products: some of its compounds are fire retardants, some melt only at extremely high temperatures and are used as refractory ceramic materials (which find use in, e.g., plasma welding torches), and it may be used as a stabilising agent for ZrO_2 (prevents excessive crystal growth). The optical applications account for 11% of hafnium use, followed by 5% contribution by electronic applications, e.g., microchips [2].

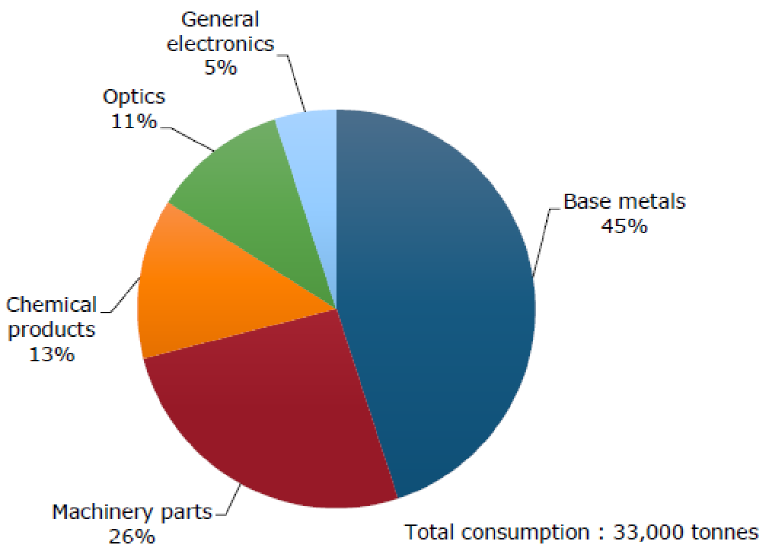

Figure 3. End uses of hafnium. [3]

Metallurgy: Base metals

Majority of hafnium is used for base metals as an alloying element (45 % of hafnium use globally, Figure 2). Here, the main focus area is high-temperature alloys, including superalloys.

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The high melting point of hafnium, 2233°C (4,051°F), helps to strengthen grain boundaries, thus considerably improving both high-temperature creep and tensile strength. In addition, with its high affinity for carbon, nitrogen and oxygen, the metal also provides strengthening through second-phase particle dispersion.

One of the most common uses of hafnium is in nickel-based superalloys for environments with very high temperatures, pressure and high stress. Such conditions are found in the turbine blades and vanes "hot end" of jet engines in aerospace industry and in industrial gas turbines. For example, MAR-M 247, a polycrystalline nickel-based superalloy developed by Martin-Marietta Corp. and used by Siemens in land-based turbines that operated at temperatures up to 1038°C, contains 1.5% hafnium. In addition to superalloys, hafnium can be found in a number of other alloys, such as iron-based alloys and those of niobium, tantalum and titanium. Hafnium-niobium alloys, for example, are heat resistant and are used in aerospace applications, such as space rocket engines. Some examples of hafnium alloying are as follows: tantalum-based T111 (Ta-8%W-2%Hf); tantalum/tungsten-based T222 (Ta-10%W-2.5%Hf-0.01%C) and molybdenum-based MHC, or molybdenum-hafnium-carbide, which breaks into Mo-1.2%Hf-0.1%C. In addition, it can be found in a number of niobium-based alloys: C-103 (10% Hf-1%Ti-1%Zr); C-129Y (10%W-10%Hf-0.7%Y) and WC-3015 (30%Hf-15%W-1.5%Zr). Among other applications, niobium-based alloys containing hafnium have been used as coatings for cutting tools, while C-103 and hafnium-tantalum-carbide have been used in the fabrication of rocket engine thruster nozzles. With the melting point of over 3890°C, hafnium carbide (HfC) is one of the most thermally stable refractory binary materials around [2] [3].

Nuclear applications

The second important application sector is nuclear industry, accounting for 26% of hafnium use (indicated in the category of "machine parts" in Fig. 2). Hafnium shows a good absorption capability of neutrons and this end use makes use of this capability along with the good mechanical and corrosion resistance qualities. Indeed, hafnium is used as a neutron absorber in control rods in nuclear reactors and nuclear submarines. The purify of hafnium in the nuclear control rod applications is vital in order to work effectively [2] [3].

Table 13. General information concerning Hf products and applications.

CRM	Product	Application	Substitute
Hafnium	Nuclear control rods	Nuclear reactors, nuclear submarines	Silver-indium-cadmium alloy (Ag-In-Cd)
	Nuclear control rods	Nuclear reactors, nuclear submarines	Boron carbide B_4C
	Superalloys	Aerospace, industrial gas turbines	Niobium (Nb), tantalum (Ta), cobalt (Co), chromium (Cr)

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2. SUBSTITUTE MATERIALS

Metallurgy: Base metals

In alloying applications (superalloys), hafnium can generally be substituted by other alloy metals, such as niobium, tantalum, cobalt and chromium. [2] In the following, a short description of each is given.

Niobium is a transition refractory metal with a very high melting point of 2477ºC and good resistance to corrosion and chemical attack. [2] Currently, 86% of niobium is consumed in the production of high-strength low-alloy (HSLA) steels. 8% of niobium ends up in high-performance alloys with high Nb-contents, e.g, superalloys or special-purpose alloys. Niobium is also considered as a Critical Raw Material and it relies 100% on the import outside from EU. The average production of niobium ores and concentrates is 113 000 tonnes a year [4]. The market for niobium is expected to witness a compound annual growth rate (CAGR) of 5.90 % during the period of 2019-2024. Major factors driving the market are the increased consumption of niobium in structural steel and extensive utilization of niobium-based alloys in manufacturing aircraft engines [5].

Tantalum is another substitution candidate in base metal applications. It has an even higher melting point than niobium, 3017ºC, and a high permittivity and corrosion resistance. [6] At present, capacitor applications (making use of the high permittivity of the material) account for the major end use of tantalum (33%), followed by superalloy applications (22%) and sputtering targets (17%) that are a tantalum source for depositing tantalum thin films. [6] The global tantalum market was estimated at 1803.5 tons in 2017. The market is expected to reach 2949.29 tons by 2023, at an estimated CAGR of 5.81 % during 2018-2023 [7]. Nevertheless, tantalum is also a Critical Raw Material and and is fully reliant on import to EU, mainly from Nigeria, Rwanda and China. Total annual production worldwide is approximately 1800 tonnes [2], i.e., all produced tantalum ends up in consumption.

Cobalt is also an alternative material solution to replace hafnium in base metal applications. Cobalt metal has a melting point of 1495ªC, good corrosion resistance and high-temperature strength as well as magnetic properties with the highest known Curie point. [8] Cobalt is one of the key battery chemicals, with battery applications accounting for 42% of cobalt end use [8]. However, due to electrification of traffic, the global demand for cobalt is expected to double in the future years (by 2025) to the annual consumption of 272 000 t as compared to situation in 2017, 136 000 t [9]. The end uses that follow battery applications have been superalloys (23%) and hard materials (10%). It is emphasized that cobalt also has some hazardous properties including lung carcinogenicity for fine cobalt powders and some cobalt compounds, and therefore requires appropriate measures for safe handling and use.

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Chromium is one of the possible substitutes for hafnium. It has a melting point of 1907C [] and features a good corrosion resistance. Chromium is used to harden steel, to manufacture stainless steel and as an alloying element to produce several alloys. Indeed, manufacturing of stainless steel is the leading end use of chromium [10]. Chromium is also used as a plating material, to provide resistance against corrosion and wear. Annual chromium production is approximately 36 000 t, with reserves of 560 000 t. [11] The top chromium producers in the world are South Africa, Kazakhstan and India, and these also have the largest reserves. Chromium has been in the CRM list (2014), but is not included in the latest version (2017).

Nuclear applications

In nuclear control rod applications, the neutron absorption properties of the material are of key importance. Thus, only materials with high neutron capture cross-section may substitute hafnium in nuclear control rod applications. The most common alternative materials are boron carbide, B4C, and silver-indium-cadmium alloy (Ag-In-Cd). Boron carbide (B4C) is a hard, chemically stable refractory compound with a high melting point and good high temperature mechanical properties, which make it a useful ceramic material for commercial applications. It is particularly useful as an absorber in control assemblies of nuclear plants because the boron (B) has nearly 20% of the high neutron absorption 10B isotope. Boron carbide is the most widely used absorber in reactors. Ag-Cd-In alloys typically have the composition of 80% Ag, 15% In, 5% Cd. [12] However, also borates, the source of boron, and indium are CRMs. Boron is used mainly in glass industry (49%), with the annual production reaching 1 million t annually, mainly from Turkey (38%), USA (23%) and Argentina (12%). Indium, in turn, is produced only at the rate of 689 t per year. The main applications are flat panel displays (56%), solders (10%) and PV cells (8%). [2]

Table 14. General description, economic value and main applications of Hf substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Niobium	Niobium has several characteristics parallel to those of hafnium, e.g., high melting point	Niobium is also a critical raw material with no EU production	Utilised especially in the production of high-strength steel	Substitution candidate in base metal applications
Tantalum	Tantalum has a high melting point, like hafnium. However, it has also other interesting properties, such as high permittivity	Tantalum is also a critical raw material with no EU production	Tantalum is used broadly due to its high permittivity in capacitor applications	Substitution candidate in base metal applications

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Cobalt	Cobalt has a lower melting point than hafnium, yet it is still higher than for several other metals and is typical alloying element/base material in superalloys	Cobalt is also a critical raw material with limited amount of EU production	Cobalt is a battery (cathode) material so its demand will grow with electrification of traffic	Substitution candidate in base metal applications
Chromium	Chromium has a lower melting point than hafnium, yet it is still higher than for several other metals. Typical alloying element for elevated temperatures for, e.g., oxidation resistance		Alloying element also in steels (stainless steels)	Substitution candidate in base metal applications
Boron carbide, BC_4	Chemically stable refractory compound with a high melting point. Boron (B) has nearly 20% of the high neutron absorption 10B isotope, making BC_4 a suitable material for neutron absorption purposes.	Borate, the naturally occurring mineral of boron, is also a critical raw material with no EU production.	Boron is used extensively in glass and ceramics industris	Substitute material for neutron absorption applications (nuclear steering rods)
Ag-In-Cd	Alloy of the composition 80% Ag, 15% In, 5% Cd	Indium is also a critical raw material with very limited production in EU	Silver demand also in the area of renewable energy technologies (solar energy)	Substitute material for neutron absorption applications (nuclear steering rods)

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Many of the proposed substitutes are also CRMs with even smaller production amounts (tantalum, chromium) than hafnium and/or foreseen high demand (cobalt).

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Table 15. Technological and non-technological barriers to the rollout of substitutes to hafnium.

Substitute Material	Type of arrir	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Substitute 1: Niobium	Non-Technological	Metallurgy, base alloys	Niobium is also a critical raw material	5		
Substitute 2: Tantalum	Non-Technological	Metallurgy, base alloys	Tantalum is also a critical raw material	5		
Substitute 3: Cobalt	Non-Technological	Metallurgy, base alloys	Cobalt is also a critical raw material, demand expected to grow significantly in the future due to electrification of traffic	5		
Substitute 4: Chromium	Non-Technological	Metallurgy, base alloys	Already used widely in metallurgy, other demands in this area (stainless steels)	5		
Substitute 5: BC_4	Non-Technological	Nuclear steering rods: Boron carbide is the most widely used absorber in reactors	Boron (borate) is also a critical raw material	5		
Substitute 6: Ag-In-Cd	Non-technological	Nuclear steering rods: Ag-In-Cd is a common material in neutron absorption applications	Indium is also a critical raw material	5		

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4. SUMMARY

Hafnium is a raw material with exceptional chemical and physical properties, such as a very high melting point among metallic elements and a good neutron absorption capability. The use of hafnium mostly relies on in these characteristics. In the metallurgy, the high melting point and parallel benefits may be introduced by alloying with niobium, tantalum, cobalt and chromium, of which three former are also critical raw materials. In nuclear applications, which require a high neutron absorption capability, boron carbide, BC4, and Ag-In-Cd alloys at the primary substitutes. Nevertheless, also boron (borate) and indium are critical raw materials. Thus, the barriers for substitution are primary non-technical, with supply/demand dynamics and the market growth determining the future substitution possibilities.

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BISMUTH

Bismuth is a metal mined as a by-product of lead, copper and tungsten. The metal is processed mainly in China, which holds 82% share of global supply. The remaining share of Bi refining belongs to Mexico and Japan, with 11% and 7% share respectively. Bismuth has very similar properties to antimony and arsenic.

According to EU Critical Materials Report [1], bismuth is considered as an "eco-friendly" material. As a result, its first sector of application is in the pharmaceutical and animal-feed industries (62% of total uses for Bi chemicals). In modern medicine, compounds of bismuth are mainly applied clinically for gastrointestinal disorders as anti-ulcer agents. The use of bismuth (III) is also seen in nuclear medicine, anticancer, antitumor and antimicrobial studies. Fusible alloys represent the second most important use (28%). Bismuth is notably used as a replacement for more harmful metals (on top of which is lead) in solders. Other uses include metallurgical additives and a number of other industrial applications such as coatings, pigments, and electronics. Figure 3 illustrates the 3 major applications of bismuth.

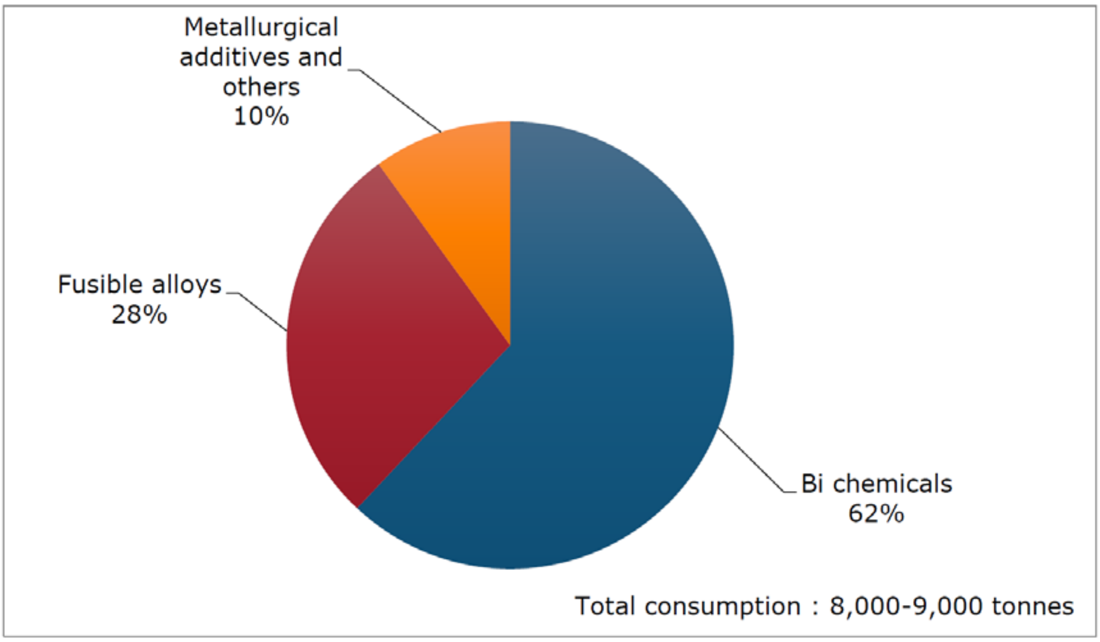

Figure 4. End-use of bismuth [1]

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The table below shows the main substitutional materials for different applications of bismuth.

Table 16. General information concerning Bi products and applications.

CRM	Product	Application	Substitute
Bismuth	Pharmaceuthical products, cosmetics, animal feed	Chemicals	Antibiotics, Alumina, Magnesia
	Electronics	Fusible alloys	Resin, Glycerine-filled glass bulbs
		Solders	Indium
	Paints, coatings	Pigment	Titanium dioxide-coated mica flakes Fish-scale extracts

Sources: [1] [2]

1. DESCRIPTION AND INDICATOR

Production and consumption in EU

EU is 100% reliant on import of refined bismuth in order to use it in manufacturing of finished products. On average 8,180 tonnes of Bi is refined globally, whereas about 0,8 tones is estimated to be processed in European Union (Bulgaria). A big actor on Bi market in EU is Canadian 5N Plus, with a subsidiary in Belgium. It specialises in production of refined bismuth, Bi-bearing chemicals and low melting point alloys. The company could have refining capacity in EU, however there is no data available to support this statement. Europe's largest producer of bismuth vanadate ($BiVO_4$), a pigment used in paints and coatings, is BASF (Germany) [1]. Geotech Internation B. V. from The Netherlands and Orrion Chemicals are other significant actors in European Bi market [3].

Future demand

According to market research prediction until 2024, global bismuth demand is expected to grow. This is driven by government's regulations to replace lead with bismuth in several applications (paints & coatings, alloys, and electronics), which has resembling properties to the harmful lead. Automotive industry is expected to increase the demand for bismuth by using it in for example rust free coatings, clutch pads and brake linings. Moreover, increase in production of tungsten, which is the main metal mined together with bismuth, is anticipated to impact the growth of Bi supply [4].

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Use in cutting edge technologies

Bismuth is used in high-tech application for example in wearable technology and as an anode in sodium-ion batteries (SIB) [4]. Example of wearable application is a flexible battery printed on fabric. Bi is mixed into electrodes in stretchable zinc-based batteries to make them rechargeable and prolong their lifetime [5].

2. SUBSTITUTE MATERIALS

According to USGS Minerals Yearbook [6], bismuth compounds can be replaced in pharmaceutical applications by alumina, antibiotics, and magnesia. Titanium dioxide-coated mica flakes and fish-scale extracts are substitutes in pigment uses. Indium can replace bismuth in low -temperature solders. Resins can replace bismuth alloys for holding metal shapes during machining, and glycerine-filled glass bulbs can replace bismuth alloys in triggering devices for fire sprinklers. Free-machining alloys can contain lead, selenium, or tellurium as a replacement for bismuth. Furthermore, bismuth is an environmentally friendly substitute for lead in plumbing and many other applications, including fishing weights, hunting ammunition, lubricating greases, and soldering alloy.

Table 17. General description, economic value and main applications of Bi substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Indium	Indium is a soft, ductile silvery metal, with low melting point, that can be superconductive. It is mainly used to produce indium-tin oxide used in final applications	Production in EU reached 48 t per year. Countries producing indium are Belgium and France. The apparent consumption was about 22 t per year during 2010-2014 (3% of global production). EU was self-sufficient with indium supply	Prices of indium were fluctuating greatly in the past, from US$65 per kg in 2002, through the highest US$1,000 in 2005 and reached current level of US$200	Flat panel displays, solders, PV cells, thermal interface material, batteries, alloys/compounds, semiconductors & LEDs

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		(0% import reliance)		
Antibiotics (replacing Bi from pharmaceutical applications)	Used in prevention and treatment of bacterial infections, by either killing or inhibiting the growth of the bacteria [7].	Mean consumption in the community in 2016 for systemic use in the community was 21.9 defined daily doses (DDD) per 1000 inhabitants per day. In 2016, consumption ranged from 10.4 (the Netherlands) to 36.3 DDD per 1000 inhabitants per day (Greece) [8].	The consumption of antibiotics in EU at community level during 2012–2016, didn't show any significant trend over all. However, large inter-country variations remained unchanged. Finland, Sweden Luxembourg and Norway showed a decreasing trend, whereas Greece and Spain showed an increasing trend [8].	Bacterial infection treatment in people and animals.
Alumina (replacing Bi from pharmaceutical applications)	White or nearly colourless crystalline substance that is used as a starting material for the smelting of aluminium metal [9].	Production in several European countries: Germany, Greece, Ireland, Romania, Spain [14].	Worldwide alumina production is growing annually.	Filler for plastics; glass; abrasive substance, among others.
Magnesia (replacing Bi from pharmaceutical applications)	Magnesia or magnesium oxide is a white solid mineral which is a source of magnesium. It is physically and chemically stable at high temperatures, has high thermal conductivity and low electrical conductivity [10].	Magnesium oxide is produced in several countries in Europe: Spain, Ireland, The Netherlands, Greece, Slovakia, Austria. Raw magnesite is traded only to a small extent.	Magnesium oxide is the most important industrial magnesium compound with its main application in the steel and refractory industry.	Used as fireproofing ingredient in construction materials, medical applications, reference white colour in colorimetry, electrical insulator in heating elements
Resin	Resin is a solid or highly viscous	Depending on the type of resin	Depending on the type of resin	Plant resins are valued for the

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(replacing Bi alloys for holding metal shapes during machining)	substance of plant or synthetic origin. Resins can replace bismuth alloys for holding metal shapes during machining [2].			production of varnishes, adhesives, and food glazing agents. Many materials are produced via the conversion of synthetic resins to solids [11].
Glycerine-filled glass bulbs (replacing Bi alloys in triggering devices for fire sprinklers)	Glycerine is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. Glycerine-filled glass bulbs can replace bismuth alloys in triggering devices for fire sprinklers [2].	Glycerine is produced in United States and Europe.	-	It is widely used in the food industry as a sweetener and humectant and in pharmaceutical formulations.
Titanium dioxide-coated mica flakes (replacing Bi use in pigments)	Free-flowing off white powder with an intense green shade and blue reflection colour [12].	Important producer in Europe is BASF	A new generation of titanium dioxide-coated synthetic mica flakes makes it possible to achieve extraordinary lustre and brilliance, important for luxury items production [13].	Used in powder coatings and inks. Recommended for coloration of plastic, general industrial paints, architectural or decorative paints as well as printing ink [12].

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

The literature regarding bismuth substitutes is limited, therefore is was not possible to find barriers and solutions for all materials. Although there are several substitute materials identified, the barriers for their implementation are not well known. Regarding medical applications, bismuth is attractive because it is not toxic. It can be deducted, that for that reason, substitution for medical purposes is difficult. In case of indium, it is a critical material as well, therefore it is not a good substitution candidate.

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Table 18. Technological and non-technological barriers to the rollout of substitutes to bismuth.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Indium	Technological	Solders	Critical raw material	9	Use different, non-critical substitute	9
Antibiotics	-	Pharmaceutical applications	-	-	-	-
Alumina	-	Pharmaceutical applications	-	-	-	-
Magnesia	-		-	-	-	-
Resin	-	Alloys for holding metal shapes during machining	-	-	-	-
Glycerine-filled glass bulbs	-	Alloys in triggering devices for fire sprinklers	-	-	-	-
Titanium dioxide-coated mica flakes	-	Pigments	-	-	-	-

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4. SUMMARY

Bismuth is a metal mined as a by-product of lead, copper and tungsten. Bismuth has very similar properties to antimony and arsenic. Since it is not toxic, it is widely used in pharmaceuticals and cosmetics. Severalsubstitutes were identified. However, there is little knowledge on bismuth substitutability. Bi can replace lead since it is not toxic, yet this does not improve its criticality performance.

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GALLIUM

Gallium, a ubiquitous element in electronic applications under the form gallium arsenide (GaAs), gallium nitride (GaN) or gallium antimony (GaSb), offers excellent electro-chemical properties as a semi-conductor with electron mobility 6x higher than silicon. This and other features have pushed the use of gallium in integrated circuits (ICs) requiring high-performance such as military applications or communications. LED lighting also requires GaN as a semiconductor material to for example provide white light. An overview from task 5.1 is given with the major applications and known substitutes for gallium.

Table 19. General information concerning Ga products and applications.

CRM	Product	Application	Substitute
Gallium	Integrated circuits (ICs)	Type III-V semiconducting compounds (GaAs, GaN, GaSb) for integrated circuits and sensors in military applications. Military applications include: radar technology, satellites, aerospace. Other applications include LEDs and solar PV.	OLED is a promising substitute for LEDs [1]. Germanium and silicon may be a substitute of GaAs in some applications albeit with a loss of performance [2].
	Permanent magnets	Additive during the manufacturing process of NdFeB type of magnets used in: Computers, wind turbines, electric and hybrid vehicles and other electronic applications.	Similar properties might be achieved by using aluminum, niobium or dysprosium.

1. DESCRIPTION AND INDICATOR

Gallium is a silvery-white, soft metal, which is one of the rarer elements in the earth's crust. It is mainly found in enriched amounts suitable for economical use in ores of aluminum (bauxite) due to gallium's chemical similarity to aluminum, but also in ores of zinc (sphalerite) and in the fly ash of coal [3]. Gallium is a low melting point metal and has one of the largest liquid ranges amongst all elements, as it melts already at 30 °C and evaporates at 2403 °C [4]. Gallium forms compounds with nitrogen (GaN) or arsenic (GaAs) exhibiting excellent semiconducting properties, which allows its use for high-frequency applications. The main use of gallium is in semiconducting form as GaAs and to a much lesser extend as GaN, due the comparatively difficult and costly production [5]. Currently, worldwide end uses for GaAs comprise

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integrated circuits (ICs), optoelectronic devices, including light emitting diodes (LEDs), laser diodes, photodetectors and copper-indium-gallium-selenium (CIGS) based thin film solar cells [10].

Within the EU the main share of manufactured gallium which is finished into products goes into sensor applications, mainly for military uses and in second place into applications using permanent magnets [6] The EU Commission considers gallium as a critical raw material since 2010 due to the limited production potential as by-product during the aluminum refining process from bauxite, its growing use and importance for low CO_2 footprint technologies [1, 7-9]. It is forecasted that until 2020, the gallium demand will strongly increase by more than 8 % annually, thereby showing the second largest demand growth rate of all classified critical raw materials after niobium in the EU mainly drive by LEDs and solar applications [1]. The substitutability of gallium was assessed by the European Commission [7], the US Geological Survey [10] and in the CRM_InnoNet project [11].

2. SUBSTITUTE MATERIALS

OLED is an emerging technology with the capacity to replace in the long-term semiconductor-based LED. OLED mostly uses organic material to provide the electroluminescence effect by means of evaporating organic layers under a glass subtract pre-coated with ITO [1]. The uptake of OLED as a replacement technology for LED will reduce demand for gallium, germanium and phosphorus elements given that its components are organic based. A layer of conductive material is needed on top the organic layers such as aluminium [1]. LED lighting is broadly used as backlight for screens such as computer screens and TVs. OLED is currently the only solution for flexible displays in smartphones and other small screens. Manufacturers of smartphones predict growth of this application for the future thus backing-up the penetration of OLED in the backlighting segment. OLED still has a 5-10 year development curve to pair with LED in terms of price, performance and lifespan [1]. Efforts are being put by OSRAM AG in terms of R&D to boost the competitiveness of OLED. A point to solve will be the need of using indium in the conductive layers [1].

Another replacement to gallium in LEDs could be zinc oxide (ZnO). This alternative has been investigated for some time although stability is still lacking thus preventing the rise of ZnO as a replacement of GaN in LED technology [1] [5] [11]. The same applied for magnesium sulphide (MgS) [1].

In terms of ICs, potential replacements for gallium include silicon-germanium (SiGe) in for example power amplifiers for midtier 3G handsets indium phosphide in infrared laser diodes and helium neon laser diodes [13]. Another potential field where gallium can be replaced by SiGe is in RF transistors as recently proved by IMEC although some improvements are still

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pending to make the substitution possible [12]. It can be concluded that only SiGe present real potential to replace GaAs in some applications [11].

For CIGS solar cells, the current scope of academic research is to find an alternative to gallium such as copper-zinc-tin-selenide (CZTS) which allows for similar performance although this is not the case yet [11].

In the case of permanent magnets, as mentioned above, gallium is used as an additive in the manufacturing process of NdFeB. Due to the criticality of REEs, much research has focused on finding replacements for Nd. In fact, a combination of manganese and gallium (MnGa) has been researched as a potential alternative to NdFeB magnets [14]. This move will increase the pressure on gallium in the long run.
A summary is presented in table below:

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Table 20. Potential substitutes for gallium and its applications.

Substitute Material	**Description of the Material**			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
OLED	Substitution for LEDs used in major electronic application such as light bulbs or back-lighting for televisions and other electronic equipment with screens. Gallium is used in the form GAN and InGaN.	Market penetration targeted for 2025 pending positive development of R&D paths.	LED lighting is expected to have an 84 % market penetration in the lighting sector in the EU by 2030 from the current 7 %. Sales of lighting are expected to decrease over time, but the share of LED sales will grow to 82 % in 2030. Sales of LED are expected to be around 500 million units per year until 2030	Low-energy consumption lighting with extended life-time when compared to incandescent or fluorescent lighting.
ZnO	Replacement of GaN in LED light and laser diodes.	ZnO accounts for 8 % of zinc flows in Europe as of 2003 [15].	Market expected to grow at CAGR of 6 % p.a. between 2015 and 2020.	White pigment in cosmetics and other applications. Additive in tire manufacturing and also commonly used in agriculture.
SiGe	Replacement of GaAs in Integrated circuits for electronic equipment such as RF transmitters.	Both silicon and germanium are listed as CRMs.	Integrated circuit market is expected to continue growing.	SiGe is a growing contester in the IC world thanks to its capabilities for mixed-signal circuits and is seen as a solution for increased size reduction [16].

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Technological and non-technological barriers to the rollout of substitutes to gallium in its main applications are elaborated in

R&D activities are pointed out as the most important steps needed to replace gallium due to its outstanding electro-chemical properties. The latter is the reason why gallium is so widely used [1] [5] [9] [11]. OLED may become a potential replacement solution for the criticality of gallium in LEDs if the lifespan and prices are improved. SiGe may replace in the future GaAs in ICs provided that the architecture of SiGe chips improves [12]. Given the similarity of price of both solutions [11], SiGe can replace GaAs in the coming future. Despite this, silicon and germanium are also CRMs.

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Table 21. Technological and non-technological barriers to the rollout of substitutes to gallium.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
OLED	Technological	LEDs and backlight for electronic devices	R&D needed extend lifespan to compete with standard LED	10	Improve R&D activities and support technological transition.	10
	Non-Technological	LEDs and backlight for devices	R&D needed to bring costs down and efficiency	8	Improve R&D activities and support technological transition.	8
ZnO	Technological	LEDs and backlight for electronic devices	P-type ZnO has limited stability. Similar happends with MgSe and ZnSe	7	Improve R&D activities and support technological transition.	9
SiGe	Technological	GaAs integrated circuits	R&D needed to raise performance of SiGe alternatives in different integrated circuit applications	10	IMEC currently develops solutions for replacement of GaAs integrated circuits based on SiGe which will lead to improved architecture of the SiGe ICs.	9
	Non-Technological	GaAs integrated circuits	Germanium and silicon are a CRM	10	Improve collection and recycling systems.	10

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4. SUMMARY

Due to its extraordinary electro-chemical properties, gallium is a broadly used element in a multitude of electronic applications. To date, no replacement exists for the large use of GaAs integrated circuits although SiGe alternatives have been reported to be a potential replacement of GaAs ICs in some applications. Another important application is LED lighting where gallium is widely used under the form GaN and InGaN. The ongoing development of OLED technology may hint soon at a possible replacement although OLED currently requires ITO to operate. In conclusion, there are no concrete replacements for gallium in its major applications and if they exist, they require other CRMs to as replacement.

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GERMANIUM

Germanium is found in diverse applications in our society. These range from optics, PV panels in space, to the manufacturing of PET polymer. The ubiquitous applications of the element, praised by its excellent transparency to infra-red (IR), make it suitable for applications dependent of IR wavelength and other applications where its optic properties lead to improvements in performance/visible color. In Table 22, a summary is shown highlighting the main applications of germanium and the potential substitutes.

Table 22. General information concerning Ge products and applications.

CRM	Product	Application	Substitute
Germanium	Infrared optics	Germanium is mostly used in lenses for: Infrared detectors and cameras, night vision devices and satellite systems.	No broad scope replacement exists and depends on application. Black DiamondTM BD-2 ($Ge_{28}Sb_{12}Se_{60}$), ZnSe, ZnS, silicon, Vacuum UV Grade CaF_2, Poly IR, CaF_2, IG6 ($As_{40}Se_{60}$), GASIR®1 and GASIR®5 chalcogenide glasses can be used but they differ in spectral range of transparency, refractive index and dependence of transmittance on coating. As an example, ZnSe can be used in thermal imaging but with lower resolution.
	Fibre optics	Transmission of light signals at high rates at high bandwidth and very low attenuation (<0.2 dB/km). Mainly used in telecommunications such as transatlantic undersea cables. Germanosilicate is used	P_2O_5 or AlO_3 can give similar high refractive index properties. Silica-core fluorine-doped has been positively tested in 2015 as a suitable replacement for germanosilicate.

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		because of its high refractive index.	
	Solar cells for satellites	Germanium used in high-performance multi-junction solar cells in space applications or in concentrated PV by means of Fresnel lenses. Germanium allows for absorption of longer wavelengths.	Substitutes exist based on other CRMs such as InGaP, AlGaInP, InGaAsP, InGaAs. Multi-junction (IMM) solar cells grown with GaAs or Ge are in the process of space qualification & characterization.
	Other uses	In electronics such as high-brightness LED and SiGe transistors. As a PET polymerization catalyst to improve transparency.	Silicon may be a substitute but with inferior performance in the same application. Antimony and titanium are progressively used as replacement for germanium as PET polymerization catalyst although potentially with a carcinogenic effect. Aluminium-based catalyst may also be a solution to offset the carcinogenic effect of Sb.

1. DESCRIPTION AND INDICATOR

Germanium is a silvery-white, hard, brittle n-type semiconductor and was only discovered in 1886. At 300 K it has a band gap of 0.67 eV, which was responsible for its earlier use in the semiconductor industry in transistors [1, 2, 3]. The abundance in the earth's crust is about 1.6 ppm (g/tonne) in continents and 1.5 ppm in ocean's crust [4]. The primary source of germanium is from by-products of zinc and copper ore mining where zinc is associated with sphalerite as well as from coal and coal combustion fly ashes [4, 5, 6]. Germanium is used mainly because of its good optical properties, i.e. transparency to infrared radiation, high refraction and dispersion indexes [2]. Germanium has been considered critical to the EU since the original assessment in 2010 [7, 8, 9].

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2. SUBSTITUTE MATERIALS

IR optics

Zinc selenide (ZnSe) can replace germanium but not without a drawback in terms of performance loss [3, 10]. ZnSe is produced from the synthesis of zinc vapour and H_2Se gas [12].

Fibre optics

Alternatives to germanium in fibre optics include phosphorous pentoxide (P_2O_5) [10]. This substance is used to increase the refractive index of silica and thus have similar performance as germanosilicate optical fibres. This alternative nevertheless implies the usage of another CRM which is phosphorous. This trade-off should be addressed when replacements of germanium are being investigated. Despite this, P_2O_5 optic fibres have been reported to have high performance.

Solar cells for satellites

Germanium is mostly used in high-performance multifunction solar cells (type III-V cells) [10]. Due to the costs associated with the use of germanium, it is mostly used in premium applications like satellites. To replace germanium, research is focused on quadruple layer cells using different substrates such as InGaP, AlGaInP, InGaAsP and InGaAs [10].

PET polymerization catalyst

Germanium dioxide is widely used as a polymerization catalyst where Sb_2O_3 or titanium-based catalysts could be potential future replacements [10]. Antimony-based alternatives may pose health risks given the toxicity of antimony although it has been reported safe. Titanium alternatives in turn give a slight yellowish coloration to the finished polymer. These two alternatives can fully replace the use of germanium in terms of technical solution but require some further research [10].

A summary is presented in table below:

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Table 23. Potential substitutes for germanium and its applications.

Substitute Material	Description of the Material			
	General description and objetive	Production and consumption in EU	Economic value/ Market trend	Technological application
ZnSe	Potential replacement for germanium in IR applications.	Isolated data for ZnSe cannot be found for Europe. According to [11], the use of zinc derivates for chemicals like ZnO is approximately 8 % (171 Gg) of the total Zn production in Europe	Zinc reserves in Europe are increasingly scarce [11]. Although zinc is not listed as a critical raw material by the EU.	ZnSe is mainly used in optical applications like lenses, mirrors, prisms or other IR applications [12].
P_2O_5	Phosporous-based doping can increase the refractive index of silica and replace germanosilicate fribre optics.	Phosphorous pentoxide is obtained from direct oxidation of phosphorous [14].	Phosphor is a CRM due to its extensive use in agriculture as a fertilizer.	Used as a potent dehydration substance based on its exothermic hydrolysis [13]. Also used in flame retardants and plasticizers or as a catalyst [14].
Multijunction solar cells	Multijunction solar cells containing non-germanium materials can replace germanium in the future.	IMM solar cells require other CRMs to be manufactured such as Ga and In.	Solar PV market will continue to experience high growth in the next decades due to the energy transition.	Solar cells for the aerospace industry.
Si	Silicon based ICs have lower performance than SiGe type of ICs.	Silicon has been listed as a CRM by the EU. Eu produces 195 tonnes of silicon metal per year although imports account to 68 % of EU consumption.	Demand for silicon will continue to grow thanks to the solar and the aluminium industries [15].	Largely used in the metallurgical industry as an alloying element in aluminum alloys and under the form of silicones and silanes in the chemical industry [15].
Sb and Ti	Antimony trioxide or titanium have been used as replacement catalysts in PET polymerization.	Antimony is a CRM where the EU relies 100% on imports. Titanium is widely abundant metal on earth's crust [16].	According to reference [15], demand for antimony will continue growing.titanium has a variety of applications. Consumption of titanium is expected to grow by 4 % per year until 2025 [17].	Antimony is mostly used as a flame retardant or in lead acid batteries. Titanium is mostly used in industries producing titanium dioxide [17].

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Technological and non-technological barriers to the rollout of substitutes to germanium in its main applications are elaborated in R&D activities are pointed out as the most important steps needed to replace germanium due to its outstanding optical properties. Despite its high-cost, cheap alternatives perform worse in the optic segment and thus replacement may be slowed down. In some IR optic applications, ZnSe can fully replace germanium. In fibre optics, phosphorus-based doping of silica fibres can lead to a similar performance compared to germanosilicate fibers – this may lead to a future replacement. In the solar cell application for aerospace, 4 layer multijunction solar cells are being researched although these use other CRMs like indium and gallium which may be a bottleneck in the future. Germanium is also used as a polymerization catalyst in PET production due to its transparency. Alternatives include antimony- or titanium-based catalyst where the first may have potential health hazards and the second gives a yellow taint to the finished polymer.

The latter is the reason why gallium is so widely used [1] [5] [9] [11]. OLED may become a potential replacement solution for the criticality of gallium in LEDs if the lifespan and prices are improved. SiGe may replace in the future GaAs in ICs provided that the architecture of SiGe chips improves [12]. Given the similarity of price of both solutions [11], SiGe can replace GaAs in the coming future. Despite this, silicon and germanium are also CRMs.

A full summary is presented in Table 24 below.

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Table 24. Technological and non-technological barriers to the rollout of substitutes to germanium.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
ZnSe	Technological	IR optics	Lower optic performance of ZnSe compared to Ge in certain applications	10	Improve R&D activities and support technological transition.	10
P_2O_5	Technological	Fibre optics	Research still at early stage	10	Improve R&D activities and support technological transition.	10
	Non-Technological	Fibre optics	Phosphorous is a CRM	6	Improve collection and recycling systems.	5
Multijunction solar cells	Technological	solar cells for satellites	R&D needed to continue developing 4 layer IMM solar cell	10	Sol Aero technologies currently develop IMM solar cells and may be a replacement in the coming years.	10
	Non-Technological	solar cells for satellites	Ga and In are a CRM	6	Improve collection and recycling systems.	5
Si	Non-Technological	Integrated circuits	Si has lower performance and lower cost compared to Ge	10	Improve R&D activities and support technological transition.	5
Sb and ti	Non-Technological	PET polymerization catalyst	Sb-catalysts require further health hazard research	10	Improve R&D activities and support technological transition.	5
	Non-Technological	PET polymerization catalyst	Ti gives a slight yellow taint.	10	Regulate and cooperate with polymer producers	10

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4. SUMMARY

Germanium offers excellent optic properties and can be simply used in many optic applications thanks to its properties. Replacement of germanium in some applications is still pending further research such as in solar cells for satellites or as a catalyst for polymerization. In IR optics, no other element and/or combination of elements offers a similar performance in a wide range of applications – different combinations for different applications may be the answer for the replacement of germanium in the long run. This is the case for ZnSe in thermal imaging where ZnSe has good properties for this application but not for the full range of applications where germanium is used. Fibre optics based on doping silicon with phosphorous pentoxide can reach high performance in terms of very low attenuation thus offering full replacement to germanosilicate fibers. R&D activities must be coordinated to find different replacements for germanium for all fields of application.

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INDIUM

Indium is produced as a by-product of zinc, mostly in China, South Korea and Japan. Production in Europe reaches 48 t and takes place in Belgium, France and Germany [1]. Indium refined within the EU accounts for about 9% of global production. Secondary resources play important role in indium supply, since about 50-60% of total production comes from recycling. Over a half of indium production is used as Indium-Tin Oxide (ITO) of conductive layers of liquid-crystal displays [2]. There are several possibilities for indium substitution, yet most of them are under development and presently not commercially available. Table below describes main applications of indium and possible substitutes.

Table 25. General information concerning In products and applications.

CRM	Product	Application	Substitute
Indium	Flat panel displays	Transparent conducting oxides (TCOs)	Aluminium doped zinc oxide (AZO); Fluorine doped tin oxide (FTO); Silver nanowires; *Under research:* Carbon nanotubes; Graphene quantum dots; Metal mesh grids *Prototype:* Poly(3,4 ethylene dioxythiophene) – PEDOT; Copper-based ITO alternative; Conductive polymer for resistive touch screen
	Thin film PV cells	Top transparent current collector electrode window layer (ITO)	CdTe and Amorphous silicon (a-Si); Aluminium doped zinc oxide (AZO); Fluorine doped tin oxide (FTO)
	Thin film solar cells	Semiconductor absorbing light (CdTe, aSi, CIGS, CIS)	No commercially available replacement *Potential substitute:* Copper-zinc-tin-selenide/sulphide (CZTS)
	Solders, alloys	Electronics	Tin-bismuth alloys
	Alkaline-manganese batteries	Alloy	Currently not available
	LEDs	Semiconductor InGaN/GaInN, InP)	Zinc oxide
	Smart windows	ITO in architectural glass	Fluorine-doped tin oxide (FTO); In moisture-protected applications: Zinc oxide (ZnO) and aluminum-doped zinc oxide (AZO)

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1. DESCRIPTION AND INDICATOR

Production and consumption in EU

Indium is refined within the EU in 3 countries, which together provide 9% of total world production. This makes the European market self-reliant in terms of the metal import. EU exported more indium than imported, which may suggest that the imported material was processed in order to export higher purity metal or other In-bearing products with higher value. Between years 2010-2014 apparent consumption of indium in the EU was over 22 tones per year, which is roughly 3% of world production and 46% of EU production [1] [2].

Future demand increasing

Indium demand is expected to grow together with ITO demand for LED technology, LCD panels and emerging displays technology using Indium Gallium Zinc Oxide from 30% to 50% by the year 2020 [2]. Demand for thin film solar cells started declining against earlier expected growth. However, it is believed that there is enough supply to support the market growth. It could be further improved by recycling activities and higher recovery during ore processing [1].

Use in cutting edge technologies

Indium is used in multiple new technologies, such as OLED (Organic Light-Emitting Diode). In this technology CRMs, except for indium, are substituted by organic compounds. It is expected to penetrate the lighting market after 2025, which will lead to very limited use of phosphors and CRMs for lighting. OLED as assumed to play very important role in small and special applications, for instance automotive displays or smartphones, due to its flexibility. The main disadvantage of this technology is short product lifetime.

2. SUBSTITUTE MATERIALS

According to USG Minerals Yearbook [3], antimony tin oxide coatings have been developed as an alternative to ITO coatings in LCDs and have been successfully annealed to LCD glass; carbon nanotube coatings have been developed as an alternative to ITO coatings in flexible displays, solar cells, and touch screens; PEDOT [poly(3,4-ethylene dioxythiophene)] has also been developed as a substitute for ITO in flexible displays and organic light-emitting diodes; and silver nanowires have been explored as a substitute for ITO in touch screens. Graphene has been developed to replace ITO electrodes in solar cells and also has been explored as a replacement for ITO in flexible touch screens. Researchers have developed a more adhesive zinc oxide nanopowder to replace ITO in LCDs. Gallium arsenide can substitute for indium phosphide in solar cells and in many semiconductor applications. Hafnium can replace indium in nuclear reactor control rod alloys.

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Table 26. Potential substitutes for indium and its applications.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Aluminium doped zinc oxide (AZO),	transparent semiconductor with high transmittance and good conductive properties	-	Issues of etching and degradation by moisture still need to be solved before commercialisation	Proposed as replacement for indium-tin oxide in transparent conducting oxide[7]
Fluorine doped tin oxide (FTO)	FTO is less expensive to produce, has lower sensitivity to surface cleaning methods and more light is obtained at a given voltage in LED than comparing to ITO[5]	-	The results from research show that the current FTO foils comply with the set project goals. Process needs to be upscaled.	Used in solar cells
Carbon nanotubes	perfectly straight tubules with diameters of nanometer size, and properties close to that of an ideal graphite fiber (high stability, strength and stiffness, combined with low density and elastic deformability)[6]	Some producers in EU: FutureCarbon GmbH Germany; ONEX Global Nanotechnologies S.A. Greece; Haydale UK; Hubron UK; Marion Technologies France; Modern Synthesis Technology Latvia[8]	Potential substitute in flexible displays and touch screens	Possible applications: electronic devices and interconnects, field emission devices, electrochemical devices, such as supercapacitors and batteries, nanoscale sensors, electromechanical actuators, separation membranes, filled polymer composites, drug-delivery systems[7]
Graphene quantum dots	A new class of nanomaterials with exceptional luminescence properties comprising one up to tens of graphene layers less than 30 nm thick	Graphene is produced in small volumes, mostly for R&D in Universities and companies. Leading Edge Materials is Canadian company with	Intensive research worldwide is considering potential applications in optoelectronic, bio-imaging and energy devices	Potential applications: displays, transistors, solar cells, diode lasers, quantum computing, and medical imaging[9]

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		mining facility in Sweden[10]		
Copper-zinc-tin-selenide/sulphide (CZTS)	Semiconducting compound with favourable optical and electronic properties. Unlike other thin film materials, it is composed of only abundant and non-toxic elements[11]	No information	It is cheaper and more abundant than CIGS and CdTe. Recent material improvements for CZTS have increased the efficiency to 12.6% in laboratory scale, yet more research is needed before their commercialization [11]	Thin film solar cells[11]
Poly(3,4 ethylene dioxythiophene) – PEDOT	Trade name: Clevios; optically transparent, electroconductive polymer, can be used in flexible displays or solar cells;	-	This material has shown good stability and is proposed as an alternative for ITO in touch screens	Applications: electrochromic displays, antistatics, photovoltaics, electroluminescent displays, printed wiring, and sensors[12]
Copper-based ITO alternative	Innovative film based on copper metal plating	Copper and copper alloy is produced in Europe (5311 kt in 2016); mine production in Poland reached about 425 kt in 2014[13]	This technology can reduce the complexity, cost and risk of manufacturing touch panels	Touch sensors
Conductive polymer for resistive touch screen	Consist of pliable and transparent organic conductive polymers instead of	-	Better endurance, cheaper and more ecological production than ITO qualifies this material particularly as pen touch-based devices	Resistive touch panels in cell phones, PDAs, tablet PCs, and other pen-based devices

Sources:
[4] (Li, Li, & Huang, 2018)
[5] (Andersson et al., 1998)
[6] (Ajayan & Zhou, 2001)
[7] (Endo, Strano, & Ajayan, 2007)
[8] (Nanowerk, 2018)
[9] (Graphene-Info, 2018a)
[10] (Graphene-Info, 2018b)
[11] (Winkler et al., 2014)
[12] (Kirchmeyer & Reuter, 2005)
[13] (Statista, 2018)

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

The most common technological barriers hindering the use of substitutes for indium is lower performance, in particular lower specific electric conductivity. Moreover, the uncertainty of substitutes development makes them impossible to consider at the moment. Indium has such good properties that immediate solutions for presented barriers are often difficult to find. It is suggested to continue research and development of currently identified substitutes and search for different options that do not compromise the performance.

Table 27. Technological and non-technological barriers to the rollout of substitutes to indium.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
aluminium doped zinc oxide (AZO)	Technological	ITO in flat panel displays	2-4 times lower specific electric conductivity	8	Use different alternative that doesn't compromise the performance	8
			less pronounced etching properties, which prevents use in high-resolution displays	7	Use different substitute for high-resolution displays	8
fluorine doped tin oxide (FTO)	Technological	ITO in flat panel displays	2-4 times lower specific electric conductivity	8	Use different alternative that doesn't compromise the performance	8
			less pronounced etching properties, which prevents use in high-resolution displays	7	Use different substitute for high-resolution displays	8
silver nanowire,	Non-Technological	ITO in flat panel displays	Current cost of ITO makes it impossible to implement those materials in mass production; remain at research level	9	More research for the alternatives and	4

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carbon nanotubes, graphene, metal mesh grids					activities to reduce their price	
copper-zinc-tin-selenide/sulphide (CZTS)	Technological	Solar cells	Low efficiency of 11.1%; not commercially used	9	Research to increase efficiency	8
	Non-Technological					
zinc oxide	Technological	LED	Under investigation due to limited stability	9	Continue research	8
Poly(3,4 ethylene dioxythiophene) – PEDOT	Technological	Flat panel display	Similar or slightly lower technical or economic performance	5	Continue research and development	7
Copper-based ITO alternative	Technological	Flat panel display	Uncertain technology status	6	Continue research and development	7
Conductive polymer for resistive touch screen	Technological	Flat panel display	Considerably lower performance	7	Continue research and use different substitute	7
Carbon nanotubes	Technological	Flat panel display	Uncertain technology status	9	Continue research and development	7
Graphene quantum dots	Technological	Flat panel display	Uncertain technology status	9	Continue research and development	7

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4. SUMMARY

There are several substitution possibilities for indium in different applications. Most of the substitutes are still under development and are not yet available. Yet, at this moment materials used instead of indium often cause lower performance of the end material. Other limitations are uncertain technology status of materials, lower efficiency or higher cost.

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PLATINUM GROUP METALS (PGMs)

PGMs dispose a number of excellent properties such as: high melting points (between 1554 °C in case of palladium and 3033 °C in case of osmium), superior catalytic activity (i.e. about the 90 wt.% of harmful vehicle off gases are catalyzed with palladium), and exceptional resistance to corrosive attack and high temperature oxidation, allowing these metals to be employed in a number of sectors including automotive (catalytic convertors, spark plugs, oxygen sensors), chemical and petroleum (catalysts and laboratory equipment), electrochemical (anode coatings), electrical and electronics (hard disk drives and multilayer ceramic capacitors), medical and dental (dental alloys, biomedical devices, and anti-cancer drugs), glass manufacturing equipment, as well as jewellery and investment areas (Table 28) [1].

Table 28. General information concerning PGM products and applications [1].

CRM	Product	Application	Substitute
PGM	Under elemental form or mixtures of: Pt-Pd-Rh, Pt-Rh, and Pd-Rh	Catalytic converters to control NO_x emissions,	Practically none at the moment. New technologies tested at laboratory scale.
	Ru, Pd, Ir	Electronic equipment (HDDs, film pastes, etc.)	Other PGMs and Ag
	Ru, Pt-Rh	Catalysis of several processes in organic industry	Fe_3O_4, nickel, cobalt
	Pt, Pd	Jewellery construction	Ni-based alloys, Au
	Ir or Ir-manganese aloys	Magnetic storage devices, crucibles for growing high purity single crystals	Mo, W
	Metallic Os or Os containing Steel aloys	Electrical contacts, pens, light filaments	None

1. DESCRIPTION AND INDICATOR

PGMs have been recently listed as a critical raw material for the EU since the original criticality assessment in 2017 [2]. Currently, there are not significant primary PGMs under exploitation in EU. Sakatti multimetallic deposit located in Sodankylä, Lapland (Finland), is believed to hold important reserves of platinum-group metals with copper and nickel. Furthermore, the recycling capacity in EU is expected improved until 2021. According to the Commission criticality assessment study, the supply risk and the economic importance of PGMs is relatively high, but much lower in comparison other significant CRMs such as rare earth elements. The annual world production of both platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), iridium (Ir), and osmium (Os) is estimated at about 470 tons per year. The demand for

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platinum group metals is at the same levels in comparison to the supply by primary and secondary production [3]. Regarding the Pt, the demand is expected to be increased at about 5% to 2021, while the production by primary resources is not forecasted to increase [3]. Currently, there are not significant primary PGMs under exploitation in EU. Sakatti multimetallic deposit located in Sodankylä, Lapland (Finland), is the only notable deposit for platinum-group metals in copper/nickel sulfide ore.

2. SUBSTITUTE MATERIALS

The use of PGMs in a wide range of applications, some of them are considered as cutting edge, coupled with their relatively high prices has led to various substitution efforts usingless expensive metals (Table 29). The investigationof suitable substitutes for the PGMs has been an ongoing concern. The crucial applications of PGMs are related with their use as catalysts in diesel and gasoline vehicle converters and in petroleum and organic chemical industry. Numerous research studies have shown that the substitution PGM catalysts is technologically feasible, however various non-technological factors render substitution implementation impractical. More specifically, it has been found out that PGMs often make the best substitutes for each other. Apart from other PGMs, Ni, Co, and Au are the elements most likely to substitute for PGMs in certain applications due to the chemical proximity between these metals and PGMs. Lately, nanotechnology offers new opportunities in PGMs substitution. Graphen doped structures and gold nanoparticles have been successfully tested at laboratory scale as substitutes of PGMs.

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Table 29. General description, economic value and main applications of PGMs substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Platinum	It has been supported that platinum in vehicle catalytic converters can be replaced by Au nanoparticles.	This PGM element is produced in EU mainly by secondary resources (mainly recycling of converters). Pt production by nickel ores is expected taking place in Kevitsa (Finland).	Its supply risk is intermediate. Production by recycling represents the 25% of the total production. The supply and the demand worldwide are quite balanced. The price of platinum per oz is about 950 $, however it can not be directly compared to the price of substitute nanomaterials as the last have not currently be commercialized.	It presents several applications such as in catalysis in vehicles emissions and in organic industry, in electronic devices and in Jewellery construction.
Palladium	Potentially replaced by nano-Au in vehicle catalytic converters.	It is not produced by primary resources. Its demand in EU is expected to increase due to its use in gasoline vehicles converters during the next years.	The world production is around 200 kg. The main producers are Russia and South Africa. Its price is variable. It has been increased from 500 $/oz in 2016 to 900 $/oz in 2017. Demand in 'consuming applications', i.e. excluding investment, is expected to increase modestly.	It is mainly used for the construction of vehicle catalytic converters, electronic devices and in jewellery.
Ruthenium	Potentially replaced by Fe_3O_4, nickel, cobalt in catalysts of chemical industry.	It is not produced by primary resources.	Its price was increased over 60% (to 275$/oz) through 2017 after the announcement	Ruthenium is used as a catalyst in organic chemical industry. It is also used for the construction

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			from a South Korean university that a ruthenium based catalyst can split water into hydrogen as effectively as the costlier Pt. Russia, Canada and South Africa are the main producers.	of chip resistors. It is a promising effective catalyst for effective in several future fuel cell and electrolysis applications.
Rhodium	Potentially replaced by nano-Au in vehicle catalytic converters.	This PGM element is produced in EU only secondary resources (mainly recycling of converters)	Only about 25 tons of rhodium are mined each year. Compare that to the 2,350 tonnes of gold mined in 2009, or the 220 tons of platinumin South Africa, which supplies over 80% of the world's demand for rhodium	Catalytic converters for automobiles, for which — especially in diesel engines — the metal has no substitute. As much as 80%-90% of annual rhodium supplies go into the production of automotive catalytic converters
Iridium	Substitutes are referred in case of a limited number of applications. Mo and W carbides and nitrides replace Ir-alumina material in liquid propellant in small rocket engines.	It is not produced by primary resources.	Iridium price rose by 45% through the f rst half of 2017, from $685/oz to $990/oz. Iridium demand and price is expected further increase during the next years.	Iridium remains an important component of electrode coatings for industrial electrolysis applications, including the inevitably cyclical global chloralkali process. It is also used as crucible for the synthesis of single crystals.
Osmium	There are no available data in the literature concerning substitute materials	It is not produced by primary resources.	The annual world production approaches 500 kg.	Electrical contacts, pens, light filaments.

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

The technological and the non-technological barriers in PGMs will be represented in the following table:

Table 30. Technological andnon-technological barriers and solutions for the substitution of PGMs.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Graphene being able to **replace platinum** as catalyst in fuel cells if doped with non-metal atoms such as nitrogen or boron [6,7].	Technological	Doped graphens/vehicle catalytic converters	There is not enough repeatability in the morphology of the synthesized graphene-supported nanocatalysts. The catalytic efficiency is strongly depended on the graphens quality. Therefore the scaling up of the synthesis process is difficult.	7	Scaling up tests using various complex graphenes	6
	Non-Technological		• Graphene doped materials have not been commercially applied and tested in large scale. • The technology of fuel cells is relatively new.	7	Pilot scale application. Policies supported by the Commission and the European automotive industry.	6

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Au nanotubes for the catalytic conversion of CO to CO_2 in diesel vehicles **replacing palladium and platinum [8]**	Technological	Au nanoparticles supported on metal oxides	Operating at high temperatures >300 °C	8	Testing of various ceramic monoliths	4
	Non technological		As in case of doped graphenes	7		6
Thin-film monolayer platinum catalysts. According to this technology a minor amount of Pt film is grown on a substrate and the required amount of **the metal is eliminated**.	Technological	Vehicle catalysts				
	Non-Technological		Technology under investigation			
Alloys produced by the combination of iron, cobalt, germanium and silicon which are going **replace iridium-manganese alloys** (horizon) [9]	Technological	Fe, Co, Ge, Si alloys in spintronic devices	There are no enough available data in the literature concerning the properties of the produced alloys.			
	Non technological		Under investigation. A EU-Japanese Horizon Project (HARFIR) took place			
Mo and W carbides and nitrides can be used as **substitues of iridium** [10]	Technological	Liquid propellant in small rocket engines used for space	Mo and W carbides and nitrides materials present a higher ignition delay in comparison to iridium-alumina material	6	Synthesis and testing Mo and W carbides and nitrides with	7

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		communication purposes			different cystallic structures	
	Non technological		There are no available data concerning the upscaling of the substitute aoolication	8	Upscaling tests	6
Rhodium and silver have been propsed as **substitutes for ruthenium**	Technological	Hard disc drives and contacts in electronic devices.	Low stability in case of silver	9	No practical solution	-
	Non techological		Rhodium consists an expensive substitute	9	No practical solution	-

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4. SUMMARY

PGMs present numerous applications including chemical and petroleum catalysts, dental, medical and biomedical devices, electrical and electronic components, electrochemical applications, and other cutting edge uses. The substitution of PGMs by other less critical and more abundant metals consists a challenging technological issue. In most of cases, PGMs can be effectively substituted only by other PGMs. None substitutes for osmium has been mentioned in the literature. Substitution strategy, in case of catalytic converters, by Co, Ni and Au can lead to more intense environmental burdens. As previously mentioned, PGM catalysts are often more active, operate under milder conditions, and are recovered and recycled with high efficiency as compared to their base metal counterparts. Substituting a PGM catalyst by a base metal with lower catalytic activity can result in the increasing of operational energy consumption, while the recycling of metals such as nickel and cobalt is going take place at lower extent. Nanotechnology and fuel cells technology could potentially led to the decreasing of PGMs demand and supply risk, however this technology is going commercialized in long term.

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HEAVY REEs

Rare earth elements (REEs) include 17 chemical elements with atomic numbers 65-71, scandium and yttrium. REEs are divided into two groups according to their atomic number. Heavy rare earth elements (HREEs) comprise the lanthanide elements europium through to lutetium and yttrium (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y). LREE group consist of 8 elements with atomic number 57 (lanthanum, with no unpaired 4f electrons) through atomic number 64 (gadolinium, with 7 unpaired 4f electrons). The European Commission has classified HREEs as critical since the original criticality assessment [2].

Table 31. General information concerning some HREEs (Europium, gadolinium, terbium) products and applications [1].

CRM	Product	Application	Substitute
Heavy REEs	Phosphor (europium, terbium)	Lightning applications (fluorescent lamps, LEDS)	None
	Permanent magnets (gadolinium, terbium)	Electric vehicles, electric motors	Dysprosium
	Contrast agent (gadolinium)	Medical technology	None

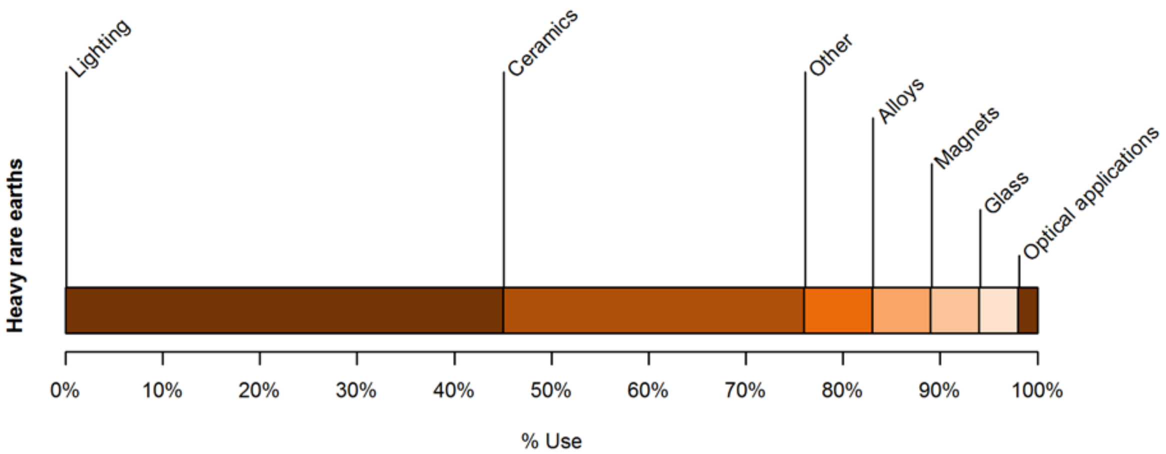

Figure 5. Distribution of recent heavy rare earth demand for manufacturing in the EU (European Commission 2017a).

1. DESCRIPTION AND INDICATOR

Heavy Rare Earth Elements, HREEs, defined as the lanthanide elements, cover the following elements: europium (Eu, atomic number 63), gadolinium (Gd, atomic number 64), terbium (Tb, atomic number 65), dysprosium (Dy, atomic number 66), holmium (Ho, atomic number 67), erbium (Er, atomic number 68), thulium (Tm, atomic number 69), ytterbium (Yb, atomic

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number 70) and lutetium (Lu, atomic number 71). However, this examination will focus on only three first elements among HREEs, namely europium, gadolinium and terbium.

All three HREEs of interest: europium, gadolinium and terbium, are soft silvery metals with a tendency to react with water (illustrating their high activity). [1] They have specific optical and magnetic properties, with the applications relying mostly on these characteristics. China accounts for more than 95 of global production of all three elements: europium, gadolinium and terbium [2].

Phosphorescent applications

96% of europium and 68% of terbium is used in phosphors [2], i.e., materials which can emit light when exposed to a light or electron source. Particularly fluorescent lights and light emitting diodes (LEDs) involve HREEs europium and terbium, and for example europium is used in the in the world and in EU almost exclusively for lighting applications. In these low-energy light bulbs, europium is employed to give a more natural (warm) light, by balancing the blue (cold) light with a little red light. Additionally, europium is used in the printing of euro banknotes as it glows red under UV light, and forgeries can be detected by the lack of this red glow. [2] Similarly, termium is used in low-energy lightbulbs and mercury lamps. It has been used to improve the safety of medical x-rays by allowing the same quality image to be produced with a much shorter exposure time [3].

Magnet applications

97% of gadolinium and 32% of terbium finds use in magnets [2]. Indeed, gadolinium is used in alloys for making magnets, electronic components and data storage disks. Additionally, its compounds are useful in magnetic resonance imaging (MRI), particularly in diagnosing cancerous tumours. [4] An alloy of terbium, dysprosium and iron lengthens and shortens in a magnetic field. This effect forms the basis of loudspeakers that sit on a flat surface, such as a window pane, which then acts as the speaker [3].

2. SUBSTITUTE MATERIALS

Phosphorescent applications

In fluorescent lamps, the coatings are made up of a phosphor material containing mix which involves rare earths as activators. Europium is often contained in fluorescent powder, which has been shown in recycling trials for fluorescent lamps. In ref [5], a fluorescent lamp was demonstrated to contain ~73 mg europium oxide. It is responsible for the red part of the light spectrum. In the luminescent lights, such as LEDs, the lights is usually brought about by substances based on yttrium. However, europium is also here added for warm light (WLED). For example, WLEDs contains europium (as Eu^{2+}) in quantities ranging from 0.4 to 0.9 µg. [6] There is no substitute to Eu in the lightning applications to introduce the effect of red (warm)

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light [2]. Nevertheless, as demonstrated by the europium quantities above, the amount of europium needed in LEDs is approximately 1000 times lower than in fluorescent lamps, thus a technology shift towards increased use of LED lights is also more resource efficient choise. These same features apply to the use of terbium in phosphor applications.

Magnet applications

As mentioned above, gadolinium and terbium are extensively used in magnet applications. For example, gadolinium and terbium are used in NdFeB permanent magnets to improve the thermal stability [7] [8] [9]. It is suggested that gadolinium can be substituted by dysprosium or terbium for its temperature compensation properties in NdFeB magnets and vice versa: terbium can be substituted by dysprosium or gadolinium for the same purpose. [2] The market for permanent magnets is expected to grow at compound annual growth rate (CAGR) of 9.0% between 2018-2024, driven by increases in the electric vehicle production [10].

Gadolinium is also used in contrast agents in magnetic resonance imaging (MRI), for example in disclosing tumours. There is no substitute for gadolinium as a contrast agent in MRI yet, although there is ongoing research to find alternatives. Alternative technologies to reduce or eliminate MRI are also sought for, due to suspicion about gadolinium toxicity cases. [11]

Table 32. General description, economic value and main applications of HREEs substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
-	Europium and terbium are used in phosphor applications to provide warm (red) light. LED lights consume much less these raw materials as compared to fluorescent lamps			Phosphor applications: no substitutes for europium and terbium exist.
Dysprosium	Dysprosium is also a heavy REE	Also a critical raw material, the production occurs primarily in China (similarly to gadolinium and terbium)		To improve thermal stability of NdFeB magnets, to substitute gadolinium and terbium

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-	Gadolinium as a contrast agent in magnetic resonance imaging (medical technology used in e.g., tumour detection)			No substitutes available currently, btu on-going research targeting in finding alternative materials

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

In phosphor applications of MRI detection applications, there are no available substitutes for europium and gadolinium, respectively.

Table 33. Technological andnon-technological barriers and solutions for the substitution of HREEs.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Substitute 1: Dysprosium	Non-Technological	Magnetic applications, NdFeB permanent magnets	Also a critical raw material with similar challenges with availability than with gadolinium and terbium	5		

4. SUMMARY

This chapter has focussed on the barriers for the substitution of europium, gadolinium and terbium. In most cases, the main challenge is that europium (phosphor applications) and gadolinium (MRI imaging) have so special properties that there are currently no substitutes available. In the magnetic applications, in improving the thermal stability of NdFeB permanent magnets, dysprosium may substitute both gadolinium and terbium. However, it is also a critical raw material with similar supply risks to gadolinium and terbium.

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OTHERS HEAVY REEs

This group of elements includes **Holmium, erbium, thulium, ytterbium** and **lutetium** which included in the Heavy Rare Earth Elements (HREE) sub-group. They present exceptional properties such as high magnetic successability, luminescennce and electrochemical ability rendering indispensable for many cutting-edge applications [1].

Although the applications [2] of this group of elements are limited, they have crucial role in the field of optics as doping elements in fibers and the construction of specific glasses. They are also used as catalysts for industrial processes, mainly to the transformation of epoxides. Around 10% of HREEs consumption is related to catalytic applications [3].
In table 34, a summary of their most significant applications is presented.

Table 34. General information concerning the applications of holmium, erbium, thulium, ytterbium and lutetium.

CRM	Product	Application	Substitute
HREEs (Ho, Er, Tm, Yb, Lu)	Er	- Refractive index enhancing agents. - Pigments sector: used in pink ceramic glazes. - Decolouring agents. - Dopant in optical fibers for communication cabling.	The substitution by InGaAlAs in lasers has been reported
		- Used in glass colour tinting providing pink colour. - Control rods. - Magnetic refrigeration technology: alloys of Gd-Er.	Currently, no substitutes have been identified in ceramic colour staining.

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			Possible substitutes in alloys: Gd-Si-Ge, Gd-Tb, Gd-Er.
	Ho	- Catalysis of several processes in organic industry. - Usually added to improve magnets performance at high temperatures.	No substitute with similar magnetic properties
	Tm	- X-ray phosphors - Electron bean tubes, visualization of images in medicine	No available data
	Yb	- Yb is used in high power optical fibres. - Industrial lighting and projectors compounds improves the lighting performance, in terms of e.g. quality and intensity (Rare Earth Technology Alliance, 2014).)	No available data
	Lu	- Single crystal scintillators	No available data
	Ho, Er, Tm, Yb	- Medical sector - Upconversion phosphors (to convert infra-red into visible light) - Crystals and garnets for microwaves and laser: Ho, Tm, Er and Yb compounds as dopant agents.	No available data data

1. DESCRIPTION AND INDICATOR

Production and consumption in EU

The European Commission has classified HREE as critical elements since the original criticality assessment [7-10]. According to the European data the uses of this sub-group of elements are limited in specific technological fields.
For example in the glass industry, erbium (Er) is one of the most widely applied HREE and it is used as a pink color additive in glass. Erbium-doped optical glass fibers are the active elements in erbium-doped fiber amplifiers (EDFA), which are widely used in optical communications [4]. Erbium containing materials are used as components in lasers, including some medical-sector devices. Erbium oxide is added in pigments, which its market is mainly focused in China and Europe (mainly in Spain and Italy).
In Europe minor reserves for HREEs have been reported, but currently there is no production by primary resources. Concerning erbium, exploitable deposits in Sweden and Greenland have been identified.World reserves are estimated at 612,000, while the annual world production is around 650 t, extracted exclusively in China [5].EU does not import any erbium concentrates or produces any material containing Er (i.e. originated by the glass industry). The annual Er consumption in Eu is estimated at 36 tonnes.Glass additives are used by the European industry

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to manufacture colored glass, which is sold mainly in the European market. The Er consumption in glass industry is relatively low and it is estimated at about 4 tonnes per year. [5].

Holmium is mainly used for the construction of magnets with extremely high magnetic susceptibility value. In fact, some of the strongest artificially created magnetic fields are the result of magnetic flux concentrators made with holmium alloys. The element is also used to provide coloring to cubic zirconia and glasses and also in nuclear control rods and microwave equipment.Thulium is used as source of the radiation device in portable X-rays and also as a component of highly efficient lasers with various uses in defense, medicine and meteorology. Lutetium is used as aluminium garnet (LuAG) phosphor in LED light bulbs, while thulium is a component of holmium-chromium-thulium triple-doped yttrium aluminum garnet.

Future demand

HREEs, including yttrium and dysprosium, are used in mature markets such as catalysts, glassmaking, lighting and metallurgy, which account the 59% of the total world consumption of rare earth elements, and in the newer, high growth ones markets such as battery alloys, ceramics and permanent magnets, which represent 41% of the total market. However, holmium, erbium, thulium, ytterbium and lutetium represent a minor part of HREEs market.

2. SUBSTITUTE MATERIALS

For decades, the research on rare earths was focused on the optimization of their applications, however the replacement and reduction of HREE consumption has been carried out the last few years. Concerning holmium, erbium, thulium, ytterbium and lutetium, the Chinese and European industries are focused on the limitation of HREEs in optical fibers and glasses taking into account the demand growth of smartphones, tablets and other electronic displays. According to the literature investigation, there are no sufficient available data concerning the replacement of holmium, erbium, thulium, ytterbium and lutetium. A limited number of studies examine the replacement of erbium by InGaAlAs semiconductor in laser diodes [11,12]. Furthermore, the substitution of erbium and other HREEs in glasses by less scarce REEs could be a challenfing technological issue. The research should be focused on the investigation of alternative materials that introduce a number of specific properties such as; absorbtion of ultraviolet light, adjustment of various refractive index values and discoloration or coloration.

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Table 35. General description, economic value and main applications of HRRE substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
InGaAlAs	As semiconductor material in laser diodes	There are no specific data concerning the production of InGaAlAs in EU, however there is a number of European leader-companies involved in the construction of semiconductors such as: Bosch, NXP and Infineon	In and Ga are also CRM. A feasibility study prior to the potential substitution should be performed	Various applications (i.e. telecommunications and medicine)
Other REEs (i.e. europium)	As additives in glasses	CRMs – Currently not produced in EU by primary resources	No research studies have been performed so far	Fluorescent glasses

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Literature data describe the potential substitution or erbium-containg semiconductors by InGaAlAs. Despite the encouranging results, the effectiveness of InGaAlAs should be tested on a wide range of laser diodes applications. Furthermore, an LCA study should prove the economic and environmental profits of erbium substitution by In and Ga, which cosist also CRMs.

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Table 36. Technological and non-technological barriers and solutions for the other HREEs substitution.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
InGaAlAs	Technological	Lasers	Not tested extensively	4	Further experimental tests	8
	Non-Technological		Substitutes consists also CRM	9	study comparing the supply risk and the cost between Er and substitutes	1

4. SUMMARY

The HREEs holmium, erbium, thulium, ytterbium and lutetium present limited applications mainly in the fields of optical fibres, glasses and fluorescents, while minor amounts of them are added in specific magnetic alloys. Currently, there are no sufficient available data in the literature concerning the existence of substitute materials. Few studies quote the replacement of erbium by InGaAlAs semiconductor in lasers. The future research should be focused on the replacement of HREEs is glasses.

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YTTRIUM

As a trivalent transition metal belonging to the rare earth element, yttrium forms various inorganic compounds, generally in the oxidation state of +3, by giving up all three of its valence electrons. A good example is yttrium (III) oxide (Y_2O_3), also known as yttria.

1. DESCRIPTION AND INDICATOR

The leading end uses of yttrium were in ceramics, metallurgy, and phosphors [1] [2].

- In ceramic applications, yttrium compounds were used in abrasives, bearings and seals, high-temperature refractories for continuous-casting nozzles, jet-engine coatings (thermal barrier base on yttria stabilized zirconia), oxygen sensors in automobile engines, high temperature ionic conductor (SOFC, SOEC), and wear-resistant and corrosion-resistant cutting tools.

- In metallurgical applications, yttrium was used as a grain-refining additive and as a deoxidizer. Yttrium was used in heating-element alloys, high-temperature superconductors, and superalloys.

- In electronics, yttrium-iron garnets were components in microwave radar to control high-frequency signals. Yttrium was an important component in yttrium aluminum-garnet laser crystals used in (dental and medical) surgical procedures, digital communications, distance and temperature sensing, industrial cutting and welding, nonlinear optics, photochemistry, and photoluminescence.

Globally, yttrium was mainly consumed in the form of oxide compounds for ceramics and phosphors. Lesser amounts were consumed in electronic devices, lasers, optical glass, and metallurgical applications.

The evolution of the use of yttrium in the form of yttria stabilized zirconia will depend on the penetration of the electrical vehicle and therefore on the reduction of the thermal engines

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vehicle. In addition the deployment of hydrogen sector, through the solid oxide fuel cells will conduct to an increase of the use of yttria stabilized zirconia that are used to make the solid electrolyte [3].

Table 37. General information concerning Y products and applications.

CRM	Product	Application	Substitute
Yttrium	Thermal barrier	Aeronautics	Y act as an additive or dopant, other trivalent or divalent ions could be use as substitute
	Oxygen sensors	Non electrical car industry	
	SOFC/SOEC	Hydrogen conversion	
	Metallurgy	Additive in alloys	No substitute
	Laser	radar	No substitute

2. SUBSTITUTE MATERIALS

Substitutes for yttrium are available for some applications but generally are much less effective. In most uses, especially in electronics, lasers, and phosphors, yttrium is generally not subject to direct substitution by other elements. As a stabilizer in zirconia ceramics, yttrium oxide may be substituted with calcium oxide or magnesium oxide, but the substitutes generally lead to lower toughness. Other stabilizer could be ceria or scandia that gives closer toughness performances.

Table 38. General description, economic value and main applications of yttrium substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Sc, Ca, Ce	Cationic substitution			- Thermal barrier, oxygen sensors, SOFC/SOEC

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

There is no strong technical barrier to replace Y by substitute, but reserves may be sufficient to satisfy near-term demand at current rates of production makes replacement unlikely.

Table 39. Technological and non-technological barriers to the rollout of substitutes to yttrium.

Substitute Material	Type of Barrier	Product/ Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Sc, Ca, Ce	Technological	Thermal barrier, oxygen sensors, SOFC/SOEC	Loss of performance of the substitute	3	Novel design of the device to cope with thesubstitute	6

4. SUMMARY

Yttrium applications are not numerous, its substitution could be envision for some of them. A shortage in the supply is not a near term option, thus no driving force is pushing the substitution process. The progressive conversion of thermal engine to electrical motors in cars will reduce the need of Y, but the emergence of hydrogen sector would lead to an increase of Y in electrochemical devices even if still some substitution option are possible.

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LANTHANUM

Lanthanum (La) is considered as a light Rare Earth Elements (REE). Although it is classified as a rare earth element, lanthanum is the 28th most abundant element in the Earth's crust, almost three times as abundant as lead. It is the second most common of the lanthanides after cerium. Lanthanum is used for a variety of applications; its three main uses are in fluid craking catalyst (FCCs), nickel-metal hydride batteries and glass & ceramics. Other uses for lanthanum include autocatalysts, polishing powders, lighting applications, metallurgical uses, fertiliser, algal, control and cement [1].

Table 40. General information concerning others La products and applications.

CRM	Product/End-use	Application	Substitute
Lanthanum	Oil refining	Fluid craking catalyst (FCCs)	Cerium can substitute Lanthanum as FCCs
	Hybrid automobiles, electrical products	Nickel-metal hydride (NiMH) batteries	Cerium, praseodymium (Pr) and neodymium can substitute Lanthanum in NiMH batteries. Typically Misch metal is used which is an alloy consisting only of rare-earth metals. Li-ion batteries can substitute nickel-metal hydride (NiMH) batteries
	Polishing powders	Glass & ceramics	Cerium, iron oxide and alumina powders

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1. DESCRIPTION AND INDICATOR

The main uses and consume in EU:

Fluid cracking catalyst (FCCs)

The single largest application of rare earths is the manufacture of rare earth-containing zeolite cracking catalysts required in petroleum refining [2] Process is known as Fluid Catalytic Cracking (FCC) and Alkylation. The catalysts primarily consist of manufactured zeolite to which Lanthanum is added to stabilize the zeolite structure and improve catalytic activity. FCC units are an essential operation in oil refining to convert heavy, high boiling point fractions of crude oil into lighter more valuable gasoline fractions. The raw zeolite is not very stable at conditions experienced in the cracking unit and without treatment, the catalyst will break down and lose catalytic effect. The stability is improved by the addition of Lanthanum up to 3% by weight. The rare earth atom has a slightly smaller size and fits neatly within the "cages" of the zeolite where it acts to stabilize the zeolite structure [3].

Nickel-metal hydride (NiMH) batteries

REEs are used in nickel-metal hydride (NiMH) rechargeable batteries to power electronic products. Lanthanum is the main REE used in NiMH batteries being particularly important for hybrid automobiles [4]. The fundamental components for a NiMH battery are the active anode (hydrogen storage AB5 alloy) and cathode ($Ni(OH)_2$) electrode materials, separator and electrolyte (KOH/LiOH). There are many different formulations of the hydrogen storage alloy used in NiMH batteries. One of the common types is the hexagonal AB5 crystal structure. The amount of A (e.g. La, Ce, Pr, Nd) atoms are proportionally less than B (e.g. Ni, Co, Mn, Al) elements. A mixture of REEs is acceptable to use since these elements have similar chemical properties. The similar chemical properties of REEs is due to the lanthanide contraction where the atomic and ionic radii, respectively, are relatively constant from lanthanum to lutetium [5].

2. SUBSTITUTE MATERIALS

In generally, many of the applications of REEs are highly specific and substitutes are either unknown or provide significant loss of performance. If substitutes exist, they are commonly another REEs or a more expensive material such as platinum-group elements [4]. Substitution index for Lanthanum stated by the European Commission is 0.99 (substitution index for supply risk)/0.99 (substitution index for economic importance) [1].

In generally, many of the applications of REEs are highly specific and substitutes are either unknown or provide significant loss of performance. If substitutes exist, they are commonly another REEs or a more expensive material such as platinum-group elements [4]. Substitution index for Lanthanum stated by the European Commission is 0.99 (substitution index for supply risk)/0.99 (substitution index for economic importance) [1].

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Fluid craking catalyst (FCCs)

In term of FCC use, lanthanum can be replaced by cerium [1]. FCC catalysts are manufactured to have composition and shape to increase the speed of the cracking process and to yield the right mix of products. Lanthanum and Cerium are added in order to take advantage of their ability to interact with the hydrogen (H) atoms found in the long-chain hydrocarbon molecules in the starting raw materials [2].

Nickel-metal hydride batteries

Misch metal (Mm) is an alloy consisting only of rare-earth metals. Nowadays, La has been substituted by Misch metal, where lanthanum making up to 18-28% of the total mixture [6]. Cerium (Ce), praseodymium (Pr) and neodymium (Nd) can substitute Lanthanum. Substitution of the lanthanum content with Mn was very useful in improving the charge-discharge cycle life [7]. Substitution is possible because of similar chemical properties. The similar chemical properties of REEs is due to the lanthanide contraction where the atomic and ionic radii, respectively, are relatively constant from lanthanum to lutetium [5].

NiMH batteries are ahead of nickel–cadmium in performance and lithium-ion types in cost. Comparisons with other rechargeable battery systems nickel-metal hydride batteries will dominate the market for small, portable rechargeable batteries [6]. Li-ion batteries can substitute NiMH batteries in many applications due to better performance [1]. Current-generation Hybrid electric vehicles (HEVs) primarily use NiMH batteries, while lithium-ion (Li-ion) batteries are preferred for plug-in hybrid electric vehicle (PHEVs) to meet requirements of greater storage capacity and higher power ratings. Lithium batteries have performance advantages over NiMH batteries and have already been preferred in plug-in hybrid electric vehicle (PHEVs) and autonomous electric vehicles (AEVs). Rare earths are used in NiMH batteries, and their use is likely to continue in applications that favor cost savings over energy and power performance. Besides, NiMH batteries are safer (e.g., less prone to fire hazards) than the Li-ion batteries, and this may work in favor of their continued use in heavy-duty applications. For example, La–Ni–H is still a very cost-effective and reliable method of storing electricity, for applications including Prius-class HEV battery [2].

Other uses

Lanthanum used for polishing can be substituted by cerium, iron oxide and alumina powders. There is no substitute to La in fluorescent lamps. The alternative lighting technology LED, which penetration in the market is fast and important and is taking over the fluorocompact market share also uses phosphors based on rare earths, including La, but the amount of phosphor needed per LED in 1000 times lower than in fluorescent lamps. In metallurgical applications, lanthanum can be substituted by cerium, neodymium, gadolinium and calcium [1].

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Table 41. General description, economic value and main applications of La substitute materials.

Substitute Material	**Description of the Material**			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Cerium	For FCC use, lanthanum can be replaced by cerium. Cerium could also replace Lanthanum in NiMH batteries.	Production: World: 51,382 t EU: 0 t The use of cerium in the EU represents 39.4% of the total EU use of REEs, which gives an estimated 3,116 t of cerium consumed in the EU per year (average 2010 – 2014)	Supply of rare-earths in general and cerium in particular is constantly subject to changes. The market of rare-earths is opaque and it is thus very difficult to predict the future evolution of supply	Fluid cracking applications in oil refining. NiMH batteries in electric vehicles
Li-ion batteries	Li-ion batteries could replace NiMH batteries	European Commission has estimated that Lithium-ion batteries for mobility and stationary storage applications, the global market size is currently 15 billion € and it will increase to 200 billion € to 2040.		Electric vehicles

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

It is showed in the following table:

Table 42. Technological and non-technological barriers and solutions for the La substitution.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Substitute 1: Cerium	Non-Technological	For FCC use, lanthanum can be replaced by cerium. Cerium could also replace Lanthanum in NiMH batteries	Substitution with another REE	5	Cerium is extracted and produced together with more valuable REEs. It is one of the cheapest and most available Rare Earth Element.	8
Substitute 2:Li-ion batteries	Technological	Li-ion batteries could replace NiMH batteries	Rare earths are used in NiMH batteries, and their use is likely to continue in applications that favor cost savings over energy and power performance. Besides, NiMH batteries are safer (e.g., less prone to fire hazards) than the Li-ion batteries, and this may work in favor of their continued use in heavy-duty applications.	5	Lithium batteries have performance advantages over NiMH batteries and have already been preferred in plug-in hybrid electric vehicle (PHEVs) and autonomous electric vehicles (AEVs)	7-8

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4. SUMMARY

Lanthanum (La) is considered as a light Rare Earth Elements (light REEs). Although it is classified as a rare earth element, lanthanum is the 28th most abundant element in the Earth's crust, almost three times as abundant as lead. It is the second most common of the lanthanides after cerium. Lanthanum is used for a variety of applications; its three main uses are in fluid craking catalyst (FCCs), nickel-metal hydride batteries and glass & ceramics. Other uses for lanthanum include autocatalysts, polishing powders, lighting applications, metallurgical uses, fertilizer, algal control and cement.

In generally, many of the applications of REEs are highly specific and substitutes are either unknown or provide significant loss of performance. If substitutes exist, they are commonly another REEs or a more expensive material such as platinum-group elements. Substitution index for Lanthanum stated by the European Commission is 0.99 (substitution index for supply risk)/0.99 (substitution index for economic importance). As fluid cracking catalyst in oil refining, lanthanum can be replaced by cerium. Cerium could also substitute lanthanum in NiMH batteries as misch metal. Lithium batteries have performance advantages over NiMH batteries and have already been preferred in plug-in hybrid electric vehicle (PHEVs) and autonomous electric vehicles (AEVs). Rare earths are used in NiMH batteries is likely to continue in applications that favor cost savings over energy and power performance. Besides, NiMH batteries are safer (e.g., less prone to fire hazards) than the Li-ion batteries, and this may work in favor of their continued use in heavy-duty applications.

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CERIUM

Cerium (Ce) is considered as a light Rare Earth Elements (REEs). It does not occur naturally as a metallic element and is found (for commercial exploitation) mainly in the minerals bastnäsite, loparite and monazite. Because of its chemical and optical properties and relative abundance it is found in many applications such as catalytic converters, glass and ceramics, polishing powders, metallurgical alloys and nickel-metal hydride (NiMH) batteries [1].

Table 43. General information concerning others Ce products and applications.

CRM	Product/End-use	Application	Substitute
Cerium	Automobiles	Catalytic converters	Lanthanum Neodymium Praseodymium
	Monitors, mirrors	Polishing powders	Iron oxide Alumina powder
		Metallurgical applications	Calcium Lanthanum Neodymium Gadolinium

1. DESCRIPTION AND INDICATOR

The production and consumption in EU revolves around:

Catalytic converters

It is used in automobiles to convert hydrocarbons, carbon monoxide, and nitrogen oxides in the engine exhaust to water, carbon dioxide, and nitrogen. Cerium oxide CeO_2 is the primary rare-earth compound used in catalytic converters, usually in conjunction with platinum group metals. It provides oxidation resistance at high exhaust temperatures, stabilizes rhodium and palladium dispersions, minimizes the interaction of rhodium with alumina, and enhances the oxidizing ability of the system [2]. Cerium carbonate and cerium oxide are used in the catalyst substrate and as a component of the converter's oxidizing catalyst system [3].

Glass & Ceramics

REE are commonly used in the glass industry. The earliest commercial use of cerium was used as a decolorizing agent in glass. It is also used as dyes in glass. Small amount of cerium decolorize glass, about one percent turn it yellow and larger quantities brown. REE are important in glass because their ability to absorb ultraviolet lights. Cerium is used in glass bottles to protect the product and prevent browning of the glass due to radiation [3]. REE

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oxides are also essential in ceramics by adding cerium oxide as stabilizers and sintering aids in structural ceramics [3].

Polishing Powders
Cerium concentrates and oxide are used to polish glass surfaces. Cerium is suitable as a polishing agent as it removes glass by both chemical dissolution and mechanical abrasion making it more efficient than other agents such as silica and zirconia. The majority of polished glass products are finished using cerium oxide [3]. Rare earth-based polishing has been used in the manufacture of CRT, LCD, and LED monitors, as well as high-quality mirrors, decorative glass products, and the wafers used to produce silicon chips. The secondary and fast-growing use of rare earth-based polishes in electronic components maintained an 8–12% per annum growth rate over the last decade. The demand for rare earth-based polishes should continue growing faster than the global economy [2].

2. SUBSTITUTE MATERIALS

In generally, many of the applications of REEs are highly specific and substitutes are either unknown or provide significant loss of performance. If substitutes exist, they are commonly another REEs or a more expensive material such as platinum-group elements [3]. Substitution index for cerium stated by the European Commission is 0.98 (substitution index for supply risk)/0.95 (substitution index for economic importance). Cerium is extracted and produced together with more valuable REEs. It is one of the cheapest and most available Rare Earth Element. There is generally no advantage of substituting cerium in its main applications despite of the spike in prices [1]. On the other cerium could be used to substitute other REEs. The new alloy is being developed which is a potential replacement for high-performance permanent magnets found in automobile engines and wind turbines. This new alloy eliminates [4] [5].

Catalytic converters
In the auto-catalyst sector in catalytic converters cerium could be substituted by other REEs such as lanthanum, neodymium and praseodymium [1]. While the amount of cerium required per vehicle is not much, catalytic converters are used in practically every passenger vehicle. The demand for cerium in catalytic converters will continue to grow with increasing global automobile deployment and the continuing need for replacement vehicles. Cerium is the most abundant rare earth and can support the increased demand anticipated in both the short and medium terms [2].

Polishing powders
Cerium used for the purpose of polishing can be substituted by iron oxide and alumina powder in some applications [1]. Cerium as polishing agent is used for precision (optical polishing) of glass, faceplates, mirrors, optical glass, silicon microprocessors, and disk drives [2].

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Metallurgical applications

In metallurgical applications, cerium can be substituted by calcium and other REEs such as lanthanum, neodymium and gadolinium [1].

Table 44. General description, economic value and main applications of Ce substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Lanthanum	To substitute cerium in catalytic converters	Production: World: 35,146 t EU : 0 t The use of lanthanum in the EU represents 41% of the total EU use of REEs, which gives an estimated 3,660 t of lanthanum consumed in the EU per year		in the auto-catalyst sector
Neodymium	To substitute cerium in catalytic converters	Production: World : 22,391 t EU : 0 t The use of neodymium in the EU represents 6.4% of the total EU use of REEs, which gives an estimated 571 t of neodymium consumed in the EU per year		in the auto-catalyst sector
Praseodymium	To substitute cerium in catalytic converters	World : 6,514 t EU : 0 t The use of praseodymium in the EU represents 2.6% of the total EU use of REEs, which gives an estimated 232 t of praseodymium consumed in the EU per year (average 2010 – 2014)		in the auto-catalyst sector

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Table 45. Technological and non-technological barriers and solutions for the Ce substitution.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Other REEs lanthanum, neodymium and praseodymium	Non-technological	In the auto-catalyst sector in catalytic converters	Other REEs are more scarce and more expensive	8	There is generally no advantage of substituting cerium in its main applications	9

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4. SUMMARY

Cerium (Ce) is considered as a light REE. It does not occur naturally as a metallic element and is found (for commercial exploitation) mainly in the minerals bastnäsite, loparite and monazite. Because of its chemical and optical properties and relative abundance it is found in many applications such as catalytic converters, glass and ceramics, polishing powders and metallurgical alloys.

In generally, many of the applications of REEs are highly specific and substitutes are either unknown or provide significant loss of performance. If substitutes exist, they are commonly another REEs or a more expensive material such as platinum-group elements. Substitution index for cerium stated by the European Commission is 0.98 (substitution index for supply risk)/0.95 (substitution index for economic importance). Cerium is one of the cheapest and most available Rare Earth Element. There is generally no advantage of substituting cerium in its main applications despite of the spike in its prices. On the other cerium could be used to substitute other more scarce REEs. For example, the new alloy is being developed which is a potential replacement for high-performance permanent magnets found in automobile engines and wind turbines. This new alloy eliminates the use of one of the scarcest and costliest rare earth elements, dysprosium, and uses cerium instead.

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NEODYMIUM, PRASEODYMIUM, SAMARIUM, DYSPROSIUM

Neodymium is considered as a light Rare-Earth element (LREE). It is one of the most abundant REE, together with lanthanum and cerium. It is a soft silvery metal that tarnishes in air in a few days [9]. Neodymium special properties include the strong magneto-crystalline anisotropy induced in Fe-rich alloys, such as $Nd_2Fe_{14}B$, which makes it extremely important for high-performance permanent magnets [1]. Light transmitted through neodymium glasses shows unusually sharp absorption bands; the glass is used in astronomical work to produce sharp bands by which spectral lines may be calibrated. Similarly, neodymium glass filters out yellow light, resulting in a whiter light which is more like sunlight, so it is becoming widely used more directly in incandescent light bulbs. Neodymium ions in various types of ionic crystals, and also in glasses, act as a laser gain medium, typically emitting 1064 nm light from a particular atomic transition in the neodymium ion, after being "pumped" into excitation from an external source. Hence, Neodymium-doped crystals (typically $Nd:YVO_4$) can be used to generate high-powered infrared laser beams which are converted to green laser light in commercial DPSS hand-held lasers and laser pointers [10]. In Mg-alloys for metallurgical applications, Nd is added to provide heat resistance [4].

Samarium is considered as a LREE. It is a moderately hard silvery metal that readily oxidizes in air [9]. Like Nd, Samarium also induces a high magnetization and strong magneto-crystalline anisotropy, especially on Co-rich magnets as $SmCo_5$ or Sm_2Co_{17}, which makes it extremely important for current high-performance permanent magnets, especially for high temperature applications [1]. Samarium is also used as a catalyst for organic research chemists to make synthetic versions of natural products (SmI_2) and the dehydration and dehydrogenation of ethanol (Samarium oxide). In its usual oxidized form, Samarium is added to ceramics and glasses where it increases absorption of infrared light. Some isotopes of Samarium are used in nuclear energy technology, as ^{149}Sm due to its high cross-section for neutron capture (41,000 barns), and cancer treatment as radioactive ^{153}Sm, which is a beta emitter with a half-life of 46.3 hours [11].

Dysprosium is considered as a heavy REE (HREE). It is a silvery very hard metal which slowly oxidizes in air (a few years). It is mainly used to replace around 6% of the neodymium in Nd-Fe-B magnets in order to raise the coercivity for demanding applications, such as drive motors for electric vehicles and generators for wind turbines. In particular, it can increase the performance of the magnet at high temperatures. Because of dysprosium's high thermal-neutron absorption cross-section, it is also used in neutron-absorbing control rods in nuclear reactors [12]. Other main applications of Dy are laser for commercial lighting and long persistent phosphors for signage applications [4].

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Praseodymium is considered as a LREE. It is a soft, silvery, malleable and ductile metal, valued for its magnetic, electrical, chemical, and optical properties [13]. It is often used in the form of didymium (NdPr-alloy) in Nd-Fe-B magnets; sometimes used to substitute Nd, although it entails a lower magnetic strength [4]. In Mg-alloys for metallurgical applications, Pr is added to provide strength and corrosion resistance [4]. It is also used as a yellow colorant in glass, ceramics and textiles. Other applications are LED lamps for domestic lighting, Nickel-metal hydride batteries and oxidation catalyst in solid solution with ceria or ceria-zirconia [13].

Neodymium, Samarium, Dysprosium and Praseodymium have been listed as critical raw materials for the EU since the original criticality assessment in 2010 [14-16] with the highest rank for supply risk (9.5). Europe has not mines of them, in fact most of the world's commercial REE are mined in China [5], which currently monopolizes REE market. For instance, their prices peaked in 2011, this anomalous behaviour could be due to speculation and hoarding of RE-oxides, the subsequent decreases after 2011 may also be due to sell-offs by the speculators [2].

Table 46. General information concerning others Nd, Pr, Sm & Dy products and applications.

CRM	Product	Application	Substitute
Neodymium	Magnets	Wind turbines, electric vehicles, microphones, professional loudspeakers, in-ear headphones, high performance hobby DC electric motors, computer hard disks	Other REEs (Sm, Pr, Dy, Ce, Gd, Tb, Ho), Rare-Earth-free magnets (alnico, ferrite, etc)
	Laser	High-power applications, inertial confinement fusion,	Chromium, erbium, thulium, ytterbium
	Glass	Astronomy equipment, automobile rear-view mirrors, incandescent light bulbs, colorant for enamels	Led lamps, compact fluorescent lamp
	Catalyst	petroleum industry (Fluid Catalytic Cracking), automotive	La, Ce
	Nickel-metal hydride (NiMH)	Battery	La, Ce, Pr, Li-ion batteries
	Steel & Mg-alloys	Metallurgical applications	Ce, La, Pr, Gd

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	Ceramics	Temperature compensating capacitors, resistors and thermistors	Pr, La, Ce, base metal capacitors
	Pigment	It is mainly used as a blue pigment in ceramics	Cobalt blue
	Drug	Medical application: Nd-isonicotinate to treat thrombosis	Heparin
Samarium	Magnets	Wind turbines, electric vehicles, microphones, professional loudspeakers, in-ear headphones, high performance hobby DC electric motors, computer hard disks	Other REEs (Nd, Pr, Dy, Ce, Gd, Tb, Ho), Rare-Earth-free magnets (alnico, ferrite, etc)
	Catalyst	Organic research chemists to make synthetic versions of natural products (SmI_2), the dehydration and dehydrogenation of ethanol (Samarium oxide)	ZrO_2, SiO_2, Al_2O_3
	Glass	Colour filtering and tinting agents	Nd, Ce, Eu, Pr, Er, Ho, Tm
	Medicine	Radioactive ^{153}Sm is used in the treatment of cancers	^{131}Iodine, ^{89}Strontium, ^{223}Radium, ^{60}Cobalt, ^{90}Yttrium, ^{226}Radon
	Nuclear energy	Absorber in nuclear reactors	Boron, Cadmium
	Ceramics	Solid oxide fuel cells (SOFCs)	Y, Ce, Gd, La
Dysprosium	Magnets	Wind turbines, electric vehicles, computer hard disks	Other REEs (Nd, Sm, Pr, Ce, Gd, Tb, Ho), Rare-Earth-free magnets (alnico, ferrite, etc)
	Laser	Commercial lighting	Vanadium
	Nuclear energy	Absorber in nuclear reactors	Boron, Cadmium
	Phosphors	Signage applications	Eu

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Praseodymium	Magnets	Wind turbines, electric vehicles, microphones, professional loudspeakers, in-ear headphones, high performance hobby DC electric motors, computer hard disks	Other REEs (Nd, Sm, Dy, Ce, Gd, Tb, Ho), Rare-Earth-free magnets (alnico, ferrite, etc)
	Steel & Mg-alloys	Metallurgical applications, aircraft engines	Ce, La, Nd, Gd, Y
	Glass	Colour tinting agents	Nd, Er, Ce, Eu, Ho, Sm, Tm
	Ceramics	Temperature compensating capacitors, resistors and thermistors	Nd, La, Ce
	Phosphors	LED lamps for domestic lighting and for LCD backlighting	Eu, Ce, Y, Gd, Lu, Tb
	Nickel-metal hydride (NiMH)	Battery	La, Ce, Nd, Li-ion batteries
	Catalyst	Oxidation catalyst	Zr, Ce
	Pigments	Pr_6O_{11} yellow colorant	No substitutes have been identified in ceramic colour staining
	Textiles	It is used as dyes	Ce

Sources: Refs. [4] [8] [9]

1. DESCRIPTION AND INDICATOR

As for all Rare Earths Elements, there is no mining of Neodymium, Samarium, Dysprosium and Praseodymium in the EU. Supply solely depends on imports in the form of REE oxide and compounds. The use of neodymium in the EU represents 6.4% of the total EU use of REEs, which gives an estimated 571 t of neodymium consumed in the EU per year (average 2010 – 2014) [9]. The use of samarium in the EU represents 0.4% of the total EU use of REEs, which gives an estimated 35.7 t of samarium consumed in the EU per year (average 2010 – 2014). The Europe samarium cobalt magnets market is witnessing high growth on an account of increasing applications. Europe samarium cobalt magnets market was valued at $30.33 million in 2013 and is expected to reach $41.20 million by 2019, growing at a CAGR of 5.9% from 2014

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to 2019 [3]. The use of dysprosium in the EU represents 0.2% of the total EU use of REEs, which gives an estimated 18 t of dysprosium consumed in the EU per year (average 2010 – 2014). Finally, the use of praseodymium in the EU represents 2.6% of the total EU use of REEs, which gives an estimated 232 t of praseodymium consumed in the EU per year (average 2010 – 2014) [9].

2. SUBSTITUTE MATERIALS

Neodymium can be mainly substituted in magnet and batteries applications. In magnets, neodymium can be substituted either by material substitution (using other REEs) or by using alternative magnet technology (REE-free magnets). In batteries, neodymium is used in NiMH batteries, which have been progressively replaced by Li-ion batteries. Neodymium in other applications is not easily substituted [9].

Most samarium applications have possible substitutes, although with significant loss of performance. In its main use (for magnets), samarium is considered to have already been widely substituted by other types of permanent magnest such as NdFeB magnets, ferrite or AlNiCo magnets, especially in low temperature applications [9].

The main use of dysprosium is in permanent magnets NdFeB. Dysprosium is added to NdFeB magnets (2-11% w/w) to increase the Curie temperature, which means that it allows the use of those magnets at up to 200°C. The main finished products driving dysprosium consumption for magnets include new generations of wind turbines, industrial motors, etc [9].

Praseodymium can be mainly substituted in magnet and batteries applications, as well as in metallurgical applications [9].

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Table 47. General description, economic value and main applications of Nd, Pr, Sm and Dy substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Other REEs (Ce, Gd, Tb, Ho)	- Tb and Ho: Same as Dy, that is, to improve magnets performance at high temperatures - Ce and Gd: Cheaper but less magnet strength; used as an alternative for Nd are then represented by Ce and Gd, with the latter only used in China because of the high availability.	They are not produced in EU. They are CRMs which are mainly supplied by China. In 2015, the official global total REO production was 124,000 tons, of which China produced 85%, Australia 8%, and USA 4%, and the remaining small amounts were produced by India, Russia, Malaysia, and Thailand. Around 23% of the total global REEs was used for magnets.	In 2015, the global REE market value was estimated to be in the range of USD 2-4 billion. After 2010, EU total imports remained rather static around 11-12,000 t REE with a reduction in imports from China, and variances in the contributions of the second and third largest import partners, the US and Russia [4].	Automotive, actuators, speakers, electronic equipment, domestic appliances and wind turbines.
REE-free magnets	Alnico: High remanence and high Curie temperature, but low coercivity.	In 2010, only 1% of total magnet sales correspond to alnico.	The European alnico magnet market is witnessing high growth on an account of increasing applications, especially in the automotive and consumer electronics industries. This market was valued at $7,388.48 thousand in 2013 and is expected to reach $58,523.34 thousand by 2019.	Instrument panels of cars, transformer.

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	Ferrites: High coercivity, high resistant to corrosion, low cost, coercivity increases with temperature, but very low remanence.	In 2010, 34% of total magnet sales correspond to ferrites.	Europe ferrite magnets market was valued at $252.02 million in 2013 and is expected to reach $349.81 million by 2019. The applications of Ferrite magnets experienced a positive growth till 2013 and are expected to continue the same in the coming years.	Adorn refrigerator door, small motors, loudspeakers.
	FeNi: Cheap, good performance, but bulk material is very unstable, problems with synthesis and upscaling.	Presently, it is only produced in the lab. Mainly found in meteorites.	-	-
	Fe_3Sn: High saturation magnetization and Tc, but it has a strong in-plane magneto-crystalline anisotropy.	Presently, it is only produced in the lab.	-	-
	MnAl: High magnetocrystalline anisotropy, high Tc, low cost, but low remanence and small thermal phase stability.	Presently, it is only produced in the lab.	-	-

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Other REEs (La, Ce)	Fluid Catalytic Cracking (FCC). Zeolite formulation: REE can be included in the catalysts formulation by exchanging part of the zeolite. The zeolite acts to retain catalyst effectiveness and enhance the hydrothermal, structural and chemical stability, thus obtaining a high yield in valuable petroleum products by cracking the heavier oil fractions.	Catalyst sector: Around 24% of the total global REEs consumption, FCC (18%) Automotive (6%)	Trend of replacing FCC process with hydrocracking of vacuum gas oil (VGO) to produce light products.	Catalyst (FCC, Automotive)
	In automotive catalysts REEs (mostly cerium) are responsible for enhanced thermal stability and emission reduction.		Diffusion of "green technologies" (e.g. wind turbines, hybrid and electric cars) or other processes alternative to the fossil-based ones.	
Other REEs (Ce, Eu, Er, Ho, Tm) in the glass sector	REEs used to filter specific colours from the light spectrum, in applications such as safety goggles and glass containers.	Glass sector: Around 7% of the total global REEs consumption	USA represents the principal market for glass coating based on REEs (e.g. used in scientific lenses, laser cavity mirrors, laser printer mirrors, slides for electron microscopy) mainly related to the defence sector.	Glass sector (decolouring agents, refractive index enhancing agents, colour filtering & tinting agents)

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Li-ion batteries	Rechargeable battery in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging. It does not use REEs.	Electronics covers about 50% of the global market associated to Li-ion batteries. In 2013 Li-ion batteries accounted for about 20% of all batteries used in Hybrid Electric Vehicles (HEVs).	Li-ion batteries are increasingly replacing NiMH batteries. Li-ion batteries are partially replacing NiMH batteries also in PHEVs and EVs, mainly because of their higher energy density and longer lifespan.	computing, communication and consumer products (e.g. mobile phones and laptops), electric vehicles
Base metal capacitor	This technology is slightly over two decades old and uses nickel or copper.	Multilayer ceramic capacitor (MLCC) production and sales are the highest among fine-ceramic products developed in the past 30 years. The total worldwide production and sales reached 550 billion pieces and 6 billion dollars, respectively in 2000.	Base metal capacitors are gradually replacing precious metal counterparts	Capacitor, electronic devices
Other REEs (La, Ce)	The most used MH-battery is the AB_5 alloy system, where “A” and “B” represent respectively a REE or mischmetal and one or more transition metals (mainly Ni, Co or Mn). An example of REEs used in the formulation of a commercially available AB_5 alloy is: La (65%), Ce (25%), Nd (1-8%) and Pr (3-8%).	Battery sector: Around 8% of the total global REEs consumption	NiMH batteries maintain a relevant role in large-size, stationary applications in which power-to-weight is less important (e.g. back-up units), as well as in high-temperature applications where Li-ion batteries are unsafe. China currently leads the production of small-size NiMH batteries,	NiMH Batteries

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			while the large-size ones are mainly manufactured in Japan.	
	The addition of REEs (as mischmetal or as Ce-rich silicide) in cast iron (e.g. 0.1% in case of mischmetal) allows reducing or even removing impurities (e.g. oxygen, sulphur, lead, antimony) affecting morphology and properties of the cast material. The addition of 3.5% REEs to Mg alloys allows thin-wall castings.	Metallurgical sector: Around 8% of the total global REEs consumption		Metallurgy: construction and automotive sector, including Hybrid Electric Vehicles (HEV) and Electric Vehicles (EV), in portable electronics, in fuel cell components, in high strength metals for aircraft manufacture
	Temperature compensating capacitors, resistors and thermistors to customise and improves the energy density, dielectric and permeability features, and life-span. REEs are also employed into multi-layer ceramic capacitors. La and Ce: responsible for the improvement of the dielectric properties.	Ceramic sector: Around 6% of the total global REEs consumption	In the ceramic capacitor-market, base metal capacitors are gradually replacing precious metal counterparts, which will reduce the demand for Nd_2O_3 substantially.	Ceramic capacitor, electronic devices
Other REEs (Eu, Ce, Y, Gd, Lu, Tb)	LED lamps for domestic lighting. Mainly REO and RE-	Phosphor sector: Around 1.6% of the total global REEs consumption	In 2016, it was an overall market size for LED of about 41% (12% in 2011), while 51%	Phosphors, LED lamps for Domestic lighting and for LCD backlighting

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	compounds in the purity of 4-6Ns and 2-5 Ns, respectively.		(88% in 2011) was covered by other lighting technologies.	
Other REEs (Y)	To improve absorption and emission performance. Used as dopants to cause fluorescence	Other applications (laser, nuclear energy, etc): around 10% of the total global REEs consumption	Although most of these applications are associated to niche markets, the use of REEs in such technological fields increased during the years.	Laser, material processing, medical applications.
Other REEs (Gd, Eu, Dy, Er, Y)	Neutron absorbers in nuclear reactors			Nuclear energy

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Table 48. Technological and non-technological barriers and solutions for the Nd, Pr, Sm and Dy substitution.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Other REEs (Ce, Gd, Tb, Ho)	Non-Technological	Magnet. Automotive, actuators, speakers, electronic equipment, domestic appliances and wind turbines.	CRMs	7	To reduce the amount of RE in the magnet, recycling	5
	Technological		Less magnet strength	6	Improve the microstructure, add non-CRM dopants	6
Alnico	Technological	Magnet. Instrument panels of cars, transformer.	Low coercivity, low maximum energy product	9	To reduce the scale of the microstructure, which could improve anisotropy, and to reduce the interaction strength between FeCo-rich precipitates and enhance the domain wall pinning	6
Ferrites	Technological	Magnet. Adorn refrigerator door, small motors, loud speakers.	Very low remanence.	9	To reduce the magnetization of one sublattice without changing to much the Curie temperature.	6
FeNi	Technological	Magnet	Difficult to synthesize (mainly found in meteorites)	7	Improve synthesis method	8

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Fe_3Sn	Technological	Magnet	Strong in-plane magnetocrystalline anisotropy	8	Switch to out of plane magnetocrystalline anisotropy by doping	8
MnAl	Technological	Magnet	Moderate remanence, low thermal stability	5	Enhance thermal stability by doping with carbon, improve the synthesis	7
Li-ion batteries	Technological	Batteries. Computing, communication and consumer products (e.g. mobile phones and laptops), electric vehicles.	Safety issues at high temperature, lower performance	6	Improve cooling processes and security, recycling REEs from NiMH batteries	7
Base metal capacitor	Technological	Ceramics. Capacitor, electronic devices	Reliability	8	To reduce the defect concentration with improved processing control; to prevent the use of base metal capacitors under harsh external stress levels so that the extrinsic defects will never be triggered for a failure. In order to do so appropriate dielectric layer thickness must be determined for a given rated voltage [6].	8
Other REEs	Non-Technological	Catalyst Ceramics Glass Batteries Metallurgy Phosphors and pigments Other applications (laser, textile, nuclear energy, etc.)	CRMs	7	To reduce the amount of REE, recycling	5

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4. SUMMARY

As a summary, the consumption of Nd, Sm, Dy and Pr continue to increase as the amount of high-performance magnet production increases with the expansion of the applications in critical sectors of our advanced society as transport, energy, information and communications technology. Well known REE-free magnets like alnico and ferrite are cheap but their performance is much lower than Nd-based and Sm-based magnets, thus they could only be used in low demanding applications. There are novel promising REE-free magnets that are still under development as FeNi, Fe_3Sn, MnAl, etc. Nd, Sm, Dy and Pr are also used in some of the technological sectors where REEs are typically used, like catalyst, ceramics, glass, batteries, metallurgy, phosphors, pigments, laser, textile, nuclear energy, etc [4,8]. Most potential substitutions in these applications are REEs too, which have been listed as critical raw materials for the EU since the original criticality assessment in 2010 [14-16] with the highest rank for supply risk (9.5). In the ceramic capacitor-market, for example, base metal capacitors are gradually replacing precious metal (PM) counterparts, which will reduce the demand for Nd_2O_3 substantially. Similarly, Li-ion batteries are increasingly replacing NiMH batteries, which make use of Nd and Pr, in computing, communication and consumer products (e.g. mobile phones and laptops), due to their easier manufacture in special shapes. Additionally, several processing technologies have been developed by Japanese (e.g. Toyota, Honda) and European companies (e.g. Umicore, Rhodia-Solvay) aiming at recycling of REEs, from NiMH batteries, as well as to reuse batteries in different applications. In the case of magnets, it has been shown that hydrogen can be used as a very effective processing agent to decrepitate sintered NdFeB magnets from HDDs using a method called Hydrogen Processing of Magnetic Scrap (HPMS), this technique may also be applied to other devices such as electric motors, generators and actuators [7].

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SCANDIUM

Scandium (Sc) is one of the highest valued elements in the periodic table and an element which is usually grouped in REEs. This element shares many characteristics with yttrium, likewise Sc technological applications are unique.

Table 49. General information concerning scandium products and applications.

CRM	Product	Application	Substitute
Scandium	Aluminum alloys	Aerospace industry, baseball bats, bicycle frames and components	0.1-0.5 wt% addition to aluminum. Creation of high strength alloy due to the precipitated small crystals of Al_3Sc.
	scandia stabilized zirconia	Solid oxide fuel cell	gadolinium doped ceria and yttria-stabilized zirconia
	Complex alloys	Specific applications in aerospace (military aircrafts)	$Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$
	Ceramics like material	Construction of laser sources for medical purposes.	erbium-chromium-doped yttrium-scandium-gallium garnet (Er,Cr:YSGG)
	Chemical compounds	Construction of white-light sources (lamps)	scandium triiodide

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1. DESCRIPTION AND INDICATOR

The addition of scandium to aluminium decreases the grain growth in the heat zone of welded aluminium components. This phenomenon significantly improves the mechanical properties of aluminium and aluminium-magnesium alloys as: (a) the precipitation of Al_3Sc formes smaller crystals than in other aluminium alloys and (b) the volume of precipitate-free zones at the grain boundaries of age-hardening aluminium alloys is reduced [1].
Scandium has been recently listed as a critical raw material for the EU since the original criticality assessment in 2017 [2]. Scandium is not produced by primary resources in EU territory, however it has been reported the possibility of recovery by red mud wastes. According to the Commission criticality assessment study, the supply risk and the economic importance of scandium is relatively high but lower in comparison to respective values of LREEs and HREEs. The annual world production of scandium (under scandium oxide form) is estimated at about 10 tonnes per year. The demand is about 50% higher, and both the production and demand are constantly increasing. Currently, only three mines produce scandium: 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 [3] [4].

2. SUBSTITUTE MATERIALS

The main scandium application concerns its addition to aluminium for the construction of high strength alloys, therefore the main Sc substitutes are related with elements which can be alternatively added in aluminum. Some rare earth elements including ytterbium, dysprosium, gadolinium etc., as well as titanium and zirconium, can be successfully partially substitute scandium presenting similar or properties [5-7]. In Table 50, the current use, the production data, the market trend and the main technological applications of the substitute materials are summarized.

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Table 50. General description, economic value and main applications of the substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Ytterbium	Several studies have been performed on Sc substitution by ytterbium in order to reduce the scandium content in the alloy without decreasing its properties. More specifically Al–0.28 wt. % Sc can be substituted by Al–0.24 wt. % Sc–0.07 wt.% Yb alloy presenting improved corrosion resistance properties.	This rare earth element is not produced in EU. Its main primary resources are xenotime and monazite ores. China is the major producer country.	Its supply risk is high, while its recycling rate is limited. The world produced amount is going to be stabilized at 50 tonnes per year the next years.	It presents limited applications. It is mainly used as a component for the construction of gamma rays sources, high-stability atomic clocks, as well as, for the doping of stainless steel and active media.
Other REEs (Dy, Er, Gd, Sm, Y)	It can be added at concentrations between 0.04 and 0.03 wt. % partially substituting the Sc content.	REEs are mainly produced by primary resources in China.	Dysprosium price has been dramatically increased from $7 per pound in 2003, to $130 a pound in late 2010. The price increased to $1,400/kg in 2011 but fell to $240 in 2015 indicating the direct influence of the price by the political uncertainty and the market policy of China. Samarium is following a similar market trend. Gadolinium and erbium are	Dysprosium and samarium are widely used for the construction of alloys for permanent magnets. Erbium, yttrium and gadolinium have minor applications for the construction of components in cutting-edge technologies.

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			produced at small quantities worldwide (few hundred tonnes).	
Titanium and zirconium	Titanium and zirconium precipitate in aluminum alloys to form the Al-(Zr-Ti)-Sc compounds providing similar properties with the respective Al-Sc alloys. Also in this case, Ti and Zr partially substitute scandium in the aluminum alloy.	Titanium and zirconium are not produced by primary resources in EU.	About 186,000 tonnes of titanium metal sponge were produced in 2011, mostly in China (60,000 t), Japan (56,000 t), Russia (40,000 t), United States (32,000 t) and Kazakhstan (20,700 t). About 1.6 million tonnes of zirconium mineral concentrates are annually produced. Zr price was increased the last years (from $360 pert tonne in 2003 to $840 in 2007).	Titanium nitrides and carbides are used for the coating-hardening of tools. Titanium chloride is used as a catalyst in polymers industry. Zirconium dioxide (ZrO_2) is used in laboratory crucibles, in metallurgical furnaces, and as a refractory material. Elemental Zr is used for the construction of alloys exposed to corrosive environment.

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Table 51. Technological and non-technological barriers and solutions for the substitution of scandium.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Ytterbium	Technological	Al–0.24wt.%Sc–0.07 wt.% Yb	More complex process for alloy fabrication	2	Alloy casting standardization	10
	Non-Technological	Al–0.24wt.%Sc–0.07 wt.% Yb	Ytterbium-scandium-aluminum alloys have not been commercially applied and tested in large scale	4	Construction and mechanochemical testing of a commercial product (i.e. in aerospace industry)	9
			Ytterbium consists also a critical metal that it is not produced in EU	6	Investigation of Yb recovery by specific secondary resources in EU (electronic wastes etc.) Scrap collection from various electronic waste sources	4
Other REEs (Dy, Er, Gd, Sm, Y)	Technological	gadolinium doped ceria and yttria-stabilized zirconia	-	-	-	-

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	Non-Technological	gadolinium doped ceria and yttria-stabilized zirconia	Y and Gd consist also critical metals that are not produced in EU	6	Investigation of Y and Gd recovery by specific secondary resources in EU	4
Titanium and Zirconium	Technological	Al-Sc-Ti and Al-Sc-Zr	(a) Ti and Zr diffuse more slowly than Sc in Al and decrease the lattice parameter mismatch between the a-Al matrix and the precipitates [8]. (b) decrease creep resistance by reducing elastic interactions with dislocations [10].	8	Practically difficult to further improve the mechanical properties of these alloys – extensively studied in the literature.	2
	Non technological	Al-Sc-Ti and Al-Sc-Zr	There is not a significant non technological barrier	-	-	-

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4. SUMMARY

According to the previous work packages and the additional bibliographic investigation, it is concluded that scandium is applied for the construction of alloys that are used in aerospace industry. Despite its limited range of applications, scandium has a strategic importance in EU. Al–0.28 wt.% Sc is the main alloy that has been used for aerospace purposes. A number of efforts have been performed, at laboratory scale, for the substitution of Sc by other elements in Al-Sc alloy. However, three main difficulties are revealed: (a) the substitution is partial (always a small portion of Sc should be added), (b) partial substitution by other REEs, such as Dy, Er, Gd, Sm, Y, is problematic due to their scarcity and (c) partial substitution by Ti or Zr results to the production of materials with less advanced mechanical properties, in comparison to Al-Sc alloy. Therefore, the partial substitution of Sc by REEs should be combined with recycling policies (recovery of REEs by secondary resources in EU). This option could be supported by the European Commission by the systematic investigation, collection and recovery of REEs metals by electronic wastes.

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NIOBIUM

Niobium is a soft greyish-silvery metal (bluish when oxidized) that resembles fresh-cut steel. It is a relatively hard, paramagnetic, refractory transition metal. It has a density of 8.57 g/cm^3 and a very high melting temperature (2468°C) [13]. It neither tarnishes nor oxidizes in air at room temperature because of a thin coating of niobium oxide. It does readily oxidize at high temperatures (above 200°C), particularly with oxygen and halogens. Some of niobium's characteristics and properties resemble several other neighbouring elements on the periodic table, making them, as well as niobium, difficult to identify. This is particularly true for tantalum, which is located just below niobium on the periodic table.

Niobium is not attacked by cold acids but is very reactive with several hot acids such as hydrochloric, sulphuric, nitric, and phosphoric acids. It is ductile and malleable. Niobium has been listed as a critical raw material for the EU since the original assessment in 2010 [3-5]. Niobium principally is imported into the EU in the form of ferroniobium and niobium unwrought metal, alloy, and powder. The British Geological Survey listed niobium as one of the materials to most likely be in short supply globally [7]. The substitutability of niobium was assessed in the CRM_Innonet project [6] and MSP-REFRAM project [1-2].

Table 52. General information concerning niobium products and applications.

CRM	Product	Application	Substitute
Niobium	High Strength Low Alloy (HSLA) Steels	Construction, Automobile components, energy sector	Titanium, Vanadium, Molybdenum
	Stainless steels	Mechanical equipment	Titanium, Tantalum, High Nitrogen steels
	Superalloys	Aircraft gas turbine engines, rocket thruster nozzles, turbines for electricity generation	Ceramic Matrix Composites, Titanium, Vanadium, Molybdenum
	Superconductors	Superconducting magnetic coils in MRI, NMR, particle accelerators and magnetic levitation transport system	Vanadium - Gallium alloys, BSSCO alloys

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1. DESCRIPTION AND INDICATOR

Primary niobium deposits are most commonly associated with peralkaline granites or syenites, and/or carbonatites (i.e. an igneous rock that consists of more than 50% primary carbonate minerals). Secondary deposits of niobium, such as laterites, and residual placers, typically form by the weathering of primary igneous deposits [13].

Global extraction of niobium ores and concentrates currently takes place in nine countries and averages 113,000 tonnes per annum over the 2010–2014 period. However, production is heavily concentrated, with about 95 % of world production taking place in Brazil. Consumption of ferroniobium in the EU was about 12,500 tonnes per year during the period 2010–2014. None of this came from within the EU [13]. Niobium profile prices were in the order of US$40 per kilogram in 2015 [13]. The use of ferroniobium in the production of HSLA steel means that future demand is likely to be driven by the construction and automotive sectors, particularly in rapidly developing countries such as China and India.

2. SUBSTITUTE MATERIALS

Metals such as vanadium, molybdenum, tantalum and titanium may substitute for niobium in the production of HSLA steel and superalloys. However, assuming 1:1 substitution in alloys is overly simplistic, for the simple reason that the properties of a given alloy are not controlled by a single metal, but rather by several metals. In addition each metal may produce a range of effects in the alloy. For example, niobium is used in combination with small amounts of several other metals, including, but not limited to chromium, nickel, copper, vanadium, molybdenum, titanium, calcium, rare earth elements and zirconium, in the production of HSLA steel. The interaction between these additions is complex, but they can be used to modify properties such as strength, toughness, corrosion resistance and formability [13]. Therefore it cannot be reasonably assumed that the increased addition of one of these metals in the absence of niobium would produce a steel with the same properties.

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Table 53. General description, economic value and main applications of the niobium substitute materials.

Substitute Material	**Description of the Material**			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Titanium	Nb could be partially replaced by Titanium in HSLA and Stainless Steel in order to reduce the amount of Nb in these materials. Titanium prevents the formation of niobium carbo-nitride due to its higher affinity for N. This allows a higher content of Nb to be dissolved during reheating for rolling. This can lead to increased precipitation of Niobium carbide which can contribute to the strength enhancement. As Nb, Ti has also the effect of lowering the γ to α (austenite to ferrite) transformation temperature [8].	This substance is manufactured and/or imported in the European Economic Area in 100 - 1000 tonnes per year. In 2015 the Global Mine Production was around 5,610 (Ilmenite) and 6,090 (Rutile) tons [12].	Its market is expected to experience momentous growth over the next six years owing to increasing usage in residential, commercial, power generation, transportation, and industrial. Growing energy demand on account of increasing population is expected to be the major factor driving the market over the foreseeable period.	HSLA steel: Construction, Automobile components, energy sector (gas energy, pipeline) Stainless Steel: Mechanical equipment Superalloys: Aircraft gas turbine engines, rocket thruster nozzles, turbines for electricity generation.

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Molybdenum	Nb could be partially replaced by Molybdenum in HSLA and Stainless Steel in order to reduce the amount of Nb in these materials. Compared to Fe, Mo has an atomic size difference of 9.4%, which may decrease the γ to α (austenite to ferrite) transformation temperature. This lowering of transformation temperature has an effect on the thermo-mechanically rolled plus accelerated cooled plates by refining the grain size of polygonal ferrite and increasing the amount of bainite.	Europe produced four metric tons (metal content) of Molybdenum in 2012 and eight tons in 2013, all from Norway. Molybdenum consumption in Europe in 2013 was 63.5 kt. Europe is the world's second biggest consumer of Molybdenum, with an average annual consumption of 63,500 tons in 2011 and 2012, which represents 25 % of annual worldwide production.	The global molybdenum market is expected to witness a CAGR of 3.5% during the forecast period of 2018 - 2023. The growing demand for molybdenum bearings in the steel and chemical sectors is alleviating its prices.	HSLA steel: Construction, Automobile components, energy sector (gas energy, pipeline) Stainless Steel: Mechanical equipment Superalloys: Aircraft gas turbine engines, rocket thruster nozzles, turbines for electricity generation
Vanadium	Nb could be partially replaced by V in HSLA and Stainless Steel in order to reduce the amount of Nb in these materials. Compared to Fe, V has an atomic size difference of 6.2%, which can decrease the γ to α (austenite to ferrite) transformation temperature but the effect of Nb is much more pronounced than V.	The total world production of vanadium in 2016 was around 73,000 tonnes. China remains the world's largest vanadium producer, which accounted for over 56% of the total production in 2016. The total world consumption of vanadium in 2016 was around 80,000 tonnes [9]. In the EU, industry accounts for	Vanadium prices have shown a relatively high degree of volatility over the last 20 years. Demand for vanadium is rising quite strongly and supply is already less than consumption. V has seen a rapid price recovery during 2016 after hitting its lowest point at the beginning of that year and could see a price	HSLA steel: Construction, Automobile components, energy sector (gas energy, pipeline) Stainless Steel: Mechanical equipment Superalloys: Aircraft gas turbine engines, rocket thruster nozzles, turbines for electricity generation

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		around 13% of total world consumption of V.	surge in the next few years, supported by the rising interest in vanadium redox/flow batteries.	Superconducting magnetic coils in MRI, NMR, particle accelerators and magnetic levitation transport system
Ceramic Matrix Composites (CMCs)	CMCs toughen the ceramics by incorporating fibres in them and thus exploit the good qualities of ceramics without risking a catastrophic failure.	The demand for CMCs is expected to grow tenfold over the next decade [11]. North America is expected emerged as the largest market for CMC in 2016 with a share of more than 44.0% by volume. Aerospace emerged as the most significant application segment in CMC market in 2016 with a share of more than 36.0% by volume [10].	The costs of CMCs vary between some 100s to some 1000s euros/kg. Hence, they are expensive compared to other materials like metals and the initial high investment needs to pay off by longer service life or special performance features. The global CMCs market size was valued at USD 2.28 billion in 2016. The market is expected to expand at an estimated CAGR of 13.0% from 2017 to 2025 on account of increasing demand for lightweight and high-performance materials [10].	Superalloys: Aircraft gas turbine engines, rocket thruster nozzles, turbines for electricity generation.
Vanadium-Gallium alloys	Vanadium-Gallium alloys have a critical temperature of 14.2 K and the upper critical magnetic field over 19 Tesla, which make them viable alternatives to Nb-Ti alloys for superconductor applications	Within the EU the main share of manufactured gallium which is finished into products goes into sensor applications, mainly for military uses and in second	It is forecasted that until 2020, the gallium demand will strongly increase by more than 8 % annually, thereby showing the second largest demand growth rate of all classified critical raw materials	Superconducting magnetic coils in MRI, NMR, particle accelerators and magnetic levitation transport system.

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		place into applications using permanent magnets	after niobium in the EU mainly drive by LEDs and solar applications	
Tantalum	Ta has similar characteristics and properties as Nb.	Tantalum wordwide demand in 2012 is approximately 1,680t. New supply of tantalum will increase by 22% between 2016 and 2020. EU consumption of tantalum is very difficult to estimate, which is of the order of 50-100 tonnes [13].	The overall demand is expected to grow at 4.7% py until 2020 but growth rates for individual end-use markets will vary. In capacitor which is the main application area of tantalum the demand growth is projected to be below average. This results from miniaturisation and material substitution which exist.	Stainless steels, Mechanical equipment, cemented carbides, corrosion resistant coatings, optics and hard disc drives.

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Table 54. Technological and non-technological barriers and solutions for the substitution of Nb.

Substitute Material	Type of Barrier	Product/ Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Titanium	Technological	HSLA steel, stainless steel	problems of increased weight and cost, lower performance	6	Improve grain size refinement during thermomechanical hot forming, the lowering of Ar3 transformation temperature and precipitation hardening.	8
Molybdenum	Technological	HSLA steel, stainless steel	problems of increased weight and cost, lower performance	6	Improve grain size refinement during thermomechanical hot forming, the lowering of Ar3 transformation temperature and precipitation hardening.	8
Vanadium	Technological	HSLA steel, stainless steel	problems of increased weight and cost, lower performance	6	Improve grain size refinement during thermomechanical hot forming, the lowering of Ar3 transformation temperature and precipitation hardening.	8
	Non-Technological		CRM	9	Use different, non-critical substitute	9
Ceramic Matrix Composites	Non-Technological	Aircraft gas turbine engines, rocket thruster nozzles, turbines for	They are expensive compared to other materials like metals	6	Longer service life or special performance features.	8

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		electricity generation				
Vanadium-Gallium alloys	Non-Technological	Superconducting magnetic coils in MRI, NMR, particle accelerators and magnetic levitation transport system	CRM	9	Use different, non-critical substitute	9
Tantalum	Non-Technological	Stainless steels, Mechanical equipment	CRM (lower supply risk than Nb)	9	Use different, non-critical substitute	9

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4. SUMMARY

As a summary, Niobium, a grain refiner and precipitation hardener, enhances the steels' mechanical strength, toughness, high temperature strength, and corrosion resistance. This makes niobium pivotal to the automotive, construction and energy industries. Potential substitutes are titanium, vanadium, molybdenum, high nitrogen steels, ceramic composites and gallium alloys. While considering the substitution potential of Nb with other elements, it is important to factor in the global availability of those elements. EU consumption of niobium is estimated to represent 24% of global niobium consumption. Since there is no primary niobium production in Europe, scrap is the only available intra-European raw material source. It is directly processed in steel production. Ores and concentrates, oxides and niobium metal must be imported. More than 90% of niobium is produced in Brazil.

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TANTALUM

Tantalum is a shiny, silvery metal with malleable and ductile properties. Tantalum is very resistant to corrosion to most acids below 150°C due to an oxide film on its surface. It is a very good conductor of heat and electricity and has a high melting point (2996 °C). Tantalum causes no immune response in mammals, so has found wide use in the making of surgical implants and other medical applications. Tantalum also has near-zero electric resistance at low temperature, shape memory properties and high capacitance [1].

Due to these unique properties, tantalum ensures its increasing usage in different areas such as electronics, mechanical, aerospace, chemical machinery, process industry, vacuum techniques, optic and other applications [2]. One of its main uses is in the production of electronic components (i.e. automotive electronics, mobile phones and personal computers), mainly tantalum capacitors. Alloyed with other metals, tantalum is also used in making carbide cutting tools for metalworking and in the production of superalloys for turbine blades, rocket nozzles and nose caps for supersonic aircraft. Some of tantalum's characteristics and properties resemble other neighbouring elements on the periodic table like niobium.

Tantalum was classified as a Critical Raw Material for the EU in the criticality assessments of 2010 and 2017 [3, 5]. In the list of 2013 tantalum was moved out of the EU critical material list due to a lower supply risk [4].

Table 55. General information concerning tantalum products and applications.

CRM	Product	Application	Substitute
Tantalum	Capacitors	automotive electronics, portable electronic boards, mobile phones, medical electronics	Niobium, aluminium capacitors, ceramic capacitors
	Superalloys	jet engine, rocket engine nozzles, missile parts, gas turbines	Vanadium, molybdenum, hafnium, iridium, niobium, rhenium and tungsten

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	Sputtering targets	magnetic recording media, inkjet printer heads, flat panel displays, optical and industrial glass, battery chargers, power rectifiers, game consoles, and thin film resistors	Substitution of tantalum in semiconductors appears impractical
	Mill products	heat exchangers, condensers, coils, columns, vessels, reactors, bayonet heaters, furnace parts	glass, titanium and niobium
	Carbides	Teeth for excavator buckets, mining drills, high-performance bearings, refractory parts and coatings for furnaces and nuclear reactors	tungsten and titanium carbides (TiC) and nitride (TiN)
	Chemicals	Reactor coatings, heat exchangers, boilers, condensers, pressure reactors, distillation columns, pipelines	glass, platinum, titanium and zirconium

1. DESCRIPTION AND INDICATOR

With the exception of very small quantities of by-product from kaolin mining in France, there is currently no primary mine production of tantalum in the EU. There are a few processors notably in Estonia (from imported primary ore), Austria, Germany and the UK (mainly from secondary material) [6]. EU consumption of tantalum is very difficult to estimate, which is of the order of 50-100 tonnes [6]. After a spike in prices in the early 2000s, tantalite prices on the international market remained low (around 50-100 US$/kg) for most of the period 2002-2010, with another increasing episode in 2010-2012, followed by a chaotic and progressive fall until 2017.

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2. SUBSTITUTE MATERIALS

In capacitors, the vast majority of them in electronic devices do not contain tantalum, mostly because of their high prices. In terms of substitution, niobium (also considered a critical raw material for the EU since 2011) can be used to produce capacitors at lower cost, but they are usually larger and have a shorter life-span. Other alternatives are ceramic capacitors (multilayer or monolithic) or standard aluminium capacitors (both also have larger size, reduced capacitance and are more sensitive to harsh and hot operating conditions). The superior performance and robustness of tantalum capacitors thus remains the only reliable choice in applications where long term reliability, size and/or security matters (e.g. automobile anti-lock brake systems, airbag activation systems, satellites, etc.) [6].

Tantalum carbides are used in cutting tools. Other refractory metals which share similar properties of strength and resistance at high temperatures can be substitutes for carbides (tungsten, niobium, titanium, molybdenum), although prices are often comparable [6].

In many types of superalloys tantalum is one of several elements added to the base metal (nickel, cobalt or iron) in small but precise quantities. Substituting tantalum for another element would dramatically alter the properties of the superalloy. Once a particular superalloy has been engineered into an aero engine or industrial gas turbine and approved for commercial use any subsequent change to that superalloy would take many years to become established. Tantalum plays a critical role in superalloys and in this application it is a relatively minor cost, making substitution unlikely [6].

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Table 56. General description, economic value and main applications of the Ta substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Niobium	Similar characteristics and properties as Ta. Process equipment, resistance to corrosion and high temperature environment.	Global resources of niobium are very large (about 84 million tonnes) [6]. EU consumption of niobium is estimated to represent 24% of global niobium consumption. [7] Consumption of ferroniobium in the EU was about 12,500 tonnes per year during the period 2010–2014. [6]	Niobium prices were in the order of US$40 per kilogram in 2015. Niobium prices have decreased of more than 40% since 2015 compared to the period 2011-2015 [6].	Heat exchangers, heating elements, evaporators, condensers, pumps, reactors, and in prepared components such as thermal screens of furnaces and crucibles
Aluminium	Aluminium capacitor. Lower cost, higher availability, shorter production lead times, low leakage current, higher voltage range (up to 400 VDC) [7].	Primary aluminium production in Europe has rebounded following a difficult period. Production increased by 1.1% in 2016 to 4.3 million tonnes. The EU still imports roughly half of its metals supply; 5.9 Mt in 2016 [8].	The aluminium price fell further on December 2018 to US$ 1908 /tonne, the lowest level since July 2017 [9].	Automotive electronics, portable electronic boards, mobile phones, medical electronics.
Titanium	Process equipment, corrosion resistance (not very high temperature applications).	This substance is manufactured and/or imported in the European Economic Area in 100 - 1000 tonnes per year. In 2015 the Global Mine Production was around 5,610 (Ilmenite) and 6,090 (Rutile) tons [12].	Its market is expected to experience momentous growth over the next six years owing to increasing usage in residential, commercial, power generation, transportation, and industrial. Growing energy demand on account of increasing population is expected to be the major factor driving the market over the foreseeable period.	heat exchangers, heating elements, evaporators, condensers, pumps, reactors, and in prepared components such as thermal screens of furnaces and crucibles

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Molybdenum	Ta could be partially replaced by Molybdenum in high temperature applications, like steel super-alloy applications where strength is required at high temperature [7].	Europe produced four metric tons (metal content) of Molybdenum in 2012 and eight tons in 2013, all from Norway. Molybdenum consumption in Europe in 2013 was 63.5 kt. Europe is the world's second biggest consumer of Molybdenum, with an average annual consumption of 63,500 tons in 2011 and 2012, which represents 25 % of annual worldwide production.	The global molybdenum market is expected to witness a CAGR of 3.5% during the forecast period of 2018 - 2023. The growing demand for molybdenum bearings in the steel and chemical sectors is alleviating its prices.	Heat exchangers, heating elements, evaporators, condensers, pumps, reactors, and in prepared components such as thermal screens of furnaces and crucibles.
Vanadium	Ta could be partially replaced by V in high temperature applications, like steel super-alloy applications where strength is required at high temperature [7].	The total world production of vanadium in 2016 was around 73,000 tonnes. China remains the world's largest vanadium producer, which accounted for over 56% of the total production in 2016. The total world consumption of vanadium in 2016 was around 80,000 tonnes [9]. In the EU, industry accounts for around 13% of total world consumption of V.	Vanadium prices have shown a relatively high degree of volatility over the last 20 years. Demand for vanadium is rising quite strongly and supply is already less than consumption. V has seen a rapid price recovery during 2016 after hitting its lowest point at the beginning of that year and could see a price surge in the next few years, supported by the rising interest in vanadium redox/flow batteries.	HSLA steel: Construction, Automobile components, energy sector (gas energy, pipeline) Stainless Steel: Mechanical equipment Superalloys: Aircraft gas turbine engines, rocket thruster nozzles, turbines for electricity generation Superconducting magnetic coils in MRI, NMR, particle accelerators and magnetic levitation transport system.

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Table 57. Technological and non-technological barriers and solutions for the substitution of tantalum.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Niobium	Non-Technological	heat exchangers, heating elements, evaporators, condensers, pumps, reactors, and in prepared components such as thermal screens of furnaces and crucibles	CRM	9	Use different, non-critical substitute	9
Titanium	Technological	heat exchangers, heating elements, evaporators, condensers, pumps, reactors, and in prepared components such as thermal	problems of increased weight and cost, lower performance, not very high temperature applications	6	Improve grain size refinement during thermomechanical hot forming, the lowering of Ar3 transformation temperature and precipitation hardening.	8

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		screens of furnaces and crucibles.				
Molybdenum	Technological	HSLA steel, stainless steel.	problems of increased weight and cost, lower performance.	6	Improve grain size refinement during thermomechanical hot forming, the lowering of Ar3 transformation temperature and precipitation hardening.	8
Vanadium	Technological	HSLA steel, stainless steel.	problems of increased weight and cost, lower performance.	6	Improve grain size refinement during thermomechanical hot forming, the lowering of Ar3 transformation temperature and precipitation hardening.	8
	Non-Technological		CRM	9	Use different, non-critical substitute.	9
Aluminium	Technological	Capacitor. Automotive electronics, portable electronic boards, mobile phones, medical electronics.	More sensitive to harsh and hot operating conditions.	6	Improve the design of the capacitor.	8

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4. SUMMARY

Due to the physical and chemical similarities of niobium and tantalum, both metals can be substituted for each other in a large number of applications, for example in cemented carbides, corrosion resistant coatings, optics and hard disc drives. In cases where strength at high temperature is required in steel, metals such as molybdenum and vanadium could be used to substitute tantalum. In superalloys hafnium, iridium, molybdenum, niobium, rhenium and tungsten could substitute tantalum [7].

All in all, though there are substitutes available for most applications of tantalum and its compounds, the use of these substitutes often incurs a cost or performance penalty or less versatility. The core use of tantalum in capacitors has several possible substitutes (aluminium, ceramic or niobium-based capacitors) that are likely to answer most common needs [1]. However, it is expected that tantalum capacitors will remain first-choice for applications requiring high reliability and resistance to elevated temperature where cost is not a primary consideration. Substitutes are also available in the case of mill products (e.g. glass, titanium, niobium) and high-temperature applications (e.g. niobium, tungsten, hafnium).

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TUNGSTEN

Tungsten special properties include the highest melting point, the lowest coefficient of thermal expansion and the lowest vapour pressure of any non-alloyed metal [1]. In addition, tungsten is the heaviest metal with a density similar to that of gold and presents a high modulus of compression, high wear resistance, high tensile strength and high thermal and electrical conductivity [2]. These properties make it extremely important for a variety of products, in particular in cemented carbides.

Table 58. General information concerning tungsten products and applications.

CRM	Product	Application	Substitute
Tungsten	Cemented carbides	Mining petroleum construction metal-working industries in drill bits and in machine tools for shaping metals, wood, composites, plastics and ceramics.	Tool Steel, Ceramics, Ceramic-metallic composites, Molybdenum carbide, Niobium Carbide, Titanium carbide, Titanium cabonitride in metallic binder phase (Ni and/or Co) possible with toughening additives.
	Steel alloys	Thermal and radiation shields of space vehicles, electrodes for welding in noble gas atmosphere, X-ray emitting cathodes, heating elements for industrial furnaces High-speed, tool and matrix.	Molybdenum combined with alloying with chromium, vanadium and nickel ASS (Alumina, silicon nitride, sialon) AZS (Alumina, zirconia, silicon carbide).
	Superalloys	Corrosion resistance turbines blades, marine vehicles.	Molybdenum Ceramic matrix composites (CMCs) Tantalum fiber.
	Mill products	Lighting filaments, audio-visual projectors, fibre-optical systems, video camera lights, airport runway markers, photoprinters, medical and scientific instruments, and stage or studio systems, electron emitters, heating technology.	Carbon nanotube filaments, induction technology, light-emitting diodes (LED).
	Chemical compounds	paints, dyes, enamels, painted glass, catalysts	Molybdenum carbide catalyst.

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1. DESCRIPTION AND INDICATOR

Tungsten has been listed as a critical raw material for the EU since the original criticality assessment in 2010 [3] [4] [5]. Europe has mines of tungsten in its territory but the mine production still does not meet the demand of the European industries. The British Geological Survey's risk list ranked tungsten in the top ten materials facing potential supply disruptions [6] [7] [8]. The substitutability of niobium was assessed in the CRM_Innonet project [9] and MSP-REFRAM project [10] [11].

2. SUBSTITUTE MATERIALS

The following table shows the substitutes of tungsten:

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Table 59. General description, economic value and main applications of the tungsten substitute materials.

Substitute Material	**Description of the Material**			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Titanium	Substitution of tungsten carbide for cemented carbides. TiC is also more lightweight, useful in tribotechnical and machining applications. TiC hard metal grades shows a higher hardness and fracture toughness.	This substance is manufactured and/or imported in the European Economic Area in 100 - 1000 tonnes per year.	Its market is expected to experience momentous growth over the next six years owing to increasing usage in residential, commercial, power generation, transportation, and industrial. Growing energy demand on account of increasing population is expected to be the major factor driving the market over the foreseeable period.	Metal surface treatment products, non-metal-surface treatment products, inks and toners, laboratory chemicals, polymers, welding & soldering products, metals, coating products, fillers, putties, plasters, modelling clay, metal working fluids and paper chemicals and dyes.
Molybdenum	Molybdenum combined with alloying with chromium, vanadium and nickel for steel alloy applications	Europe produced four metric tons (metal content) of Molybdenum in 2012 and eight tons in 2013, all from Norway. Molybdenum consumption in Europe in 2013 was 63.5 kt. Europe is the world's second biggest consumer of Molybdenum, with an average annual consumption of 63,500 tons in 2011 and 2012, which represents 25 % of annual worldwide production.	The global molybdenum market is expected to witness a CAGR of 3.5% during the forecast period of 2018 - 2023. The growing demand for molybdenum bearings in the steel and chemical sectors is alleviating its prices.	Thermal and radiation shields of space vehicles, electrodes for welding in noble gas atmosphere, X-ray emitting cathodes, heating elements for industrial furnaces high-speed, tool and matrix
	Molybdenum Ceramic matrix composites for corrosion resistance turbines blades, marine vehicles			Turbines blades, marine vehicles
	Molybdenum carbide catalyst			Lubricant (MoS_2), catalyst

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Table 60. Technological and non-technological barriers and solutions for the substitution of tungsten.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Titanium	Technological	cemented carbides	the technology is not competitive at the moment	6	Improve the performance of TiC	7
	Non-Technological	cemented carbides	Implies higher costs	7		
Molybdenum	Technological					
	Non-Technological	steel alloy applications	High dependance of the EU on Mo supply (Raw Material)	6	Establishing more efficient sorting and recovery systems	5
		corrosion resistance				
		catalyst			Redesign of the value chain: Using recycling tungsten from tailing and waste and scrap	6
					Develop a more environmental friendly process to replace the present	4

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					oxidative roasting process. This will increase Mo competitiveness.	
					Using generated residual materials as by-products as well as wastes	5
					Potential innovations on recovery from secondary resources (mill scale, dust, slag, etc) are needed.	3
Niobium	Non-Technological	catalyst	Critical Raw Material	8	Improve collection and recycling systems	4
Silicon carbide/nitride		Ceramic Matrix Composites for gas turbine engines				
FeTa	Technological	Super-alloy applications	Low TRL (3-4)	6	Increase TRL by further technological development	7
	Non-Technological	Super-alloy applications	Ta is a Critical Raw Material	8	Improve collection and recycling systems	4

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4. SUMMARY

As a summary, the consumption of W continues to increase as the amount of carbide tool production increases with the expansion of markets in developing countries. For tungsten's main application, WC-based cemented carbides, substitution appears technically possible but implies higher costs and, in some cases, a decrease in performance. Titanium carbides (TiC) and nitride (TiN) are potential substitute but the technology is not competitive at the moment. Tungsten can be replaced by other refractory metals such as niobium (CRM) or molybdenum in steel products. In other application areas, possible substitution of tungsten is affordable, as super-alloys substituted by Ceramic Matrix Composites (CMCs) made from a silicon carbide/nitride matrix for gas turbine engines. Also, substitution with nanostructured n-alloys such as FeTa, is could be possible in 10 year since current TRLs are very low (TRL 3-4). Substitution in the lighting sector is well underway [9] [10] [11].

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VANADIUM

As described in D4.1 and D5.1, vanadium is mainly used as additive in HSLA (high-strength-low-alloyed) steel and special alloys to improve their strength and resistance to corrosion; vanadium oxide is also used as catalyst and as pigment for ceramics and glass. The vanadium in HSLA steels can be substituted by, for example, niobium to only a few degrees; while the substitution element, niobium, is also listed as one of the critical raw materials by EU.

The product, application and substitution of vanadium is summarized in the table below. [1]

Table 61. General information concerning vanadium products and applications.

CRM	Product	Application	Substitute
Vanadium	Ferrovanadium	HSLA steel	Nb, Mn, Mo, Ti and W
		Special alloys	Nb
	Vanadium pentoxide	Catalyst	Pt, Ni, etc.

1. DESCRIPTION AND INDICATOR

Production and consumption in EU and future demand

Vanadium is typically recovered as a by-product or coproduct from the vanadium-containing slag generated from the hot metal production. According to USGS, world resources of vanadium exceed 63 million tons. In EU there is no complete and harmonised dataset that presents total EU resource and reserve estimates for vanadium. Minerals4EU website only provides resources data for Sweden, with 24.6 million tonnes vanadium, or 140 million tonnes at 0.2% of V of inferred resources. The EU import reliance on vanadium is 84%. [1]

The future demand on vanadium is driven by the market need of lighter weight and higher strength steels. The addition of just 0.2% vanadium to steel increases steel strength by up to 100% and reduces weight in relevant applications by up to 30%.[2]

2. SUBSTITUTE MATERIALS

The V-containing steel can be replaced by some other types of steels containing completely no vanadium. Further, vanadium as an alloying component in steels can be replaced by Mn, Mo, Nb, Ti, Nb and W to some extent. One of the main factors that defines the substitution of

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vanadium is the relative price difference between vanadium and the substitution elements. Further, as mentioned earlier, sometimes the substitution element is also in the CRM list. The description of niobium as a substitute of vanadium in steel is described in the table below. [1]

Table 62. General description, economic value and main applications of the vanadium substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Niobium	One of the CRMs; High price	No production in EU Consumption ca. 12,500 ton/year FeNb	High economic value	Steels Superalloys

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

In the application of HSLA steels, niobium can be used to replace vanadium. However, niobium is also listed one of the CRMs and the price of niobium is high. In EU there is no production of niobium and the EU import reliance on niobium is 100%. Similar as vanadium, the application of niobium in HSLA steels is dissipative, which means that the recovery of niobium from secondary materials is almost zero. All these factors are barriers for the substitution of vanadium by niobium.

Table 63. Technological and non-technological barriers and solutions for the substitution of vanadium.

Substitute Material	Type of Barrier	Product/ Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Niobium	Technological	Steels	Dissipative in the applications and almost no recovery	2 2	Increase the recovery rate of Nb from secondary materials	4
		Superalloys		2 2		
	Non-Technological	Steels	Higher price; Higher import reliance	8		
		Superalloys		8		

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4. SUMMARY

Vanadium is largely used in HSLA steels and special alloys. Due to the market demand of lighter weight and higher strength steels, vanadium becomes indispensable in HSLA steels. Vanadium as an alloying component in steels can be replaced by several other elements to some extent; however, sometimes the higher price of the substitution elements than vanadium makes the substitution less economic.

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SILICON

The element silicon is a very abundant element in the earth's crust and has several applications that are summarized in the following table:

Table 64. General information concerning Silicon products and applications.

CRM	Product	Application	Substitute
Silicon	Silicone	Construction, energy, health care, transport, kitchen appliances	Rubber, thermoplastics
	Silane	Adhesion layer in structures, paints, …	-
	Aluminium alloy	Automotive, aerospace, kitchen, other industries	Magnesium, copper
	Solar cells	Renewable energy production	Copper indium gallium selenide, CdTe, hybrid technologies
	Semiconductors	Electronic applications	Germanium, GaAs

1. DESCRIPTION AND INDICATOR

Silicon metal (symbol Si) is the second most abundant element in the Earth's crust in the form of silicate minerals (27.5%, after oxygen). It occurs in nature combined with oxygen, as the oxide (silica) and silicates (minerals, in which aluminium or other tetravalent atoms replace some of the silicon atoms). Elemental silicon is produced commercially by reducing vein quartz/silica sand with carbon in an electric furnace. High-purity silicon, for the electronics

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industry, is prepared by the thermal decomposition of ultra-pure trichlorosilane, followed by recrystallisation. Silicon has no metallic properties but is known as silicon metal in the industry because of its lustrous appearance when ultra-pure. [1]

Two grades of silicon metal exist: metallurgical grade silicon (typically around 99%), representing the majority of the volumes produced, and polysilicon (with a 6N to 11N purity). The former is applied in metallurgy and in the chemical industry in the production of silicones and silanes, covering more than 90% of the total world and European silicon metal consumption, whereas the latter is used as a semiconductor in photovoltaic applications or in microelectronics. Despite the overall low share of electronic applications in the silicon consumption, 2%, ultra-high purity grade silicon is used extensively in silicon semiconductors, transistors, printed circuit boards and integrated circuits. [1] Additionally, silicon is seen as one of the most attractive anode materials for future lithium-ion batteries. [2]

Silicon has been included in the List of Critical Raw Materials for the EU in the assessment of 2014 and again in 2017 [3]. The annual production of refined silicon metal is 2.3 million tons, with China accounting for 61%.

Silicon in silicones, silanes and other chemical applications

Chemical industry accounts for 54 % of silicon end use [3]. Much of this is consumed for the production of silicones, silanes and other silicon-bearing chemicals. Silicone is an inert polymer that comprises silicon with oxygen, carbon, hydrogen, and other elements. The silicon-based monomeric chemical includes four substituents, and at least one carbon-silicon bond structure. Some of the common forms of silicones are resin, grease, oil, and rubber, which are used across automobile, medical, construction and electronics industries. On the contrary, silane is an organic compound containing a single or multiple siliconcarbon bonds. Silane is produced by reacting silica sand with magnesium and then adding hydrochloric acid. One of the primary applications of silane is to bond two compounds together.

Silane is increasingly adopted in paints & coatings, adhesives & sealants, rubber & plastics, and fiber treatment activities. The growth of the overall silicones & silanes market is driven by rise in demand from end-use industries, such as electronics & semiconductor. They are preferred because of their temperature stability and outstanding insulation. The market for silicones and silanes is expected to grow with a compound annual growth rate (CAGR) of 5.4% from 2018-2025. [4]

Alloying element in aluminium alloys

Silicon is added into aluminium to improve lower the melting temperature, improve the viscosity of the liquid alloy and to crease strength, corrosion resistance and machinability. Indeed, 38 % of silicon is consumed in the production of aluminium alloys [3]. Aluminium alloys

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are produced as wrought alloys and cast alloys. Wrought alloys vary in the silicon contents up to 13.5 %, with the exact amount of silicon alloying depending on whether silicon is the major or minor alloying element. 4000 series alloys have silicon as the main alloying element (5-13.5 wt.%), whereas 6000 series alloys contain both silicon (0.2-1.8 wt.%) and magnesium, and 2000 series alloys involve copper and silicon (typically < 1 wt.%). [5] Equally, in cast alloys, silicon improves the casting properties of aluminium. 4xx.x series involves silicon as the main alloying element, while 3xx.x series contains silicon with copper and/or magnesium. In the cast 4xx.x series alloys, silicon contents are typically between 5 and 13 wt.%. [6] The primary use is in castings in the automotive industry due to improved casting characteristics described above and the reduced weight of the components.

Solar applications

Solar applications correspond to 6% of silicon end use in Europe [3].Ultrahigh-purity grade silicon is used for the production of solar panels. Crystalline silicon is the most mature photovoltaic material, and is the long-term market leader. There is very widespread and deep skill and infrastructure available in crystalline silicon technology [7]. Indeed , crystalline silicon is one of the most widely used semiconductor material in photovoltaic (PV) technology to manufacture solar cells. It occupies more than 90% of the total PV market revenue owing to its several benefits, such as high efficiency. The expected compund annual growth rate of crystalline silicon solar cell technologies is 11.3 % (between 2016-2022) [8].

Electronic applications

Ultra-high purity grade silicon is used extensively in electronic devices such as silicon semiconductors, transistors, printed circuit boards and integrated circuits, and the value of silicon in electronic applications surpasses that in, e.g., metallurgy (aluminium alloys). These applications make use of the semiconducting properties of silicon. For example, semiconductor-grade silicon metal used in making computer chips is crucial to modern technology. One reason is the established and reliable technology related to manufacturing of silicon-based computer chips. [3]

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2. SUBSTITUTE MATERIALS

In the case of silicon metal, there are no materials that can replace any of the main uses of metallurgical silicon without serious loss of end performance or increase of cost.

Silicones, silanes and other chemical applications

There is no material for the substitution of silicon in silicones and silanes, or in end-use products based on these chemicals. Indeed, silicones are durable and heat resistant. In comparison, materials such as rubber or thermoplastics do not pose as good durability and heat resistance thus a compromise in materials performance is expected upon substitution.

Aluminium alloys

Silicon is used to lower the melting point in aluminium manufacturing and to increase strength, machineability and corrosion resistance in aluminium products. There is currently no substitute to silicon metal for this application to introduce exactly the same property combination in aluminium alloys. [3] For example, in the case of cast alloys involving copper, high strength may be achieved yet the castability and corrosion performance of the alloys poorer than for silicon-containing alloys. In turn, aluminium magnesium alloys pose good machinability and high corrosion resistance, but moderate castability. [6]

Solar applications

Substitutive technologies to silicon based technologies for solar applications exist, with reduced performance, and alternative technologies are continuously being developed. However, these do not represent a material-to-material substitution but rather an alternative equivalent technology. It is estimated that Si technology represents 92% of the EU market; the reminder is shared between CdTe and copper indium gallium selenide (CIGS) technologies. [3] Among these two technologies, CIGS shows higher efficiency than CdTe [9] and it is loaded with very positive market growth expectations [10]. Additionally, new hybrid, 'tandem', technologies are currently being developed, but not on the market yet [11].

Electronic applications

For silicon in the microelectronics industry, in transistors, silicon be substituted by germanium of bismuth. In some cases, germanium may be used in combination with silicon, i.e., silicon remains as physical support for the germanium layer on the top. In integrated circuit applications, GaAs and GaN are the possible substitutes for Si. [3]

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Table 65. General description, economic value and main applications of the silicon substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Rubber, thermoplastics	Rubber and thermoplastics considered a potential substitute for silicone in some applications, yet the properties are different.	Natural rubber is also a critical raw material with no EU production		Substitute for silicone in chemical industry. Different chemical behaviour, thus compromised performance
Copper	In aluminium alloys, copper introduces precipitation hardening, i.e., strength improvement based on the formation of intermetallic precipitates.		Demand for copper is expected to boom with the electrification of traffic (electric conductor material)	Substitute for Al-Si alloys, but with much poorer castability/higher melting point and lower corrosion resistance.

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Table 66. Technological and non-technological barriers and solutions for the substitution of silicon.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Substitute 1: Rubber	Technological	Chemical industry: silicones, silanes	Chemistry of silicon is quite unique with its high affinity of oxygen, thus chemicals imitating silicone and silanes are hard to manufacture by other means.	10		
Substitute 2: Magnesium	Technological, non-technological	Metallurgy: aluminium alloys	Silicon and magnesium have different properties, so they introduce different effects in aluminium alloys. Magnesium is light, similar to silicon, but the castability of their aluminium alloys is different. Magnesium is also a critical raw material.	7	Development of replacive Al-alloys (e.g., scandium)	
Substitute 3: CIGS (Copper indium gallium selenide)	Technological	Solar applications	Solar technology based on silicon is very established. CIGS technology is a thin-film technology with good potential in the future.	7	More research efforts on alternative solar technologies, incentives to invest on alternative technologies	9-10
Substitute 4: Germanium, GaAs	Non-technological	Seniconducting applications, electronics	Germanium and GaAs are the principal substitutes for silicon in electronics industry. Both germanium and gallium are also critical raw materials, thus their supply is limited.	5		

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4. SUMMARY

Silicon is the second most abundant element in earth's crust, but in compounds, typically with oxygen. The extraction of silicon metal requires several steps and energy. Semiconductor applications (solar, electronic) make use of high-purity or ultra-pure silicon metal. The largest use sectors of silicon metal are chemical industry (silicone, silanes) and metallurgical industry (aluminium alloys). In the former, practically no substitutes exist, while in the latter other alloying elements, such as magnesium, may provide some of the properties also introduced by silicon alloying. In semiconducting applications, solar sector has a potential replacive technology based on thin film of copper indium gallium selenide (CIGS), with great marker growth expectations, whereas the electronic industry already uses germanium and gallium arsenide, GaAs, in parallel to silicon technologies. Some of the technological challenges may be overcome by extensive R&D in alternative technologies, yet non-technological barriers are related to the supply/demand -dynamics of substitutive materials (magnesium, germanium, and gallium).

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COKING COAL

As described in D4.1 and D4.2, coking coal is mainly used as raw material for metallurgical coke production. Substitution is presently possible only to minor degree and there are innovations needed to develop innovative technologies that can allow increased substitution of coking coals with e.g. thermal coals, bio-coals and secondary materials (e.g. coke fines, petroleum coke, plastics etc.) without significant effect on the coke quality.
The product, application and substitution of coking coal is summarized in the table below.

Table 67. General information concerning coking coal products and applications.

CRM	Product	Application	Substitute
Coking coal	Metallurgical coke	Blast furance ironmaking	Thermal coals
			Bio-coals
			Secondary materials

1. DESCRIPTION AND INDICATOR

There has been a decrease in coking coal use within EU due to increased import of finishes steel products from Asia. The Minerals Council of Australia [1] foresee a further minor decrease of approximately 3% foreseen until 2030. However, the significant increased needs foreseen in China and India will have effect on the availability of coking coal on the market. The metallurgical coal import is foreseen to grow with 7.5 Mt/year resulting in a total growth by 97 Mt from 2017 to 2030. A large part of these high-quality coking coals needed are supplied from Australia but some from USA. Occasionally the supply is lowered by weather disasters or reduce production adaptation due to lower market demand and prices.

The forseen need for import of coking coals [1] are:

Country (Imports Mt)	2017	2020f	2025f	2030f	Growth
China	76	95	118	115	39
India	53	67	87	113	60
Japan	42	42	41	40	(2)
Korea	24	25	25	25	1
Taiwan	9	9	9	9	-
Europe	55	54	53	52	(3)
Brazil	16	17	17	18	2
Total	**275**	**309**	**350**	**372**	**97**

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There are mining of coking coal in EU-28, mainly in UK, Germany, Czech Republic, Spain and Turkey but the European mines produces less than half of the coking coals needed in EU. The coke is mainly used in metal production as for ironmaking, lead production and at foundries.

High quality coke is important for resource efficient metal production and although that there is research in the metallurgical sector making research for fossil free or low carbon metal production most of the plants will still require coking coal for their steel plants. With lowered coke rate its residence time in the process will increase and the coke quality becomes even more important. For this, high quality coking coal will be needed.

2. SUBSTITUTE MATERIALS

As pointed out in D6.1 and D 6.2 coking coals may be partly replaced by thermal coals and bio-coals as well as secondary materials. However, these materials are all inert and therefore the cokemaking needs to be modified and adapted to maintain the coke quality. Research and innovation is needed in this field. Methods as stamp charging, also with binder, addition of a binder as hypercoal when using density charging, new type of coke making processes but also modification of the temperature program and coal blend can improve the plasticity development during cooking. [2]-[8].
The description of substitutes for coking coal is described in the table below.

Table 68. General description, economic value and main applications of the coking coal substitute materials.

Substitute Materials	**Description of the Materials**			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Thermal coals	Limited replacement for metallurgical use	Small production in EU and decreased consumption	Low economic value	Fuel in power station
Bio coals	Limited replacement for metallurgical use	Small amount of production in EU, expected increase in consumption	High cost for substitution of coking coals	Fuel for ironmaking, power station, etc.
Secondary materials	Limited replacement for metallurgical use	Small amount available	High economic value	Fuel for ironmaking, power station, etc.

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

In metallurgical application, thermal coals, bio coals and secondary materials can be partially used to replace the coking coals. However, the replacement ratio at the moment is very limited, because: (a) the used of thermal coals and bio coals may deteriorate the coke quality and/or the ironmaking process; (b) the quality and the quantities of the supplied secondary materials may vary from time to time and from one source to another. Among these secondary materials, the bio coals could have the highest potential in the future with the development of the bio coal production process.

Table 69. Technological and non-technological barriers and solutions for the substitution of coking coal.

Substitute Material	Type of Barrier	Product/ Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Thermal coals	Technological	Blast furnace ironmaking	Reduced coke quality with addition in coking process	8	Reducing addition in the coking process	8
	Non-Technological		/	/	/	/
Bio coals	Technological		Reduced coke quality with addition ; Low production capacity	6	Production and technology development	8
	Non-Technological		High price	9		
Secondary materials	Technological		Low quality or sometimes high impurities	9	N. A.	5
	Non-Technological		Big variations in quality and quantity.	6	N. A.	5

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4. SUMMARY

High quality coking coals are required for metal production and especial for ironmaking. The availability of coking coal is crucial for operation of modern blast furnaces with high injection rate of pulverised coals. The major production route for steel is via the ironmaking blast furnace and production via this route also has increased most. From economic and technical reasons, it is foreseen that most of the modern blast furnaces furnace will sustain as the major production route for many years and therefore new technologies for substitution important.

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FLUORSPAR

The main usage of fluorspar is in the production of hydrofluoric but it has other applications summarized in the following table (Table 70):

Table 70. General information concerning flourspar products and applications.

CRM	Product	Application	Substitute
Fluorspar	Acid-grade fluorspar “acidspar”	Fluorochemicals, fluorocarbons (fluorinated hydrocarbons, HFCs) as refrigerants for refrigeration (refrigerator) and air conditioning	Hydrocarbons such as propane CO_2 Ammonia

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	Acid-grade fluorspar "acidspar"	In the production of hydrofluoric acid (hydrogen fluoride, HF)	Fluorosilicic acid (FSA) Calcium fluoride Depleted uranium hexafluoride Sodium fluoride Sodium fluorosilicate
	Acid-grade fluorspar "acidspar"	In the production of Aluminium fluoride (AlF_3) - component of the molten bath in the electrolytic reduction of alumina to aluminium metal	Fluorosilicic acid (FSA)
	Metallurgical grade fluorspar "Metspar"	As flux in steel smelting	Calcium aluminate Aluminium smelting dross Borax Calcium chloride Iron oxides Manganese ore Silica sand Titanium dioxide

1. DESCRIPTION AND INDICATOR

Fluorspar is the commercial name for the mineral fluorite (calcium fluoride, CaF_2). Fluorite is a colourful, widely occurring mineral that occurs globally with significant deposits in over 9,000 areas. It is the principal industrial source of the element fluorine. Commercial fluorspar is graded according to quality ad specification into acid-grade "acidspar" (minimum 97% CaF_2), metallurgical grade "metspar" (minimum 80% CaF_2) and ceramic grade (80-96% CaF_2). The grade of fluorspar determines its end-use. Nearly two thirds of the world's fluorspar production is for the manufacture of the hydrofluoric acid (hydrogen fluoride, HF) which is the basis for all fluorine-bearing compounds and fluorinated chemicals including fluorocarbons, fluoropolymers, fluoroaromatics and inorganic fluorine compounds. Fluorspar has a low melting point, and when added to metallurgical slags, it imparts greater fluidity at lower temperatures, thus making it valuable as flux in smelting. Approximately one third of the fluorspar produced worldwide is of metallurgical grade and is used primarily as a flux in steelmaking and in the production of aluminium. A small proportion of fluorspar produced is ceramic grade which is used in the production of opaque glass and enamels [1] [2].

Acid-grade fluorspar, Fluorine-bearing compounds and chemicals

Nearly two thirds of the world's fluorspar production is for the manufacture of the hydrofluoric acid (hydrogen fluoride, HF) which is the basis for all fluorine-bearing compounds. Historically, the largest group of chemicals that requires HF in their manufacture are chlorofluorocarbons (CFCs) in refrigeration units. Hydrogen-containing chlorofluorocarbons (HCFCs) were introduced as transitory replacements for CFCs. Nowadays, HCFCs are being replaced by fluorocarbons, fluorinated hydrocarbons HFCs which contain no chloride and even more fluorine. HFCs are mainly used as refrigerant in stationary and mobile air conditioners and heat pumps offering special advantageous properties as refrigerant: low toxicity, non- or low- flammability and a moderate global warming potential. Furthermore, HFCs show good thermodynamic properties and can be tailor-made to specific operation conditions required for process scalability, thereby increasing system efficiency [1] [3].

Metallurgical grade fluorspar, Metallurgical use

Metallurgical grade fluorspar is used as a flux in oxygen and electric arc furnaces where it acts to reduces slag viscosity, lowers the melting point and removes impurities such as sulphur and phosphorus from steel. Metallurgical grade fluorspar is also used in the production of aluminium, as aluminium fluoride (AlF_3) is a component of the molten bath in the electrolytic reduction of alumina to aluminium metal [1]. Hydrogen fluoride is also used to produce synthetic cryolite (Na_3AlF_6) [4].

Other uses

Ceramic grade fluorspar is used in the glass and ceramic industries where it is needed to produce opal glass and opaque enamels. New uses of fluorine in the form of fluoropolymers in the plastics and electronic industries have emerged in the past decade which could replace demand lost due to declining CFC production. Fluoropolymers are remarkable for the their thermal stability, high chemical inertness, strong electrical insulation and very low coefficient of friction. A second rapidly growing market is nitrogen trifluoride (NF_3), which is widely used as as an inert cleaning gas in the manufacture of semiconductors and LCD-screens. It is also used in a wide range of chemicals vital for the manufacture of electrical components in the form of silicon based semiconductors, catalyst in petrochemical production, pharmaceuticals, herbicides, pesticides, crystal glass and the processing of uranium for nuclear fuel [1].

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2. SUBSTITUTE MATERIALS

The EU report dedicated to CRMs confirms that fluorspar is hard to substitute (substitution index for fluorspar is equal to 0.98/0.97). [5] Large-scale commercial substitutes do not exist [6].

Fluorine-based compounds as refrigerants

There is currently a major drive to replace fluorine-based compounds used in many applications with more environmental friendly alternatives. Available substitutes for HFCs refrigerants are CO_2, ammonia and hydrocarbons (butane, propane). However, those may not be suitable for each application or as performant as HFCs as e.g. ammonia is toxic, hydrocarbons are flammable and CO_2 needs to be compressed to high pressures to be able to use it as refrigerant [1] [5]. Future demand for fluorspar will highly depend on the development and use of fluorocarbon substitutes [6].

Alternative sources of HF

There are several alternatives sources of HF, including calcium fluoride, depleted uranium hexafluoride, sodium fluoride and sodium fluorosilicate. However, the use of fluorosilicic acid (FSA) is the only one, which could have a significant impact. Fluorosilicic acid is used to produce aluminium fluoride (AlF_3), but because of differing physical properties, AlF_3 produced from FSA is not readily substituted for AlF_3 produced from fluorspar [7]. Until recently, the FSA route to produce HF was more expensive than the fluorspar route, but this situation is changing as new technologies make production of HF from FSA cheaper [1].

Metallurgical grade fluorspar

Substitutes for fluorspar fluxes includes aluminium smelting dross, borax, calcium chloride, iron oxides, manganese ore, silica sand, and titanium dioxide [8]. Aluminium dross is a by-product of the aluminium smelting process [9].

Table 71. General description, economic value and main applications of the fluorspar substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Substitutes for fluorine-based air conditioning and refrigeration compounds	Ammonia for air conditioning and refrigeration applications	The EU-27 has a total capacity for the industrial production of ammonia equal to about 21 million tonnes [10].		Refrigeration applications
	Hydrocarbons (butane, propane) for air conditioning	The decline in global oil prices resulted in similar price declines in	Historically, propane prices have been very closely linked to	Refrigeration applications

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	and refrigeration applications	petroleum products such as gasoline, diesel, and propane [11].	oil prices in both domestic and international markets [11].	
Substitute fluorspar in aluminium fluoride manufacturing	Fluorosilicic acid, FSA to produce Aluminium Fluoride. Aluminium fluoride is manufactured from anhydrous hydrofluoric acid generated either from fluorspar or fluosilicic acid.		The theoretical price of FSA would be USD 600.-/ton if fluorine F contained in FSA is assumed at the same value of F contained in fluorspar [9].	Aluminium fluoride production
Substitutes for fluorspar fluxes	Aluminium smelting dross	Dross generation from the primary aluminium smelting process normally represents 0.5 – 1.5% of the aluminium production [12].		Fluxes in steelmaking

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Ammonia, CO2 and hydrocarbons for refrigeration solutions

Ammonia was used for refrigeration already in 1876 and also other refrigerants like CO_2, SO_2 were commonly used until 1920s [13]. However, the development of CFC's (Chlorofluorocarbons) decrease the use of these refrigerants. But the stopped use of HCFC refrigerants, have again increase the use of refrigerants like Ammonia and CO_2 and they are being considered for various new applications as well. Ammonia is a toxic refrigerant, and it is also flammable at certain concentrations. That is why it has to be handled with care, and all ammonia systems have to be designed with safety. In case it is necessary to reduce ammonia charge, combination of ammonia and CO_2 (as cascade or as brine) could be a good and efficient option. The cost of ammonia (per kg) is considerably lower than the cost of HFCs. This advantage is even multiplied by the fact that ammonia has a lower density in liquid phase. Furthermore, as any leakage of ammonia will be detected very quickly due to the odor, hence any potential loss of refrigerant will also be lower. Ammonia is mainly suitable for industrial and heavy commercial applications [13].

The following types of hydrocarbons are commonly used as refrigerants: Propane, Isobutane and Propylene. A number of other hydrocarbons, such as blends containing ethane, propane or butane, are also used Propane has been proposed since the late 1980s as a replacement for CFCs and especially HCFC [14]. Except its high flammability, propane has very similar

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properties as HCFC. The relative cost of a system using hydrocarbons largely depends on the application but e.g. in domestic and light commercial applications, the cost of the system is similar to that of systems with HFCs. In commercial and industrial refrigeration applications, systems with hydrocarbons tend to be relatively expensive due to the need for explosion-proof enclosures for electrical equipment [14].

Fluxes in steelmaking

Fluorspar is a common raw material used at ironmaking and steelmaking facilities being a powerful fluxing agent. Despite of its benefits there are also health and environmental concerns. Fluor can be lost from industrial slags due to the reaction:

$2CaF_{2\,(slag)} + SiO_{2\,(slag)} \rightarrow SiF_{4\,(g)} + 2CaO_{\,(slag)}$.

Depending on temperature and slag composition compound such as NaF(g), KF(g) and (SiF_4), AlF_3, CaF_2, BF_3 can be emitted [15]. These contributes to environmental problems and corrosion of metallic structures. Use of fluorspar in steel refining operations is one of the environmental concerns and for that reason substitution is one of the objectives in that field [16].

Fluorosilicic acid, FSA

Fluorosilicic acid finds its main application in the manufacture of low bulk density (LBD) aluminum fluoride being a large volume chemical, which is mostly produced from fluorspar as high bulk density (HBD) aluminum fluoride. From fluosilicic acid only a small amount HBD is produced. Aluminum fluoride is used as a flux for smelting aluminum by volumetric addition to the cells of aluminium smelters in order to regenerate the cryolite bath. Aluminum fluoride technology often referred to as the Dry/FSA Process which is a gas phase process using a fluidized bed reactor [9].

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Table 72. Technological and non-technological barriers and solutions for the substitution of fluorspar.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Substitute 1: CO_2	Technological	to substitute fluorine-based air conditioning and refrigeration compounds	Needs to be compressed to high pressures →used only in very limited applications	5		
Substitute 2: Hydrocarbons	Technological	to substitute fluorine-based air conditioning and refrigeration compounds	Flammable → limits the use, higher costs because of explosion-proof enclosures	5	Future demand for fluorspar will highly depend on the development and use of fluorocarbon substitutes	
Substitute 3: Ammonia	Technological	to substitute fluorine-based air conditioning and refrigeration compounds	Toxic →used only in very limited applications in industrial and heavy commercial applications	5		
Substitute 4: FSA	Technological	Fluorosilicic acid finds its main application in the manufacture of low bulk density (LBD) aluminum fluoride	New process technologies need to be developed to manufacture aluminum fluoride of high density	5		
Substitute 5: Alumina smelting dross	Technological	to replace fluorspar flux	The ilmenite and aluminum dross mixtures showed similar behavior when compared to the fluorspar mixture.			

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4. SUMMARY

Fluorspar is the commercial name for the mineral fluorite (calcium fluoride, CaF_2). Commercial fluorspar is graded according to quality ad specification into acid-grade “acidspar” (mininum 97% CaF_2), metallurgical grade “metspar” (minimum 80% CaF_2) and ceramic grade (80-96% CaF_2). The grade of fluorspar determines its end-use. Nearly two thirds of the world’s fluorspar production is for the manufacture of the hydrofluoric acid (hydrogen fluoride, HF) which is the basis for all fluorine-bearing compounds and fluorinated chemicals including fluorocarbons, fluoropolymers, fluoraromatics and inorganic fluorine compounds. Approximately one third of the fluorspar produced worldwide is of metallurgical grade and is used primarily as a flux in steelmaking and in the production of aluminium.

The EU report dedicated to CRMs confirms that fluorspar is hard to substitute (substitution index for fluorspar is equal to 0.98/0.97) and large scale commercial alternatives do not exist. There is currently a major drive to replace fluorine-based compounds used in many applications with more environmental friendly alternatives. Available substitutes for fluorine based refrigerants are CO_2, ammonia and hydrocarbons (butane, propane). Future demand for fluorspar will highly depend on the development and use of fluorocarbon substitutes.

Partial or total replacement of fluorspar fluxes is very beneficial both from economic and environmental points of view. The generation of SiF_4 using fluorspar fluxes contributes to environmental problems and corrosion of metallic structures. Substitutes for fluorspar fluxes includes aluminium smelting dross, borax, calcium chloride, iron oxides, manganese ore, silica sand, and titanium dioxide.

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NATURAL GRAPHITE

As described in D4.1 and D5.1, natural graphite is mainly used as refractory materials for steelmaking/foundries (56%) and batteries (8%); the other applications of natural graphite include friction products, lubricants, etc. Due to the rise of the electric vehicles, it is expected that the share of natural graphite in Li-ion batteries will increase largely in the future. Natural graphite used in the refractory applications can hardly be substituted due to the unique combination of physical and chemical properties of natural graphite. Natural graphite used in the batteries can be replaced by synthetic graphite; however, the synthetic graphite normally is much more expensive. The product, application and substitution of natural graphite is summarized in the table below.

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Table 73. General information concerning natural graphite products and applications.

CRM	Product	Application	Substitute
Natural graphite	Refractory	Steelmaking/foundries	Not available
	Anode material	Batteries	Synthetic graphite

1. DESCRIPTION AND INDICATOR

Production and consumption in EU

In EU there are 3 active mines: the Kaisersberg mine in Austria (Grafitbergbau Kaisersberg GmbH), the Kropfmüh mine (Graphit Kropfmühl, a subsidiary of AMG Advanced Metallurgical Group) in Germany, and the Woxna Mine (Leading Edge Materials) in Sweden which operated only a few months during 2014 producing about 500 tonnes. Due to low price, production at the Woxna mine has been suspended since 2015. The EU-28 produced 561.8 tonnes per year of natural graphite (C content) on average, during the period 2010-2014. EU import reliance on natural graphite is 99%. During the period 2010-2014 the imports of graphite amounted to about 95,000 tonnes per year on average. Two-thirds of the EU-28 imports came from China and 20% from Brazil and Norway (as shown in Figure 6). [1]

Future demand

Graphite demand is expected to grow in near future, especially when considering the rise of Li-ion battery market (as shown in Figure 5), which will have impact on the price of the flake graphite. Graphite pricing is determined by chemical and physical characteristics: the carbon content and particle size, as well as the form of graphite. In general, the price increases with increasing particle size and carbon content. The price trend for the flake graphite can be seen in Figure 6, which shows that the price of the graphite will be increasing until 2022 and then level out.

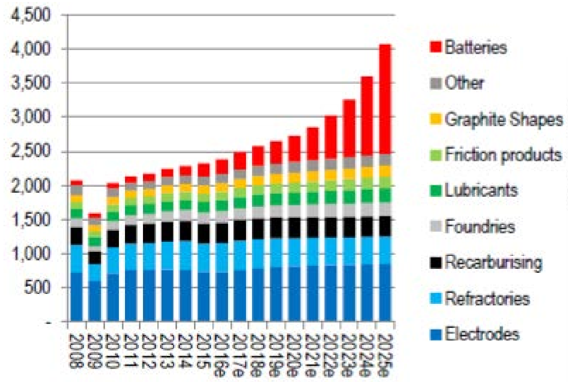

Figure 6. Global graphite demands [2].

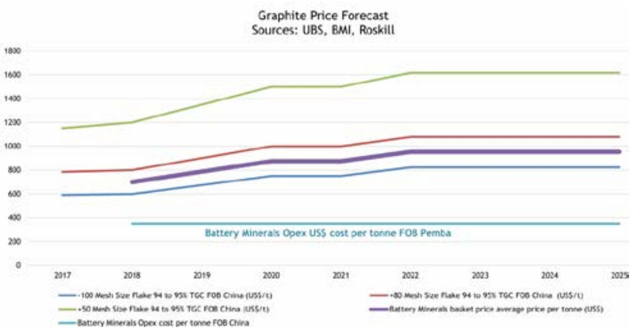

Figure 7. Price trend for the flake graphite [2].

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2. SUBSTITUTE MATERIALS

Synthetic graphite is a material consisting of graphitic carbon which has been obtained by graphitizing of non-graphitic carbon, by CVD from hydrocarbons at temperatures above 2500 K, by decomposition of thermally unstable carbides or by crystallizing from metal melts supersaturated with carbon.[3] Compared to the natural graphite production process, all these synthetic graphite manufacturing processes are complex and/or requires multiple processing steps. Figure 7 shows a typical production process of synthetic graphite by the graphitization method. The raw materials used in the process are petroleum coke (needle type is preferred) and coal tar pitch. It is seen that the synthetic graphite has quite critical production condition (high temperature) and quite long production time.[4] The purity of synthetic graphite will depend on the purity of the starting raw materials. The synthetic graphite can be used in Li-ion batteries, LEDs and other cutting-edge applications (solar, electronics, etc.). However, synthetic graphite cannot compete with natural graphite in the massive refractory applications due to the cost.

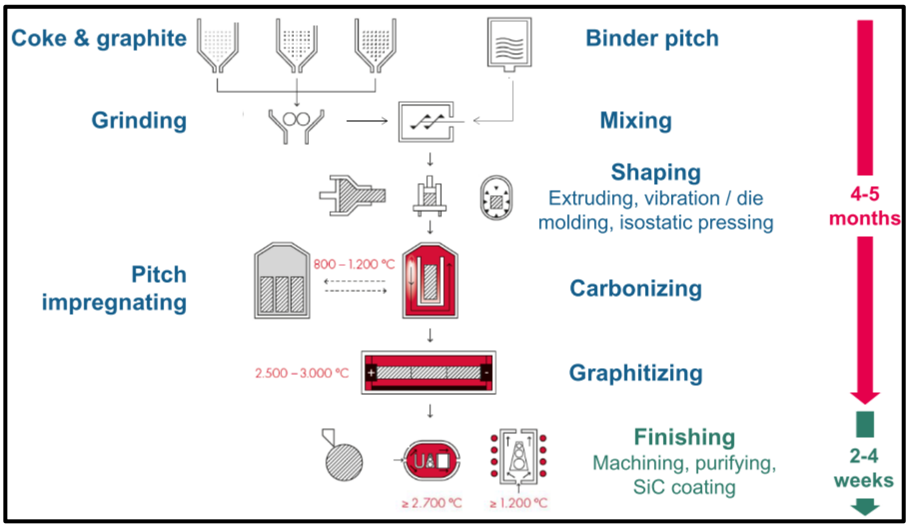

Figure 8. Manufacturing process of synthetic graphite [4].

Synthetic graphite vs natural graphtie in li-ion battery application

For Li-ion battery application, synthetic graphite performs as well as the natural graphite. While in certain Li-ion battery cells, synthetic graphite is even better than natural graphite.[5] The two types of graphite in Li-ion battery application compete actively in price and performance. Natural graphite as anode material in Li-ion batteries shows excellent performance under rapid charging and discharging cycles; while, synthetic graphite has large capacity with improved battery life. Natural graphite is cheaper than synthetic graphite and the production process for natural graphite is more environment friendly. In the future the need for both natural graphite and synthetic graphite will increase.

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The description of synthetic graphite is summarized in the table below.

Table 74. General description, economic value and main applications of the natural graphite substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Synthetic graphite	High quality but also high price	N.A.	High economic value; the market is expected to be larger	Batteries

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Synthetic graphite can be used to replace natural graphite in the application of batteries. However, more R&D work will be required to further improve the quality of the synthetic graphite to meet the specific needs for batteries. Synthetic graphite may be partially used to replace the natural graphite in the refractory applications (e.g. electrode). However, synthetic graphite is not going to replace most of applications in refractories, as the production of synthetic graphite is costly and less environment friendly.

Table 75. Technological and non-technological barriers and solutions for the substitution of natural graphite.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Synthetic graphite	Technological	Batteries	Quality	6	Technology development	8
	Non-Technological	Batteries and refracotries	Economic	10	Technology breakthrough	5
		Batteries and refracotries	Environmental	8	Technology breakthrough	7

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4. SUMMARY

Natural graphite is largely used in refractory and Li-ion battery. Due to the rapid growth of the Li-ion battery industry, the share of natural graphite application in Li-ion battery is becoming large in the future. EU has high import reliance on natural graphite. Due to the high production costs of synthetic graphite, the substitution of natural graphite by synthetic is limited in the refractory application. In Li-ion battery application, the natural graphite can be replaced by synthetic graphite. However, this sitution is challenged by the improvment of performance of natural graphite, which is comparable to synthetic graphite in properties but with lower price and smaller environmental impacts.

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BARYTE

Baryte (or barite) is a naturally occurring barium sulphate mineral ($BaSO_4$). It is inert, non-toxic and almost insoluble in water. Baryte has a high density of 4,5 g/cm^3, high fusion point (1580°C) and brightness, and a low oil adsorption. Baryte is white, grey or black in colour depending on the presence of any impurities.

Table 76. General information concerning Baryte products and applications.

CRM	Product/End-use	Application	Substitute
Baryte	Oil and gas industry as drilling fluids	Weighting agent in drilling fluids	Hematite (Fe_2O_3), ilmenite ($FeTiO_3$)
	Fillers in rubbers, plastics, paints & paper	Fillers	Calcium carbonate ($CaCO_3$) and clays (kaolin, talc)
	Automotive industry	As a soundproofing material	
	Construction Industry	Building materials or concrete with special features, like x-ray protection and sound insulation	
	Chemical industry	Barium carbonate ($BaCO_3$)	Strontium carbonate ($SrCO_3$)

1. DESCRIPTION AND INDICATOR

It is mainly used as a weighting agent in drilling fluids by the oil and gas industry. Baryte and barium compounds are also used as a fillers or additives in industrial products including rubber, paint, ceramics and glass, high density concrete and plaster, dielectrics, medical application [1].

Weighting agent in drilling fluids

Baryte is primarily used as a standard weighting agent in drilling fluid industry where baryte high specific gravity assists in containing pressures and preventing blowouts. Ground baryte is combined with bentonite, water, and other materials to manufacture “mud” which is pumped down the drill hole. Drillings muds remove cuttings up to the surface while cooling and lubricating the drill bit [1] [2].

Fillers and additives

Baryte is used as heavy filler in rubber, paint and plastics applications. In the automotive industry, it is used mostly as a soundproofing material in moulded components, floor mats, and in friction products such as breaks and clutches pads. In the construction sector, baryte is used for the production of building materials or concrete with special features, like x-ray protection and sound insulation [3]. Baryte is also used as filler in asphalt, in high quality primers and anti-corrosion coatings, resistant to abrasion paint such as bituminous paints etc [1].

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Chemical industry
In the chemical industry, baryte is used for the preparation of barium compounds, notably barium carbonate ($BaCO_3$) that is used in the production of special glass, as an ingredient in high-fire glazes, and in the brick and tile industry. $BaCO_3$ is increasingly used in electronic components, such as electronics ceramics and capacitors. Barium meal (barium sulphate) is used in radiodiagnosis [1].

2. SUBSTITUTE MATERIALS

The EU report dedicated to CRMs confirms that baryte is hard to substitute (substitution index for baryte is equal to 0.94/0.93) [1]. Baryte is an environmentally friendly material as it is a natural product and not manufactured; and not subject to registration under the EU REACH regulations. Substitution potential in the oil industry exists but the alternates are economically less attractive. None of these substitutes, however, has had a major impact on the barite drilling mud industry [4]. In some filler applications, cheaper alternatives exist where quality or technical considerations are less stringent [5].

Weighting agent in oil and gas well drilling fluids
Substitutes suggested for baryte used as a weighting agent for the oil and gas industry are hematite (Fe_2O_3), and ilmenite ($FeTiO_3$) [2]. In the drilling mud market, also celestite ($SrSO_4$) is suggested [6]. Hematite has a higher density and can be used to reduce solids percentage for rheology control, and ilmenite can be used when drilling activities take place close to a cheap supply source. Also relatively high hardness of hematite and ilmenite can give rise to abrasion/erosion in the tubular and surface equipment. Also the magnetic characteristic of iron oxide-containing minerals need to be addressed. This has the potential to affect the operation of direction drilling and some other downhole tools [1] [2].

Fillers
For fillers, the main substitutes for baryte are calcium carbonate ($CaCO_3$) and clays (kaolin, talc). They are used for general purpose fillers where quality or technical considerations for fillers are less stringent. They do not match quality aspects for heaviness, sound proofing and radiation shielding to barite [1].

Chemical sector
In chemical sector, there are various acceptable substitutes for barium carbonate in several applications. Strontium carbonate is sometimes used as a substitute in ceramic glaze. There is no alternate for barium carbonate in dielectrics and no safe substitute for medical applications [1].

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Table 77. General description, economic value and main applications of the baryte substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Hematite (Fe_2O_3)	Hematite has a higher density and can be used to reduce solids percentage for rheology control.	Manufactured and/or imported in the European Economic Area in 10 000 - 100 000 tonnes per year [7].		Substitute for baryte used as a weighting agent for the oil and gas industry. Economically less attractive.
Ilmenite ($FeTiO_3$)	Ilmenite can be used when drilling activities take place close to a cheap supply source.			Substitute for baryte used as a weighting agent for the oil and gas industry. Economically less attractive.
Calcium carbonate ($CaCO_3$)	Used for general purpose fillers where quality or technical considerations are less stringent.	The global calcium carbonate market size was valued at USD 20.69 billion in 2016 [8].		Substitute for baryte for fillers. do not match quality aspects for heaviness, sound proofing and radiation shielding.
Clays (kaolin, talc)	Used for general purpose fillers where quality or technical considerations are less stringent.			Substitute for baryte for fillers. Do not match quality aspects for heaviness, sound proofing and radiation shielding

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

The principal barrier that has limited the massive use of hematite as weighting agent in drilling fluid systems has been its erosive and abrasive wear effect over metallic and non-metallic components of the fluid circulation system (valves, pumps, pipes) and downhole tools (directional tools, motors, turbines) of a drilling rig. This effect increases when drilling fluids are operated at high densities and high pumping rates. Since the introduction of Brazilian hematite in South Texas in the early 1970s, several attempts have been made to reduce the wear potential of hematite, which have shown that erosive potential depends on the particle sizes, fluid densities (solid content) and rheological properties of the fluid system [9].

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Table 78. Technological and non-technological barriers and solutions for the substitution of baryte.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Substitute 1: Hematite (Fe_2O_3)	Technological	Substitute for baryte used as a weighting agent for the oil and gas industry	Erosive and abrasive wear effect over metallic and non-metallic components of the fluid circulation system (valves, pumps, pipes) and downhole tools (directional tools, motors, turbines) of a drilling rig.	5	Improve the performance of the oil based drilling fluids weighted with hematite	
Substitute 2: Calcium carbonate ($CaCO_3$)	Technological	Substitute for baryte for fillers	Used for general purpose fillers where quality or technical considerations are less stringent. do not match quality aspects for heaviness, sound proofing and radiation shielding	5		

4. SUMMARY

Baryte (or barite) is a naturally occurring barium sulphate mineral (BaSO4). It is mainly used as a weighting agent in drilling fluids by the oil and gas industry. Baryte and barium compounds are also used as a fillers or additives in industrial products.

The EU report dedicated to CRMs confirms that baryte is hard to substitute (substitution index for baryte is equal to 0.94/0.93)(European Commission, 2017) Substitution potential for baryte in the oil industry exist but the alternates, hematite (Fe_2O_3), and ilmenite ($FeTiO_3$), are economically less attractive. Thus, these substitutes has only minor impact on the barite drilling mud industry.

In some filler applications, cheaper alternatives such as calcium carbonate (CaCO3) and clays (kaolin, talc) exist where quality or technical considerations are less stringent.

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NATURAL RUBBER

Natural rubber (NR) consists an elastomer (elastic hydrocarbon polymer) which is collected by specific plant species in tropical environments. Its main applications are related with the construction of materials for pathogens protection in medicine, tires in automobile and aerospace industry, clothing and as adhesives (Table 79). The current options concerning the decreasing of NR supply are based on; (a) the examination of alternative non-tropical plant species from which it can be synthesized (substitution of the raw source), (b) its production via biochemical processing (alternative processing route) and (c) its direct substitution by synthetic elastomer materials.

Table 79. General information concerning natural rubber products and applications [1].

CRM	Product	Application	Substitute
Natural rubber	Latex	Medicine - best barrier against pathogens such as the AIDS virus (condoms and surgical gloves)	1) Production of natural rubber by alternatives plants (Guayule) or via biosynthesis)
	Composites (petroleum products,	Automobile and aircraft tires	2) EPDM rubber ethylene

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	carbon black) containing 50-100% of natural rubber		propylene diene methylene rubber
	Rubber-textile composites	rainwear, diving gear	
	As an additive in adhesives	Paper and carpet industries	

1. DESCRIPTION AND INDICATOR

NR can be produced from hundreds of different plant species. However, the most important source is from a tropical tree known as Hevea brasiliensis, which is native to the tropical Americas. This tree grows in environments with an annual rainfall of about 2000mm and at temperatures of 21-28 degrees. However, it is also cultivated further north in China, Mexico, and Guatemala. Malaysia, Indonesia, and Thailand Hevea cultivations represent the 90% of globally produced natural rubber. These countries lie within a band lying from 5° to 15° north or south of the equator and hence suitable for Hevea growing. World Natural Rubber (NR) consumption is expected to be 17 million tonnes by 2025. More than 1 million tonnes of NR is used in the EU in which no primary production has been reported. NR has been recently listed as a critical raw material for the EU since the original criticality assessment in 2017 [2]. The NR demand is expected to be increased during the next years due to the expanding of automotive fleet in Asia as a significant percentage of NR is used for the construction of vehicle tires.

2. SUBSTITUTE MATERIALS

Natural rubber displays various unique properties rendering its direct substitution by synthetic materials challenging and in some cases impossible. The most significant physical properties of natural rubber include [1,3]:

- High strength with outstanding resistance to fatigue.
- Ability to stick to itself and to other materials which makes it easier to fabricate.
- Moderate resistance to environmental damage by heat, light and ozone.
- Low hysteresis which leads to low heat and high resistance to cutting, chipping and tearing.

On the contrary, synthetic elastomer materials present lower heat resistance and shorter lifetime under their exposure sunlight, ozone and chemicals. The main substitution strategy which is worldwide examined is indirect and it is related with the investigation of alternative plants from which latex can be extracted. Guayule consists the most promising candidate as it has been proved that high quality latex can be extracted that can be appropriately used in several applications (Figure 8) [4].

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Table 80. General description, economic value and main applications of the substitute materials [4-7].

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Guayule (alternative raw source)	The plant is well adapted to semi-arid and Mediterranean areas, growing well under temperatures from -9°C to 40°C with 350-640 mm of rainfall/year.	2.000 hectares of guayule fields are going to be planted in Mediterranean countries within the framework of EU-NARS-G project (final results will be announced in 2022).	Currently, not commercially developed in EU.	Guayule commercial latex is going to mainly supply the automotive tire industry.
Biosynthesis (alternative production route)	The process has been tested at low scale.	Not commercial production	-	Comparative properties with natural rubber by Hevea – substitution in the whole range of applications.
Synthetic rubbers (alternative material)	Synthetic rubbers are already used in automotive tire industry and clothing (spandex -polyether-polyurea copolymer products)	According to the International Rubber Study Group, the EU is self-sufficient in synthetic rubber, producing 2.8 million tonnes of synthetic rubber in 2007 (corresponding to 20.5 % of world production) but consuming 2.6 million tonnes	The price of synthetic rubber is related with the price evolution of the petrochemical products. The synthetic rubber demand is expected to be increased, especially in China, due to automotive industry applications.	The substitution of natural rubber in specific applications (such as medical) is not expected.

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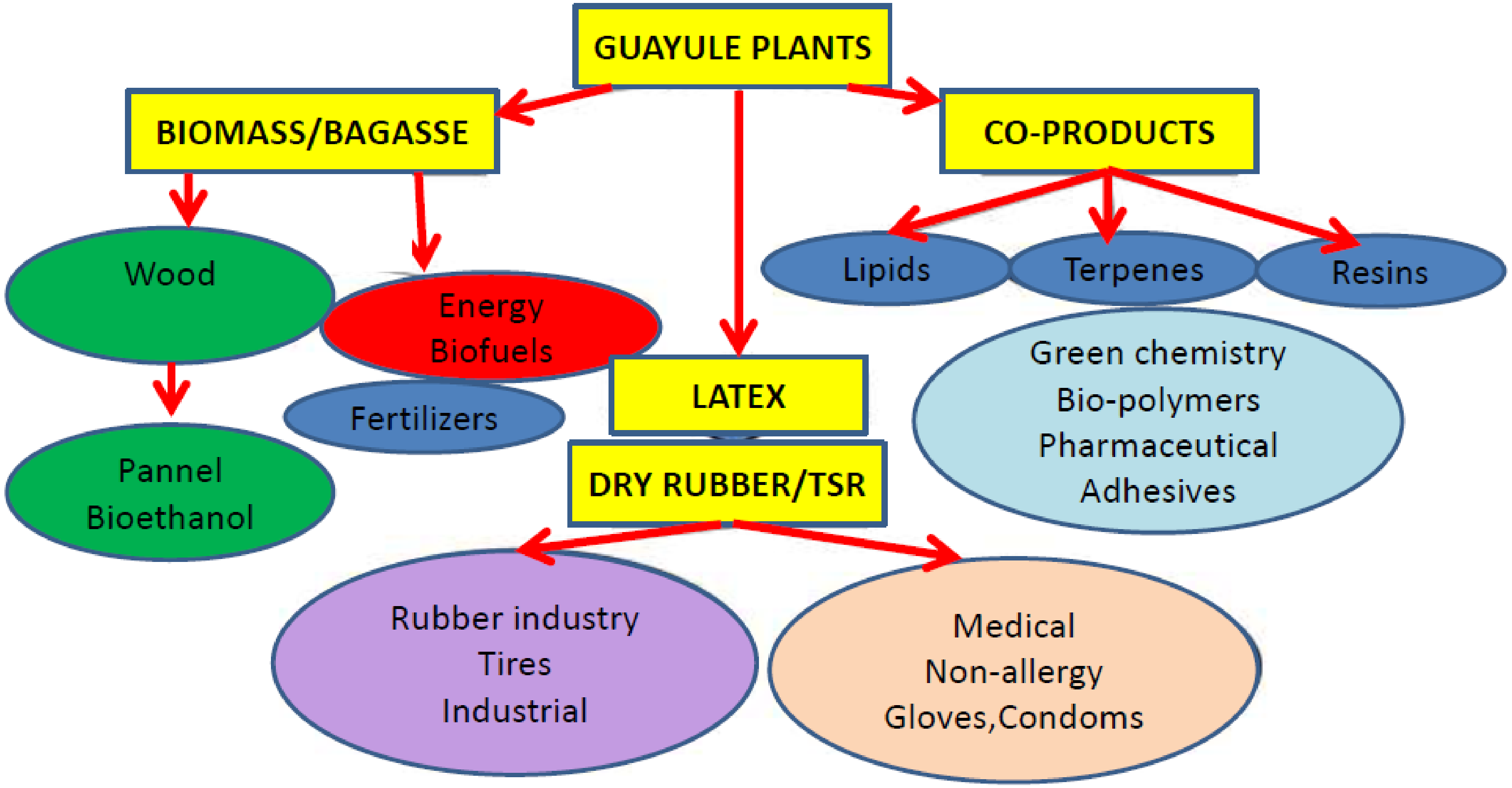

Figure 9. The industry sectors that can be potentially supplied by the products of Guayule processing [4].

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

The technological and the non-technological barriers, as well as, a short description of proposed solutions for the substitution of natural rubber are presented in Table 3. The evaluation of the barriers and the possibility of their solution are quantified according to the following graduation:

Table 81. Technological and non-technological barriers and solutions for the substitution of natural rubber [4-7].

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Guayule (***alternative raw source***)	Technological	Tires, gloves, clothing	Latex synthesized by Guayule presents a lower stress at break (7 MPa) in comparison with latex prepared by Hevea (17 MPa). However, the strain at break value is comparable. Therefore, guayule products is still impossible to be used in specific applications such as heavy duty tires and condoms.	8	Testing of modified hybrid plants.	5
	Non technological	Tires, gloves, clothing	Promotion of Guayule cultivation in south European countries – new investments are necessary.	5	Specific EU policies taking into account national stakeholders demands.	8

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Polymerization of oligomeric allylic pyrophosphates initiators such as dimethylallyl pyrophosphate (***alternative production route***)	Technological	Tires, gloves, clothing	Low yield of rubber or low molecular weight of the polymer – the exact mechanism of natural rubber biosynthesis has not totally been revealed so far. Biosynthesis processing is extremely sensitive to physicochemical parameter changes.	8	➢ Identification of key regulatory and catalytic genes ➢ Improvement of high yield variants ➢ Reconstruction of functional artificial rubber particles in vitro	5
	Non technological	Tires, gloves, clothing	High investment cost for the biosynthesis reactors	8	The increase of reaction yield consists a precondition for this barrier.	-
Synthetic rubber (***alternative material***)	Technological	Car tires (mainly)	Lower heat resistance in comparison to natural rubber, decreased time exposure to sunlight, ozone and chemicals	8 (in case of specific medical applications)	-	2
	Non technological	Car tires (mainly)	Non technological barriers have not been referred	-	-	-

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4. SUMMARY

Natural rubber are biopolymers from rubber-producing plants (mainly Hevea) presenting unique properties such as resilience, elasticity, abrasion and impact resistance, efficient heat dispersion, and malleability at cold temperatures. The substitution by synthetic elastomers is problematic in several cases and it is limited by the low heat resistance and the decreased lifetime of the synthetic materials under sunlight, ozone and chemicals exposure. The increasing demand for natural rubber in EU can be balanced by the cultivation of Guayule plant. It has been proved that Guayule cultivation is possible in the Mediterranean Sea environments. The expected yield has been estimated at about 0.5-1.0 kg/ha/an, while the harvest production is possible after 2 years versus 6-8 y. for Hevea. The production of latex by Guayule has been successfully performed at pilot scale. Currently EU-NARS-G project (EUropean NAtural Rubber Substitute from Guayule) is under progress. The project aims to the cultivation of 2.000 hectares of guayule fields in Mediterranean countries (Greece, Spain, Italy, Turkey, Morocco, etc.), while the production of rubber by Guayule will be attempted by the improvement of existing EU "green" processes. A 5 tonne/day plant to produce latex and dry rubber will be operated. A third alternative substitution strategy involved the production of natural rubber via the polymerization of oligomeric allylic pyrophosphates (biosynthesis), however this methodology presents a number of technological difficulties such as a low yield and a parameters complexity.

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PHOSPHOROUS – PHOSPAHTE ROCK

The term phosphate rock, also known as phosphorite, is used to refer to any rock with a high phosphorus content. There are rocks that contain around 300 phosphate minerals, usually apatite, that can be exploited commercially, either directly or after processing. The largest and most expensive sources of phosphorus are obtained by extracting and concentrating the phosphate rock from the numerous existing reserves.

In terms of applications, it should be noted that some phosphate rocks are used to make nutritional supplements of calcium phosphate for animals; also, pure phosphorus is used in the industry to make chemical products, produce elemental phosphorus and other industrial phosphates. But the most important use of phosphate rock, however, is in the production of phosphate fertilizers for use in agriculture because phosphorus is an essential element in common fertilizers for the capture of energy, the correct functioning of the plant and photosynthesis process. Approximately around 91% of the phosphate rock is used to produce mineral fertilizers and animal feed and food additives; phosphate rock, in addition to organic sources such as bone meal and guano, is the only source of phosphorus that is fundamental to modern agriculture.

Table 82. General information concerning phosphate rock products and applications [1].

CRM	Product	Application	Substitute
Phosphate rock	Phosphate fertilizers (P contained)	Agriculture and crop soils	There exist no substitutes for phosphate rock in the agricultural sector (USGS 2017b).
	Chemical products	Industry of detergents and other chemicals	
	Source of elemental phosphorus and salts	Soils and breeding ground	
	Nutritional additives and supplements	Animal feed and food	

1. DESCRIPTION AND INDICATOR

Production and consumption in EU

The European industry is thus highly dependent largely on imports from other countries such as the US, China, Morocco, Peru and Russia.

On the other hand, the main use of worldwide-mined phosphate rock (about 91%) is the production of mineral phosphate fertilizers. The total production amounts to 1,000 kt in phosphorus content, of which 800 kt is sold in the EU market. Most of these materials are used to make mineral fertilizers; the main part is sent for use in the EU (668 kt of phosphorus content), the rest is exported (209 kt of P content). A share of 85% of European demand is for

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this purpose [5], also EU has agreed on a new regulation for the use of fertilizers that will be implemented by the year 2022, which will include all types of fertilizers, biostimulants, organic and inorganic fertilizers and other by-products derived from the industrial sector. A minor part of phosphate rock demand in the EU (about 8%) is for detergents and other chemicals. A smaller fraction of phosphate rock (approx. 7%) is processed into nutritional supplements for animal feed mainly in form of calcium phosphate [5]. These uses of phosphate: detergents, chemical products, followed by animal feed and food additives, approximately 10% of total production, is exported for both. In addition, imports of finished products in the EU represent a total of 1,000 kt of phosphorus content, for a phosphate EU of 1,800 kt of P content. The total stock of phosphates in use in the EU amounts to 264 kt of P content, mainly as fertilizers (224 kt of P content) [5].

Future demand

Since the industrial production of fertilizers began, the constant increase in demand has gone almost in parallel with the increase in volumes of extracted phosphate rock. It is clear that in the future, the world population will increase and it will be necessary to obtain more food from the harvests, which implies that they try to improve crop yields and increase the volume of fertilizers used. Currently, there is concern about this scarce element, but the aim is to improve the quality of fertilizer safety and the transparency of the content of fertilizers through labelling, in compliance with fertilizer legislation [6]. On the other hand, detergent regulations restrict the use of phosphates and other phosphorus compounds in laundry detergents and dishwashing detergents, which will also help reduce non-essential uses and limit the release of phosphorus by improper use of detergents.

Another aspect to take into account is that, at present, the stages of the life cycle of phosphorus, waste and losses are generated, which is cause for concern in the EU due to the future demand and the presence of phosphates in the pollution of water and soil.

Use in cutting edge technologies

In this sense, due to the importance of this element, it is difficult to think of other synthetic elements that could replace the application of rock phosphate in fertilizers with phosphate or other types of fertilizers that do not contain P, such as fertilizers based on N-K and phosphorus in smaller measure.

2. SUBSTITUTE MATERIALS

Phosphorus is not only an essential element for life, but also an essential component for its applications in improving the modern agriculture needed to produce fertilizers [7].

The phosphorus used for this service is extracted from rocks with high phosphorus content, however, for some years, it has been extracted at a much greater capacity than the recovery

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capacity. Therefore, it seems clear that, in the case of phosphates, a mineral resource that is extracted from the phosphate rock mines begins to decrease in its availability. Usually, phosphate fertilizers are applied without care, and The United States Geological Survey (USGS) indicates: "there are no substitutes for phosphorus in agriculture", referring to the geological service to "phosphate obtained from mines", since it is a non-renewable resource. However, as the authors say, "fortunately, phosphorus can be recycled" [1]. In comparison, it is different from nitrate fertilizers from which nitrogen can be extracted well from the atmosphere (around 78% of N) because it is not such a minor element.

On another scale it has been considered that alternative sources to phosphorus rocks for the production of phosphate fertilizers can be guano, bone meal or other sources such as vegetable waste, animal faeces, urine, and manure and mud, but they are not economically profitable due to the higher costs per unit, since that its potential is negligible to supply the total amount of material. In the absence of adequate substitutes, with efficient production and use, as well as with recycling and minimization of waste, important advances in the sustainable use of phosphorus could be achieved, advancing towards a world of efficient use of resources and guaranteeing the availability of reserves and for future generations, guaranteeing the slogan of sustainable development.

Table 83. General description, economic value and main applications of the substitute materials.

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Other fertilizers (although to a minor extent from another sources: bone meal animal excrements and guano)	The phosphorus is a fundamental element for the crops, it is not replaceable and the only solution is a reasonable use as if it can be recycled and integrated again in the so-called phosphorus cycle. Good agricultural practices in the case of use as fertilizers for proper use and in the case of nutritional additives substitute others and making	Fertilizers (91 %), 85% of European demand. Detergents (8 %) Nutritional supplements for animal feed (7 %)	Price increase of phosphorate fertilizers	Non technological application, but in the EU, some initiatives such as codes of good practice and action programs have been achieved and phosphorus has been used more efficiently and

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	reasonable use of the P in them			redistribution of phosphorus losses in agriculture.

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

Currently, work is being done to improve the quality of fertilizers, but the escalation of prices and the depletion of optimal reserves are the factors that drive the development of numerous innovations. Technologies that are already applied or that are in the development phase, however, continue there is a large amount of margin to make future improvements in the use of phosphorus and its efficiency in agriculture [8]. Some techniques such as "precision agriculture", or the injection of manure and the incorporation of inorganic fertilizers. Also new technologies that are already marketed or that are marketed shortly.

It can increase the yield of the fertilizers, especially through enzymatic techniques with microbial inoculants to improve the efficiency of phosphorus absorption by the plant.

In the case of nutritional additives in feeding stuffs, the strategies of "phased feeding" or by stages of the life of the animal have been followed, with the aim of reducing the phosphorus content of the feed, and thus the animals process phosphorus more efficiently. In addition, new techniques with phytase enzyme are being studied in the EU for this field.

The main barriers that are found for a greater diffusion of these technologies are the high costs and the most practical application; we will have to investigate in depth other technologies and perform specific field tests. In this sense, the new European policies are oriented in the coming years to look for solutions for a more efficient use and the conservation of phosphorus in agriculture.

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Table 84. Technological and non-technological barriers and solutions for the substitution.

Substitute Material	Type of Barrier	Product/ Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
	Technological	Fertilizers	The technology is not competitive at the moment	3	Non-adequate substitutes, only other sources in a minor scale.	2
	Non-Technological	Fertilizers	Difficulty to look for a substitute element for P in fertilizers given its importance in living beings	6	Look for a new studies and search for more economical techniques and new policies and regulations	7
	Technological	Animal food additives	Cost and difficulty to the practical implementation of the new studies with enzymes	4	Dedicate economic funds and deepen new studies	6
	Non-Technological	Animal food additives	Difficulty to look for a P substitute	6	Develop of new policies and regulations	8

4. SUMMARY

Phosphorus is a minority element and is only obtained from mineral sources such as phosphate rocks; however, its importance is crucial for the proper development of plants (photosynthesis) and living beings (enzymes); and eventually to ensure the food sustenance, via agricultural crops, of the future population. There are no substitutes as such for their main applications (fertilizers, detergents or food additives), only small-scale sources. The only effective way is to facilitate or recreate their life cycle, because it must be used and recycled systematically.

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HELIUM

Terrestrial helium is formed by natural radioactive decadence of heavier elements. Most of this helium migrates to the surface and enters the atmosphere, however, its low molecular weight allows it to escape into space at a speed equivalent to that of its formation.

It is one of the noble gases and is the second lightest element of the periodic table. It is also a colorless, odorless and tasteless gas. It has lower solubility in water than any other gas. It is the least reactive element and does not combine with other chemical compounds. It is of low density and vapor viscosity and in contrast the thermal conductivity and the caloric content are exceptionally high. Helium can liquefy, but its condensation temperature is the lowest [1].

On the other hand, it is necessary to emphasize the helium was the first balloon filling gas and airships and is an application that continues today, in the investigation of high altitude and for meteorological balloons. The main use of helium is inert gas welding protection, but its greatest potential is found in applications at very low temperatures. Helium is the only refrigerant capable of reaching very low temperatures, which facilitates a state of superconductivity. Other applications are its use as a pressurizing gas in liquid rocket fuels, in

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helium-oxygen mixtures for divers, as a working fluid in nuclear reactors cooled by gas and as a carrier gas in chemical analyzes by gas chromatography.

Table 85. General information concerning helium products and applications [2] [3].

CRM	Product	Application	Substitute
Helium		Cryogenics	Liquid Nitrogen
		Aerostatics and balloons	Argon
	Shielding gas	Weldings	Argon
		Metal spraying	Nitrogen
		Semiconductors	Argon and hidrogen
	Purge gas	Purging mechanisms	Argon and nitrogen
		Controlled-atmosphere processes	Nitrogen
		Deep sea diving gases	Hydrogen/Oxygen mixtures
		Gas chromatography	Hydrogen
		Leak detection	Hydrogen/Nitrogen mixtures

1. DESCRIPTION AND INDICATOR

Production and consumption in EU

Helium resources of the world, exclusive of the United States, were estimated to be about 31.3 billion cubic meters. The locations and volumes of the major deposits, in billion cubic meters, are Qatar, 10.1; Algeria, 8.2; Russia, 6.8; Canada, 2.0; and China; also, according to the UE reports [4], recently, the largest countries producing helium worldwide are the United States (73%) Qatar (12%) Algeria (10%). Regarding the main importers to the EU, the following stand out: United States (53%) Algeria (29%) Qatar (8%) Russia (8%), being these the sources of supply of the EU: United States (51%) Algeria (29%) Qatar (8%) Russia (7%) Poland (3%). That said, the index of dependence on these imports revolves around 96%, since helium is not recyclable due to its particular properties (1%) [5].

On the other hand, the substitution index that measures difficulty to replace the material, whose values are between 0 and 1, where 1 indicates the lowest substitutability, is quite high, between 0.94 and 0.96 [5].

Future demand and use in cutting edge technologies

Some industrialized countries, such as China, have increased demand a lot, which means that we are heading for a shortage all over the world. This means that prices increase and supply problems as private companies struggle to meet demand. It is foreseeable that the situation for the future demand and the supply of helium to the EU follow similarly, since the United States has the largest sources of He to meet the European demands; however, the global demand far exceeds production and, therefore, alternatives to helium must be found for

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several technologies and it is foreseeable that the applications where the He is used look for new alternatives and reorient them towards new markets.

2. SUBSTITUTE MATERIALS

Terrestrial helium is formed by natural radioactive decay of heavier elements and as it is a thin element, most of this helium migrates to the surface and reaches the atmosphere.

Earth helium is formed by natural radioactive decay of heavier elements and as it is a thin element, most of this helium migrates to the surface and reaches the atmosphere.

One of the most important use is in cryogenics, as for the substitutes say that there are not many substitutes for helium in cryogenic applications, maybe liquid nitrogen, and even more so if temperatures below -429 ° F are required. In welding, argon can be replaced by helium and in some aerostatic applications, hydrogen can be replaced by helium because it is lighter than the air.

While it is true that they must be applications in which the flammable nature of hydrogen is not objectionable. Hydrogen is also being investigated as a substitute for helium in deepwater diving applications of less than 1,000 feet.

As the cooling of superconducting magnets for magnetic resonance images in medicine, and in cavities and superconducting magnets for high energy particles and accelerators is replaced by argon and hydrogen. Only then in applications that include lifting, such as in balloons or airships, is hydrogen used.

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Table 86. General description, economic value and main applications of the He substitute materials [3].

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Hydrogen	It is applied as a carrier gas and purge gas for gas chromatography, and inert, high purity, chemically inert gases similar to helium are required. Respiratory respiration mixtures substituted for hydrogen / oxygen helium are used instead of nitrogen / oxygen breathing mixtures to avoid nitrogen narcosis or the accumulation of nitrogen in the blood.	Mixtures as: heliair, trimix y heliox are being manufactured.	Upward trend due to the easy availability and low prince.	- Chromatography - Diving cylinders - Leak detection
Nitrogen	Used in several cryogenic applications as a refrigerant in magnetic resonance techniques in medicine or in the acceleration of particles, in nuclear physics. Also in magnetohydrodynamic superconducting generators, power transmission, magnetic levitation transport, superconducting sensors, mass spectrometers, superconducting magnets, strong field magnetic separator, toroidal field superconducting magnets for fusion reactors. Metal spraying, hot and cold, approaching its properties as high speed of sound and its chemically inertness.		Price increase	- Cryogenics - Metal spraying - Controlled-atmosphere - Purge gas
Argon	As a lifting gas, helium can be replaced by hydrogen or mixtures of gases such as argon, hydrogen and nitrogen.		Price increase for lack of efficient substitutes	- Aerostatics balloons - Weldings - Semiconductors - Purge gas

3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

In the table belong it is showed the types of barriers and its possible solutions for the main applications of helium [3]:

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Table 87. Technological and non-technological barriers and solutions for the He substitution.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Nitrogen	Technological	Cryogenics	Helium as super coolant can not be substituted in this application, if the temperatures are below (under 17K). It needs more studies.	6	It needs more studies.	7
	Non-Technological	Cryogenics		6	Look for a new studies and search for more economical techniques	7
Argon	Technological	Aerostatics	It is heavier than helium and the performance in this application is lower.	7	Need to look for new gas mixtures to optimize performance.	7
	Non-Technological	Aerostatics			Dedicate economic funds and deepen new studies	6
	Technological	Weldings & Semiconductors	Great potential of ionization and thermal potential in comparison with other elements, for welding and semiconduction applications in naval and aeronautical industry.	7		
	Non-Technological	Weldings & Semiconductors			Allocates new funds for space and naval research.	6
Hydrogen	Technological	Leak detection & Gas chromatography	In leak detection is easier to substitute, but it must be careful with the flash point according to the application.	7	To ensure a good work atmosphere for a job in ideal conditions	6

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	Non-Technological	Leak detection & Gas chromatography				

4. SUMMARY

Helium is the second most abundant element in the Universe, but on Earth it is rare because it escapes into the atmosphere. On the other hand, it is used for several technical applications, such as pressurization and purging, welding cover gas, controlled atmospheres or leak detection, in cryogenics for the cooling of superconducting magnets for magnetic resonance imaging. The substitutes are not very abundant but in a certain way they are used mainly, hydrogen, argon and nitrogen.

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MAGNESIUM

The main applications of elemental magnesium, magnesia and magnesium components are quoted in Table 1 and Figure 1. It is evident that the most critical applications are related with the fabrication of Al-Mg alloys in the automotive and aircraft industries. The substitution of Al-Mg alloys in automotive and aerospace is not possible as they are no alternative materials with similar properties. On the contrary, the use of Al-Mg alloys in automotive industry is expected to escalated aiming to the production of lower-weight and less CO2-generating

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vehicles [3,4]. Carbon-fiber based materials can be used for the construction of various vehicle components, however their cost is currently high.

Table 88. Products and applications of magnesium [1] [2].

CRM	Product/End-use	Application	Substitute
Magnesium	Al-Mg alloys	Automotive and aircraft industries, electronics	None
	Mg-Zn-Al alloys	Several applications for high resistance to corrosion	None
	Elemental	Reducing metallothermic agent, for Ti production via Kroll process, reducing agent for uranium separation, for S removal in steel	None
	Magnesium oxide (magnesia)	Additive in cements and refractory material in furnace linings for producing iron, steel, nonferrous metals, glass, and cement	Alumina, kaoline
	Magnesium salts	Fertilizers	No avaliable data
	Magnesium sulfite	Manufacture of paper	None

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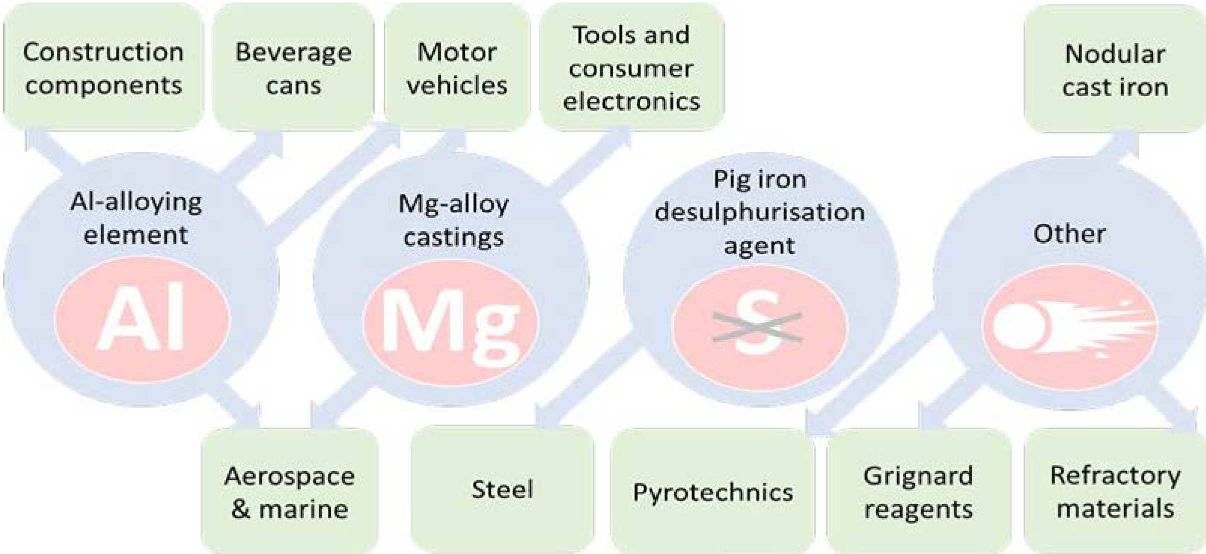

Figure 10. The main applications of metallic magnesium and magnesia [2]

1. DESCRIPTION AND INDICATOR

Magnesium is the third-most-commonly-used structural metal, following iron and aluminium. It is widely used for the strengthening of various aluminium lightweight alloys. It is also applied as a metallothermic, reducing agent at the titanium metallurgical process. Metallic magnesium is extracted by magnesium chloride (produced by magnesite ore) via electrolysis. The addition of magnesium in aluminum alloys is irreplaceable due to the advanced mechanical properties which introduces. No substitutes of magnesium have been proposed in iron and titanium industries for the purification of steel and the metallothermic extraction of titanium respectively. Therefore, the main magnesium replacement efforts should be mainly focused in the non-metallic products and especially in magnesite additive in the cement industry.

2. SUBSTITUTE MATERIALS

Cements

Magnesium phosphate cements have been identified as a potential low-CO_2 alternative to Portland cement and they have actually been used in industrial practice for more than 150 years. Magnesium phosphate cements produced by reacting magnesia with soluble phosphates. They present significant resistance to water and freeze—thaw cycles and better dimensional stability than Sorel cements [5,6]. A number of studies have indicated that

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magnesia can be partially replaced by alumina in phosphate cements. The total replacement of magnesia is not possible as the solubility of alumina in water low. However, the solubility can be increased in mild thermal environments. At the same time, alumina significantly improves the compressive strength of the paste during all the hardening periods. Thermogravimetric tests have shown a distinct increase in the reaction degree in the paste due to the addition of alumina [7]. Similar advanced properties have been obtained by the replacement of magnesia by metakaolin. It was found out that the addition of metakaolin improves the mechanical properties and durability, while it decreases the porosity of the cement [8].

Table 89. General description, economic value and main applications of the Mg substitute materials [3].

Substitute Material	Description of the Material			
	General description and objective	Production and consumption in EU	Economic value/ Market trend	Technological application
Alumina	Partial replacement of magnesia by alumina in magnesium phosphate cements	There are no data concerning the consumption of magnesite in magnesium phosphate cements	The use of magnesium phosphate cements is expected to be increased due to their relatively low energy amount required for their production	As alternatives to conventional Portland cements
Meta-kaolin	Partial replacement of magnesia by kaoline in magnesium phosphate cements			

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3. TECHNOLOGICAL AND NON-TECHNOLOGICAL BARRIERS AND PROPOSED SOLUTIONS

The principal barrier that should be limited in case of magnesite replacement in magnesium phosphate cements is the optimization of the mechanical properties of the cements containing alumina or metakaolin in relation to various parameters including the curing time, the environment temperature and the content of Al_2O_3 and metakaolin.

Table 90. Technological and non-technological barriers and solutions for the He substitution.

Substitute Material	Type of Barrier	Product/Application	Barrier	Importance of the barrier (1 Low – 10 High)	Potential solution	Sucessful of potential solution (1 low-10 high)
Alumina	Technological	Substitute for magnesite in magnesium phosphate cements	The properties of alumina-containing cement have not been tested in large scale and different environments.	5	The performance of pilot-scale tests	8
Meta-kaolin	Technological	Substitute for magnesite in magnesium phosphate cements	The properties of metakaoline-containing cement have not been tested in large scale and different environments.	5	The performance of pilot-scale tests	8

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4. SUMMARY

Literature investigation has shown that magnesium replacement in short term can be attempted only in case of non-metallic products. More specifically, additive magnesite in phosphate cements can be partially substituted by alumina and metakaolin. Furthermore, the perspective of magnesite substitution in refractories should be examined and documented in future studies.

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